

POWER UNIT COMPRISING DISTINCT DROPLETS SEPARATED BY AN AMPHIPHILIC MEMBRANE

Field

The invention relates to a power unit comprising a series of droplets, a method of
5 producing such a power unit, a method of activating such a power unit, an active power
unit obtainable from the power unit, a device comprising the power unit or active power
unit, a method of generating electric current using the power unit or active power unit, and
method of modulating the activities of one or more cells or tissues using the power unit or
active power unit.

10

Background

Devices need power sources to operate. Despite widely used technologies that can
provide power to large-scale targets, such as wired energy supplies from batteries or
wireless energy transduction, there is a need for miniaturized power sources for powering
15 very small devices, for instance bio-integrated devices (for which the need to efficiently
stimulate cells and tissues on the microscale is still pressing). The ideal miniaturized power
source should be mechanically flexible, and — for bio-integrated purposes —
biocompatible and able to generate an ionic current for biological stimulation, instead of
using electron flow as in conventional electronic devices. An intriguing approach is to use
20 soft power sources inspired by the electrical eel; however, power sources that combine the
required capabilities have not yet been produced, because it is challenging to obtain
miniaturized units that both conserve contained energy before usage and are easily
triggered to produce an energy output.

Thus, there is a pressing need to provide miniaturized power units that are suitable
25 for use in powering devices, particularly bio-integrated devices.

Summary

The present invention addresses the problems outlined above. In particular, the
present invention provides a soft, miniaturized power unit capable of powering devices and
30 modulating the activities of cells. The power unit may be activated on-demand in a
straightforward manner. The power unit stores energy at high density, and is mechanically

flexible, scalable, and portable after encapsulation. The power device may be made biocompatible.

In a first aspect, the present invention provides a power unit comprising a series of droplets, wherein said series of droplets comprises:

- 5 one or more first droplets, and
 one or more second droplets,
 wherein there is a potential energy difference between the one or more first droplets
and the one or more second droplets, and wherein
 each droplet is separated from its one or more neighbouring droplets by an
10 amphiphilic membrane.

In a first particularly preferred embodiment of the first aspect, the present invention provides a power unit comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more high salt fluids,
15 (b) one or more droplets of one or more cation selective fluids,
 (c) one or more droplets of one or more salt diffusion target fluids,
 (d) one or more droplets of one or more anion selective fluids, and
 (e) one or more droplets of one or more high salt fluids;
 wherein the one or more droplets of the above (a) may be the same one or more
20 droplets as the one or more droplets of the above (e), and wherein
 each droplet is separated from its one or more neighbouring droplets by an
amphiphilic membrane.

In a second particularly preferred embodiment of the first aspect, the present invention provides a power unit comprising a series of droplets, wherein said series of
25 droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more discharge cathodic fluids containing a
first ion donor/acceptor material,
 (b) one or more droplets of one or more separator fluids, and
 (c) one or more droplets of one or more discharge anodic fluids containing a
30 second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor
material each donate/accept the same ions,

- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,

- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein

5 each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane. In a second aspect, the present invention provides a method for producing a power unit of the first aspect of the invention, the method comprising the steps of:

- 10 • providing one or more amphipathic molecule-coated first droplets, and one or more amphipathic molecule-coated second droplets; and
- contacting said one or more amphipathic molecule-coated first droplets and said one or more amphipathic molecule-coated second droplets in series to provide a power unit of the first aspect.

15 In a first preferred embodiment of the second aspect, the present invention provides a method for producing the power unit of the above first particularly preferred embodiment of the first aspect, the method comprising the steps of:

- providing:
 - 20 (a) one or more amphipathic molecule-coated droplets of one or more high salt fluids,
 - (b) one or more amphipathic molecule-coated droplets of one or more cation selective fluids,
 - (c) one or more amphipathic molecule-coated droplets of one or more salt diffusion target fluids, and
 - 25 (d) one or more amphipathic molecule-coated droplets of one or more anion selective fluids; and
- contacting said one or more amphipathic molecule-coated droplets of the above (a), one or more amphipathic molecule-coated droplets of the above (b), one or more amphipathic molecule-coated droplets (c), and one or more amphipathic molecule-coated droplets of the above (d) in series to provide a power unit of the
30 above first particularly preferred embodiment of the first aspect.

In a second preferred embodiment of the second aspect, the present invention provides a method for producing the power unit of the above second particularly preferred embodiment of the first aspect, the method comprising the steps of:

- providing:
 - 5 (a) one or more amphipathic molecule-coated droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
 - (b) one or more amphipathic molecule-coated droplets of one or more separator fluids, and
 - (c) one or more amphipathic molecule-coated droplets of one or more
 - 10 discharge anodic fluids containing a second ion donor/acceptor material,
- contacting said one or more amphipathic molecule-coated droplets of the above (a), one or more amphipathic molecule-coated droplets of the above (b), and one or more amphipathic molecule-coated droplets (c) in series to provide a power unit of the above second particularly preferred embodiment of the first aspect.

15

In a third aspect, the present invention provides a method for activating a power unit of the invention, the method comprising the step of transforming the series of droplets into a series of compartments wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

20 In a fourth aspect, the present invention provides an active power unit obtainable by the method of the third aspect.

In a fifth aspect, the present invention provides an active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

- 25 (a) one or more high salt biocompatible gel compartments,
- (b) one or more cation selective biocompatible gel compartments,
- (c) one or more diffusion target biocompatible gel compartments,
- (d) one or more anion selective biocompatible gel compartments, and
- (e) one or more high salt biocompatible gel compartments;
- 30 wherein the one or more high salt biocompatible gel compartments of the above (a) may be the same one or more high salt biocompatible gel compartments as the one or more high salt biocompatible gel compartments of the above (e); and wherein

each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.

In a sixth aspect, the present invention provides an active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

- (a) one or more discharge cathodic biocompatible gel compartments containing a first ion donor/acceptor material,
 - (b) one or more separator biocompatible gel compartments, and
 - (c) one or more discharge anodic biocompatible gel compartments containing a second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein
- each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.

In a seventh aspect, the present invention provides a device comprising:

- (a) the power unit according to invention, or an active power unit according to the invention, and
- (b) one or more electronic components.

In an eighth aspect, the present invention provides a method of generating an electric current, said method comprising the steps of either:

- (i) providing a power unit according to invention, connecting two droplets within the series of droplets with electronically conductive means, and activating the power unit by the method for activating a power unit according to the invention, or
- (ii) providing an active power unit according to the invention, and connecting two compartments within the series of compartments with electronically conductive means.

- In an ninth aspect, the present invention provides a method of modulating the activities of one or more cells or tissues, the method comprising a step of either:

- (i) providing a power unit according to the invention and activating the power unit by the method for activating a power unit according to the invention, or
- (ii) providing an active power unit according to the invention,
- wherein one or more cells or tissues are contained within, or are in the presence of,
- 5 the power unit according to the invention, or the active power unit according to the invention.

Brief description of the Figures

Figures 1 to 29 relate to the experiments described in Example 1 and the
 10 supplementary information thereto.

Figures 30 to 62 relate to the experiments described in Example 2 and the supplementary information thereto.

Figure 63 relates to an alternative battery chemistry embodiment of the power source of the invention.

15 **Fig. 1 Structure and output performance of the droplet power source. a–c,** Fabrication process for a power unit formed by depositing hydrogel droplets: pre-gel droplets were submerged in lipid-containing oil and acquired lipid monolayer coatings, which subsequently formed lipid bilayers when droplets were placed in contact (a); the insulating lipid prevented ion flux between droplets when they were connected to form a
 20 single unit (b). Ag/AgCl electrodes were used to measure electrical output. The power source was activated by transfer into lipid-free oil and thermal gelation to rupture the lipid bilayers (Methods) (c). d, Bright-field images of the formation process of a droplet power unit. In (i) to (iii), the volume of each droplet was 50 nL. Scale bars, 500 μ m. Panel (iii) shows the insertion of Ag/AgCl electrodes. In (iv) and (v), droplets were encapsulated in a
 25 flexible and compressible organogel to demonstrate energy preservation in a portable unit. The volume of each droplet was 500 nL. Scale bars, 10 mm. e, Output open-circuit voltage (V_{OC}) during the transition from pre-gel (i), to gel (ii), to continuous hydrogel network (iii), as shown in (d). Inset, output short-circuit current (I_{SC}) of a droplet power unit after formation of a continuous hydrogel network (iii). f, Variation of normalized V_{OC} and mean
 30 droplet diameter of single power units with different length of storage time in oil before the formation of continuous hydrogel networks. Normalization was with respect to the initial values of each experiment. The diameter of the droplets decreased over time most likely

due to the evaporation of water. Data in (e) and (f) are mean values $\pm$ standard deviation (s.d.) ($n = 7$).

Fig. 2 Effect of droplet volume on the electrical characteristics of droplet power sources. **a**, Initial ($t = 0$) V_{OC} and I_{SC} values. Droplet volumes below 100 nL were calculated based on diameters measured by microscopy. **b**, Calculated power densities and total released charge of single power units with various droplet volumes. The power source volume and length were five times of a single droplet volume and diameter. **c**, Normalized V_{OC} , I_{SC} , and total released charge of power units formed into droplet networks in series and/or in parallel. The volume of each droplet was 1.84 nL. 2 $\times$ 2 stands for two sets of two paralleled power units in series. Inset, schematics showing the power units were formed into continuous droplet networks during measurements. The normalization was with respect to the outputs of a single unit. Data are mean values $\pm$ s.d. ($n = 5$).

Fig. 3 Template-assisted droplet network fabrication and output. **a** and **b**, Preparation of a large-scale patterned power source network. First, 7 droplets were deposited in a mould, by using a programmable micro-injector, and formed a hexagonal 'flower-like' structure (**a**). Droplet networks can be drawn into a truncated pipette tip by capillary action and arranged in three dimensions. Hexagonal assemblies of droplets were layered to form larger droplet networks (**b**). **c**, Bright-field images of a mould with multiple droplet hexagons. The volume of each droplet was ~ 4 nL. Scale bar, 600 μm . **d**, Zoom-in of a single hexagonal layer. Scale bar, 200 μm . **e**, Stacks of 7 and 28 power units. Scale bar, 600 μm . **f**, After 4-step sequential deposition into a spiral mould, droplets self-assembled into a chain of power units (Methods). **g** and **h**, 20 power units were connected (**g**, Scale bar, 1.2 mm) to generate an output voltage sufficient to light up a red LED (**h**).

Fig. 4 Ionic droplet device induced neuronal modulation. **a**, The triggering strategy used to modulate neuronal activity by generating ionic current from a droplet device. The high-salt and ion-selective droplets together acted as a droplet device, which was attached to droplets that contained neural microtissues or brain slices. Droplets #1, #2, and #3 received a cation influx from the left and an anion influx from the right. **b**, The ionic current modulated neuronal activity as reflected by intracellular Fluo-4 fluorescence. **c**, Output of the droplet device across the low-salt droplets. The voltage readout was conducted in open circuit mode to ensure that the continuous hydrogel network was the only current path ($n = 5$). The volume of each droplet was 500 nL. The average voltage

during the first 10 min was 120 mV. The corresponding ionic current was $\sim 2.6 \mu\text{A}$. **d**, Frames at various time-points showing neurons embedded in the #1 droplet. Neurons were cultured for different periods (at day 3 and 17), reflecting a change of neuronal network activities. The high-salt droplets contained 0.5 M CaCl_2 . Ionic current flowed from left to right into the #1 droplet. Orange dashed lines mark the modulated area. Scale bars, 150 μm . **e**, Relative fluorescence intensities at different time-points along the white dashed lines indicated in (**d**). The black dot in each plot indicates the center of fluorescence (weighted-mean distance) at the corresponding time-point. **f**, Relative displacement of the center of fluorescence over 90 s for neuronal networks after different culture periods and in *ex vivo* brain slices from mice. GABA treatment was used on the day 17 neural tissues to suppress activities of neuronal networks ($n = 3$, *denotes $P < 0.05$ and **denotes $P < 0.01$, unpaired one-tail t-test). Data in (**f**) are presented as mean values $\pm$ s.d.

Fig. 5 - Extended Data Fig. 1 Electricity-generating mechanism of the electric eel. a, Location of the electric organ in the electric eel (*Electrophorus electricus*). **b**, Electrococytes stacked within the organ generate an electrical potential, which arises as depicted from directional ion fluxes through sodium and potassium channels.

Fig. 6 - Extended Data Fig. 2 Measurement of power source activation during DIB rupture. a, The integration of a Peltier cooler and a heat sink to the bottom of the droplet measurement system enabled electrical readouts during temperature-triggered droplet gelation and oil transfer. **b**, Output V_{OC} during droplet network formation (i) and activation process (ii and iii). Five independent droplet power sources were all activated within 60 s (iv).

Fig. 7 - Extended Data Fig. 3 SEBS organogel encapsulation enabled preservation of droplet network in physiological environments. a, Schematic showing the SEBS organogel encapsulation. **b**, Photographs of a droplet power source formed from 500 nL droplets and encapsulated in an organogel cube. **a**, Comparison with a one-penny coin (20.3 mm diameter). **c**, The encapsulated droplet power source is soft and can withstand repeated bending and twisting by hand. **d**, The open-circuit voltages are shown for droplet power sources encapsulated in organogel after 30 min immersion in phosphate buffered saline (pH 7.4, Gibco) or rabbit blood (New Zealand white rabbit strain, Envigo).

Fig. 8 - Extended Data Fig. 4 Optimization of the droplet power source for maximal output. a, V_{OC} and I_{SC} of single power units with different concentration

gradients between the high-salt and low-salt droplets, with the high-salt droplets set at 2 M CaCl_2 . **b**, V_{OC} and I_{SC} of single power units with different salt concentrations in the low-salt droplets, with the concentration gradient set at 10-fold (see Supplementary Note 3 for detailed discussion). **c**, The dependence of output voltage, current, and power of a single power unit on the external loading resistance. The instantaneous output power reached a maximum (75 nW for 50 nL droplets) when the loading resistance was set around 78 k Ω . The output voltage, current, and power were typical of a concentration cell, showing a positive correlation between voltage and load resistance, while the current followed a reverse trend¹⁷. Data are presented as mean $\pm$ s.d. (n = 5).

Fig. 9 - Extended Data Fig. 5 Cell viability study and immunofluorescence staining of neural microtissues before and after droplet device modulation. **a**, Cell viability in neuron-containing droplets, which had been connected to droplet devices for 10 min and then cultured in medium for 4, 12, 24, and 48 h. The control group was neural microtissues only embedded in agarose droplets and had not been in contact with a droplet device. Salt concentrations in the high-salt droplets (CaCl_2) were: 0.5 M (50-fold gradient, light blue); 1 M (100-fold gradient, dark blue). Data are presented as mean $\pm$ s.d. (n = 5). **b**, Overlaid bright-field (top) and fluorescence (bottom) live/dead imaging of microtissues embedded in agarose droplets. Calcein-AM (live, green) and PI (dead, red) staining were conducted after droplet device (0.5 M) modulation. Scale bars, 600 μm . **c** and **d**, RFP-labelled microtissues were stained for the neuronal cell marker TUJ1 and the apoptosis marker caspase 3. The RFP are expressed by live cells; the TUJ1 staining reveals the neuronal cells including their processes; the caspase 3 staining reveals apoptotic cells. The control group (**c**, Day 10) was not contacted with a droplet device. The experimental group had been connected with the droplet device for 10 min and then cultured in medium for 48 h (**d**, Day 12). Salt concentrations in the high-salt droplets (CaCl_2) were 0.5 M (50-fold gradient). **e**, The number of apoptotic cells per unit area of $100 \times 100 \mu\text{m}^2$. Data are presented as mean $\pm$ s.d. (n = 6).

Fig. 10 - Extended Data Fig. 6 Various droplet configurations for verification of the modulatory effects of droplet devices on neural microtissues. **a**, Direct contact of neuron-containing droplets (neurons cultured for 3 days) with high-salt droplets (0.5 M CaCl_2). **b**, Frames at various time-points showing stable fluorescence. Scale bar, 300 μm . **c**, Applying an external voltage to Ag/AgCl electrodes in Ca^{2+} -free hydrogel droplets to

modulate neural microtissues within connected droplets. Droplet #1 received a relatively positive input voltage compared to droplet #3. The input current was $\sim 2.6 \mu\text{A}$ that approximately equaled to our droplet device. **d**, Frames at various time-points showing neurons embedded in the #1 droplet. The neurons had been cultured for different periods (3 and 17 days). Ionic current flowed from left to right into the #1 droplet. Red dashed lines mark the border of the modulated area of Ca^{2+} wave. Scale bars, $150 \mu\text{m}$. **e**, Relative fluorescence changes for neural microtissues after modulation by various means. The control group was neuron-containing droplets in direct contact with high-salt droplets (**a**). The "electrical" group was subjected to an external voltage source (**b**). The droplet device group is documented in Fig. 4.

Fig. 11 - Extended Data Fig. 7 Monitoring the change of neuronal membrane potential under droplet device modulation. **a**, Neuronal membrane potential was measured by confocal imaging using FluoVolt™, a voltage-sensitive fluorescent probe (Methods). Scale bar, $200 \mu\text{m}$. **b**, Frames at various time-points of a zoom-in area in (**a**) showing the fluorescence change corresponding to the droplet device modulation. Ionic current flowed from top-left to bottom-right of the selected area. Scale bar, $50 \mu\text{m}$. **c**, Relative fluorescence change of individual neurons under different conditions. The black curve represents neurons in direct contact with high-salt droplets (0.5 M CaCl_2). The stable fluorescence indicates that the neurons remain in a resting state. The red curve represents neurons under droplet device modulation (see **b**) and the blue curve represents neurons depolarized by adding 20 mM KCl solution. Three neural microtissues were tested under each condition and five cells from each were randomly selected for fluorescence quantification.

Fig. 12 - Extended Data Fig. 8 Modulation of various neuronal networks. **a**, Neuronal network cultured for 10 days. High-salt droplets contained 0.5 M CaCl_2 . Ionic current flowed from left to right into the #1 droplet. Orange dashed lines mark the modulated area with increased fluorescence intensity. **b**, Profile plots of relative fluorescence intensities at different time-points along the white dashed line indicated in (**a**). Ionic current flowed from left to right. The black dot in each plot indicates the Weighted-mean Distance at that time-point. **c**, In the same setup, part of an *ex vivo* mouse brain slice was embedded in a hydrogel droplet for ionic current modulation. **d**, Profile plots for (**c**) and the Weighted-mean Distances at each time-point. **e**, In the same setup, day

17 neurons were treated with GABA before ionic current modulation. **f**, Profile plots for (e) and the Weighted-mean Distances at each time-point. Scale bars in (a), (c), and (e), 300 μm .

Fig. 13 - Extended Data Fig. 9 Direct attachment of the droplet device to a

5 **mouse brain slice. a**, Direct modulation of a mouse brain slice without hydrogel coating by using the droplet device. High-salt droplets contained 0.5 M CaCl_2 . The two ion-selective droplets were separated with a distance of $\sim 300 \mu\text{m}$. **b**, Orange dashed lines mark the modulated area, which has increased fluorescence intensity. The fluorescence response of the brain slice modulation was less directional and uneven compared to the neural
10 microtissues, which might be due to the different neuronal wirings or tissue structures at different regions of the brain slice. Scale bar, 150 μm .

Fig. 14 - Schematic S1 Schematic illustrations of the basic electrochemical and electrical mechanisms of the droplet power source and a measurement circuit. a, The

ion fluxes inside a droplet power source can be simplified into four components. (1) The
15 ionic gradient between a high-salt and a low-salt droplet gives rise to an electromotive force and an ion flux across the charge-selective droplet; (2) inflowing ions (blue and red arrows) move at rates that maintain electroneutrality; (3) ions in the terminal high-salt droplets react at the electrodes to convert the ion flux into electron flow in an external circuit; (4) the internal ionic current affects the activities of embedded neurons. **b**, The
20 equivalent electric circuit of the droplet power source, connected electrodes, and the measuring meter, corresponding to parts (1), (2), and (3) in (a).

Fig. 15 - Schematic S2 Model of regenerative Ca^{2+} release and wave propagation (SI ref 21)

Fig. 16 - Supplementary Fig. 1 Rupture of the lipid bilayer between two pre-

25 **gel droplets**. After gelation and oil transfer, a continuous hydrogel is formed. Schematic (top) and fluorescence microscopy images (bottom) of a droplet pair before and after formation of the continuous hydrogel. The droplet pair was formed from an agarose pre-gel droplet and an agarose pre-gel droplet that contained the bilayer-impermeable dye ATTO-488 (1 μM , Sigma-Aldrich). Following gelation and oil transfer with lipid-free oil, the dye
30 diffused into the adjacent droplet, indicating bilayer rupture. Scale bars, 250 μm .

Fig. 17 - Supplementary Fig. 2 The gelling temperature of the SEBS organogel.

We used undecane/hexadecane (50% v/v) for the oil transfer process, achieving a gelling

temperature below 37 °C. The encapsulation was conducted by replacing the silicone oil with the molten organogel at the last oil transfer step.

Fig. 18 - Supplementary Fig. 3 Simulation of I_{sc} to support the experimental results. **a**, The simulation layout with a droplet radius of 258 μm , corresponding to 50 nL in volume. **b**, Comparison of simulated and experimental results.

Fig. 19 - Supplementary Fig. 4 Variation of the volume ratio over time. The hydrogel droplet diameters were measured from photographs, and the droplet volumes were calculated with the assumption of spherical geometry. Volume ratio was with respect to the initial volume values (0 h) of each experiment. Data are presented as mean $\pm$ s.d. (n = 3).

Fig. 20 - Supplementary Fig. 5 Influence of the cations in the high- and low-salt droplets on electrical output. Na^+ , K^+ , Ca^{2+} and the cationic forms of pyronine Y and GABA were examined, all as chloride salts. **a**, Divalent Ca^{2+} ions carry more charge than the monovalent ions and therefore produce a higher voltage under the same concentration gradient (200-fold). The combined effects of a higher aqueous ionic mobility (SI ref 14) (K^+ : $7.62 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, Na^+ : $5.19 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$) and a higher affinity for the cation-selective polystyrene sulfonate chain (SI Ref 23) (K^+ : 2.27, Na^+ : 1.58) produce a higher output voltage for K^+ . **b**, Comparison with Ca^{2+} ions of the V_{OC} values of the cationic forms of pyronine Y and GABA at the concentrations shown.

Fig. 21 - Supplementary Fig. 6 I_{sc} versus time for two droplet power units with different volumes. We integrated the current traces over time to calculate the capacity of the droplet power sources during each discharge. **a**, Experimental results. **b**, Simulations based on the same structural setup as the experimental droplet power sources (Supplementary Fig. 3).

Fig. 22 - Supplementary Fig. 7 Charging of electronic components and circuits. **a**, Charging a capacitor and lighting an LED with the droplet power source. **b**, The charging current of a 0.47 μF capacitor. The blue area shows the integration area of the current trace over time, indicating the accumulated charge in the capacitor ($\sim 1.57 \mu\text{C}$) during one charging cycle. **c**, Charging a pulse generator circuit with the droplet power source. The pulse generator circuit was connected with the droplet power source using a capacitor for charge collection. Inset, a photograph of the pulse generator circuit based on a 555-timer chip. **d**, By tuning the value of R_H and R_L , the pulse frequency was tuned from 3

to 10 Hz. Higher frequencies led to the faster energy consumption of the droplet power source.

Fig. 23 - Supplementary Fig. 8 Recharging a droplet power source network. A droplet power source network (Fig. 3e and h) was recharged with a reversed 200 mV voltage for 5 min. I_{SC} was recorded and the cycle was repeated 10 times. Data are presented as mean $\pm$ s.d. ($n = 5$).

Fig. 24 - Supplementary Fig. 9 Fluorescence monitoring of ion fluxes from droplet devices. **a**, In the front three low-salt droplets (red), inflowing cations will move from left to right and inflowing anions right to left, creating an ionic current in the three droplets. **b** Relative concentration distributions of Ca^{2+} (orange) and Cl^- (green) across the three low-salt droplets, calculated from line scans of fluorogenic Ca^{2+} and Cl^- indicators at 5 min (Methods). The volume of each droplet was ~ 500 nL. **c**, Line scans of the fluorescence signals across the three low-salt droplets (red in 'a'), showing the Ca^{2+} concentration with time. **d**, The salt concentration in the high-salt droplets affects the speed and intensity of the cation flux. Data were from the front left droplet. **e**, Line scans of the fluorescence signals across the three low-salt droplets, showing the Cl^- concentration with time. Decreased fluorescence indicates increased Cl^- . **f**, The salt concentration in the high-salt droplets affects the speed and intensity of the anion flux. Data were from the front right droplet. All data are presented as mean $\pm$ s.d. ($n = 3$).

Fig. 25 - Supplementary Fig. 10 3D neural microtissues in culture. **a-d**, Microscopy images of neural microtissues at: **a**, day 0 (right after generation by a microfluidic system); **b**, day 3; **c**, day 10; **d**, day 17. The red arrows mark stretched and entangled neural processes, which indicate the formation of neuronal connections. **e** and **f**, Bright-field microscopy (**e**) and overlaid confocal (**f**) image of agarose droplets that contained neural microtissues at day 10. Neurons were stained with Calcein-AM. Scale bars, 250 μm .

Fig. 26 - Supplementary Fig. 11 Images of the droplet ring for triggering neuronal modulation. **a**, A droplet device attached to droplets containing neural microtissues (three bottom droplets, #1, #2, and #3). **b**, A zoom-in view of droplet #3, which contains a neural microtissue at day 3. Scale bars, 500 μm .

Fig. 27 - Supplementary Fig. 12 XYZ scanning of a neuron-containing droplet (day 17) by confocal microscopy. **a**, Schematic of the three Z stacks. **b**, Dark-field

images. The bottom of the embedded neural microtissue was $Z = 0 \mu\text{m}$. Neurons were stained with Fluo-4 Direct™. Scale bar, $300 \mu\text{m}$. Due to limited light-penetration, deeper stacks (e.g., $Z = 140 \mu\text{m}$) could only be imaged around the boundary.

Fig. 28 - Supplementary Fig. 13 Images of mouse brain slices. **a**, A mouse brain slice in culture medium. Scale bar, 1.5 cm. **b**, Using a 1 mm biopsy punch (KAI), part of the brain slice was cut out and embedded in a droplet by coating with agarose (Methods). **c**, Bright-field image of the boundary of a brain slice, where neurons are visible. Scale bars in **(b)** and **(c)**, $65 \mu\text{m}$.

Fig. 29 - Supplementary Fig. 14 Calculation of the Ca^{2+} wave propagation speed from the fluorescence intensity of individual neurons. **a**, Selected neurons in a day 3 neural microtissue along the direction of the Ca^{2+} wave (white dashed line). **b**, Time-dependent changes of intracellular Ca^{2+} concentration in cells marked 1–6 in **(a)**. **c** and **d**, Selected neurons in a day 17 neural microtissue **(c)** and their changes in intracellular Ca^{2+} concentration **(d)**. **e**, Speeds of Ca^{2+} wave propagation at day 3 and day 17. We picked 6 neurons in each neural microtissue (5 data values), and 3 neural microtissues with the same culture times for analysis ($n = 15$). Data are presented as mean $\pm$ s.d. (**denotes $P < 0.01$, two-sample t-test). Scale bars, $150 \mu\text{m}$.

Fig. 30 – Example 2 Fig. 1 Design of the LiDB. **a–c**, Fabrication of a LiDB by consecutively depositing hydrogel droplets: silk pre-gel droplets were submerged in lipid-containing oil and acquired lipid monolayer coatings, which subsequently formed lipid bilayers when droplets were placed in contact **(a)**; the lipid insulation prevented Li-ion flux between droplets when they were connected to form a single unit **(b)**; the battery was activated by UV crosslinking of the silk hydrogel, which ruptured the lipid bilayers to form a continuous hydrogel structure **(c)**. Carbon electrodes were used to measure electrical output. **d**, Working mechanism of the LiDB. Electrons flow from electrodes to Li-particles through conductive interconnecting CNTs. Charge neutralization then occurs by the intercalation or deintercalation of Li-ions into or out of Li-particles. Accordingly, Li-ions flux throughout the negatively-charged silk hydrogel, which is formed by dityrosine crosslinking (dashed box) mediated by a small number of tris(bipyridine)ruthenium(II) (Ru), sodium persulfate (SPS), and low-intensity UV illumination (1 min). **e**, Bright-field images of a LiDB before and after UV-induced crosslinking. Droplet volumes, 30 nL. **f**,

Bright-field images of LiDBs of different droplet volumes. From top to bottom, 250, 50, and 10 nL. Scale bars, 400 μm .

Fig. 31 – Example 2 Fig. 2 Electrochemical characteristics of LiDBs. a,

Galvanostatic charge-discharge curves of LiDB at a current of 0.5 μA . **b,** Discharge curves of LiDB at different currents. **c,** Cyclic performance of LiDB at a current of 1 μA . C_0 and C correspond to the capacities before and after the cycle. **d,** Calculated volumetric capacities and released charge of LiDBs with various droplet volumes. **e,** Comparison of volumetric capacities of LiDBs (red) and reported flexible Li-ion hydrogel batteries (blue)⁹⁻¹². **f,** 6 LiDB units were connected in series by underneath screen-printed carbon electrodes to light up three red light-emitting diodes. 1 μL (**a–c**) and 0.5 μL (**f**) droplets were used. Scale bar in **f**, 2.4 mm. Data in **d** and **e** are mean values $\pm$ standard deviations (s.d.), $n = 5$.

Fig. 32 – Example 2 Fig. 3 Charged molecule translocation powered by LiDBs.

a, Bright-field image of a LiDB unit tetherlessly linked with two converting droplets (**i**, middle red box) and three hydrogel droplets (**ii**) or aqueous synthetic cells (**iii**, right blue box). The converting hydrogel droplets contained 1.1% w/v PEDOT:PSS that transformed the electron flow from a LiDB into ion flux (**i**). M^+ represents the cation in the electrolyte. The pore-forming protein αHL was used to achieve signal (charged molecule) transmission through DIBs (**iii**). Fluorescent charged molecules were cationic pyronin Y (10 μM , red) and anionic MANT-dATP (100 μM , blue). **b,** Bright-field and fluorescence microscopy overlays (background removed) of three hydrogel droplets at the start and after 10 min of the LiDB actuation. Initially, only the central cell contained pyronin Y. **c,** Fluorescence ratios indicating that pyronin Y moved toward the anode of the LiDB (the right droplet). **d** and **f,** Overlays (background removed) of hydrogel droplets (**d**) and aqueous cells (**f**) containing MANT-dATP at the start and after 10 min of the LiDB actuation. **e** and **g,** Fluorescence ratios indicating that MANT-dATP moved toward the cathode of the LiDB (the left droplet). Droplet volumes, 0.3 μL . Scale bars, 800 μm . Data are mean values $\pm$ s.d., $n = 3$.

Fig. 33 – Example 2 Fig. 4 Ex vivo murine heart stimulation by LiDBs. a,

Direct contact by a LiDB to produce electrical shock/defibrillation. Black box, an ECG signal was recorded with three electrodes to monitor the responses of the heart. Red box, the output current of the LiDB in phosphate-buffered saline, which will flow through the

heart during the contact process. The time derivative of the output current indicates that the maximum alterations occur at the times when a LiDB is attached to a heart and detached from it, which can alter the heart electrophysiological activity. **b**, Image of the direct contact. Scale bar, 1 cm. **c**, Cell viability assay of fibroblasts after 48 h attachment with fully-charged LiDBs formed from 1 μ L droplets ($n = 3$). NS, not significant; two-sample t-test. **d**, ECG traces of hearts under stimulation by LiDBs with droplet volumes of 0.2, 1, and 3 μ L. Green arrows mark the times of attachment and red arrows mark the times of detachment. **e**, Shock amplitudes and beating intervals of hearts under stimulation by LiDBs with different droplet volumes ($n = 5$). The beating interval was the time gap between the time of attachment and the next intrinsic heartbeat. Inset, comparison of mean shock amplitudes. The control group stands for fully discharged LiDBs (intrinsic heartbeats). **f** and **g**, ECG traces of heart defibrillation from ventricular tachycardia (**f**) and fibrillation (**g**). The heart was subjected to ouabain solution perfusion to induce the arrhythmia (Methods). The attachment (green arrow and dashed line) and detachment (red arrow and dashed line) of a LiDB were set as the start and end of a defibrillation process. The heart defibrillations were performed by LiDBs with 3 μ L droplets. **h**, ECG trace of a heart undergoing two sequential cycles of ouabain-induced fibrillation and LiDB-enabled defibrillation with 3 μ L droplets. Data are mean values $\pm$ s.d. in **c** and **e**.

Fig. 34 – Example 2 Fig. 5 Magnetic propulsion and steering of LiDBs. a, Incorporation of magnetic Ni-particles in the central separator droplet enabled magnetic manipulation of a LiDB (**i**). The LiDB can be manoeuvred to different target electrodes to perform energy delivery in oil (**ii**) and from oil into water (**iii**). **b**, Bright-field image of a LiDB containing Ni-particles. **c**, Relative capacities of LiDBs with and without Ni-particles. **d**, Trajectory of a LiDB navigating through a maze to perform repeated energy delivery and recharging. **e**, Charge-discharge curves of a LiDB at the first cycle and after the 10th cycle of magnetic navigation. **f**, A 2 mF capacitor was connected to the target electrodes to collect the delivered energy of each cycle. **g**, Trajectory of a LiDB crossing from oil into the aqueous phase (LiCl 1 M, blue dye for visualization). **h** and **i**, Discharge curves (**h**) and relative capacities (**i**) of LiDBs in oil and in water. **j**, Images showing the time sequence of biodegradation after the addition of Proteinase K to the aqueous phase. Droplet volumes, 0.25 μ L. Scale bars in **b** and **j**, 800 μ m. Scale bars in **d** and **g**, 3 mm. Data in **c**, **h** and **i** are mean values $\pm$ s.d., $n = 5$.

Fig. 35 – Example 2 Extended Data Fig. 1 Rupture of the lipid bilayer between two pre-gel droplets. After UV-crosslinking of the silk hydrogel, a continuous hydrogel was formed. Subsequently, the bilayer-impermeable dye ATTO-488 (1 μ M, Sigma-Aldrich) diffused into the adjacent droplet, indicating bilayer rupture. Overlaid bright-field and fluorescence microscopy images (top) and relative fluorescence intensity (bottom) of a droplet pair before (a) and after (b) formation of a continuous hydrogel.

Fig. 36 – Example 2 Extended Data Fig. 2 Electrochemical impedance spectroscopy and zeta potentials of silk hydrogels. a, Alternating current impedance spectra over a frequency range from 0.1 to 100 kHz. The electrical conductivity of the silk hydrogel was calculated by Ohm's law. The silk hydrogel with CNT had an electrical conductivity of $\sim 41.3 \text{ mS cm}^{-1}$, which was 30-fold higher than the silk hydrogel without CNT ($\sim 1.3 \text{ mS cm}^{-1}$). b, Theoretical fitting of the silk hydrogel with CNT. Inset, equivalent circuit. Charge transfer resistance (R_{ct}) of the CNT–Li-particles–electrolyte interface was $\sim 1025 \Omega$. c, Zeta potentials of the native silk solution and silk hydrogel diluted at 2.5 mg mL^{-1} .

Fig. 37 – Example 2 Extended Data Fig. 3 Relative fluorescence of the three connected droplets before and after charged molecule translocation powered by the LiDB. a, Cationic pyronin Y (10 μ M) moved toward the negative anode of the LiDB (the right droplet). b and c, Anionic MANT-dATP (100 μ M) moved toward the positive cathode of LiDB (the left droplet) in hydrogel droplets (b) and aqueous (c) synthetic cells. d, Molecular structures of pyronin Y and MANT-dATP. Control group stands for experiments using fully discharged LiDBs. Data are mean values $\pm$ s.d., $n = 3$.

Fig. 38 – Example 2 Extended Data Fig. 4 Biocompatibility of LiDBs. a and b, Live/dead imaging of 3T3 fibroblasts shows the live (green) and the dead cells (red). The control group was not contacted with a LiDB (a). Cells in experimental group were subjected to LiDBs with 1 μ L droplets (b). Red dashed line denotes the outline of the attached LiDB. Cells were attached with LiDBs for 48 hours before imaging. Scale bars, 300 μ m. c–e, Cell assays with human fibroblasts, or atrial or ventricular cardiomyocytes (derived from human iPSCs), after 7 days of co-culture with LiDBs. MTT assays reveal cell metabolic activity and viability (a). Cytotoxicity assays monitor cytotoxic effect of LiDBs (b). Caspase assays detect caspase activity and cell apoptosis (c). NS, not significant; two-sample t-test.

Fig. 39 – Example 2 Extended Data Fig. 5 Optogenetic control of heart rhythm by blue light pacing. **a**, Image of the pacing set up. Scale bar, 1.2 cm. **b**, ECG of the intrinsic heartbeats. **c**, ECG under light-regulated pacing to avoid ectopic heartbeats.

Fig. 40 – Example 2 Extended Data Fig. 6 ECG traces of hearts under direct current stimulation through wired electrodes. **a**, Image of the electrode stimulation. Scale bar, 1 cm. **b**, Green arrows mark the times of stimulation on and red arrows mark the times of stimulation off. Stimulation by a 30 μ A direct current was equivalent to the application of a LiDB with 1 μ L droplet volume, and showed a similar shock signal, heartbeat suppression, and subsequent restoration in the ECG trace.

Fig. 41 – Example 2 Extended Data Fig. 7 Activation of a pulse generator circuit by 6 LiDBs connected in series. **a**, Circuit diagram of the pulse generator circuit connected to a LiDB power pack. A reed switch was used to avoid interference. **b**, Charging curve of a 4700 μ F capacitor. **c** and **d**, By tuning the value of R_H and R_L , the pulse frequency was tuned from 2.5 to 10 Hz and the pulse width was tuned to 5 ms. **e**, Output voltage of 2.5 Hz pulses in one pacing cycle. One LiDB power pack could power 3 stimulation cycles.

Fig. 42 – Example 2 Extended Data Fig. 8 *Ex vivo* murine heart pacing by LiDBs. **a**, Wired contact for pacing. An ECG signal was monitored by three electrodes to reflect the heart responses. **b**, Image of the wired contact for atrial pacing. Scale bar, 1.2 cm. **c–e**, ECG spikes of an intrinsic heartbeat (**c**) and heartbeats during atrial (**d**) and ventricular (**e**) pacing powered by LiDBs. The arrow marks the time of the pacing signal. **f**, Upper, ECG signals of hearts under different pacing frequencies. Lower, ECG trace and the corresponding instantaneous pacing frequency during one 10 Hz pacing stimulation. **g**, Normalized counts of heart rates under 10 and 2.5 Hz pacing. 3 independent stimulations were counted.

Fig. 43 – Example 2 Supplementary Fig. 1 Infrared spectroscopy of silk pre-gel (blue) and UV-crosslinked hydrogel (red). Absorption assigned to the crystalline region increased due to the formation of β -sheet. Three absorption bands have been proposed at 1625, 1645, and 1660 cm^{-1} , associated with β -sheet, random coils, and α -helices, respectively^{6,7}. Samples were analyzed by using Fourier-transform infrared spectroscopy in attenuated total reflection mode.

Fig. 44 – Example 2 Supplementary Fig. 2 Compression responses of LiDBs. a and **b**, Cyclic compressive stress-strain curves of LiDBs under 0–50% (**a**) and 0–80% strain (**b**). **c**, Compressive modulus as a function of compressive strain. **d**, Relative capacities of LiDBs before and after 80% compressive strain. Data in **c** and **d** are mean values $\pm$ standard deviations (s.d.), $n = 5$.

Fig. 45 – Example 2 Supplementary Fig. 3 Cyclic voltammograms of the silk hydrogel (black), silk-LTO (blue) and silk-LMO (red) hydrogels at scan rates of 10 mV s⁻¹. A mass loading of 10% w/v LTO or LMO in the silk hydrogel was used.

Fig. 46 – Example 2 Supplementary Fig. 4 Scanning electron microscope images of the dehydrated silk-LMO (a) and silk-LTO (b) hydrogels. A volume loading of 30% v/v CNT and a mass loading of 10% w/v LMO or LTO in the silk hydrogel were used. Scale bars, 1 μ m.

Fig. 47 – Example 2 Supplementary Fig. 5 Volumetric capacities of LiDBs with different mass loadings of LMO in the cathode droplet and LTO in the anode droplet. Data are mean values $\pm$ s.d. ($n = 3$).

Fig. 48 – Example 2 Supplementary Fig. 6 Cyclic performance and rate capability of LiDBs at charge-discharge current of 0.5, 1, and 2 μ A. C_0 and C correspond to volumetric capacities before and after the cycle.

Fig. 49 – Example 2 Supplementary Fig. 7 Voltage-time curves measured for the LiDB. a, Output voltages of LiDBs after different storage times in oil before activation. **b**, Self-discharge of the LiDB after activation by formation of a hydrogel structure. Data are mean values $\pm$ s.d. ($n = 5$).

Fig. 50 – Example 2 Supplementary Fig. 8 Temperature of a LiDB at a charge-discharge current of 0.5 μ A. A temperature sensor with a probe size of less than 1 mm² was placed underneath the LiDB. 0.1 μ L droplets were used.

Fig. 51 – Example 2 Supplementary Fig. 9 Normalized open circuit voltage of LiDBs connected in series by underneath screen-printed carbon electrodes. 0.5 μ L droplets were used. Data are mean values $\pm$ s.d. ($n = 5$).

Fig. 52 – Example 2 Supplementary Fig. 10 6 LiDBs were connected to light up three red light-emitting diodes (a) and a liquid-crystal display timer (b).

Fig. 53 – Example 2 Supplementary Fig. 11 Measurement of the converting hydrogel droplets. a, Agarose droplets (2% w/v, 0.5 μ L) containing 100 mM potassium

chloride were used. The two terminal droplets (dark blue) contained the redox materials, such as poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS, 1.1% w/v) or I_3^- (0.6 M KI, 0.4 M I_2). The converting droplets were used to convert the electron flow from connected electrodes into the ionic flux in the central hydrogel droplet (light blue). When applying an input voltage on the electrodes, the ions in the converting droplets first formed electric double layers surrounding the electrodes (i), creating an initial current peak. Then, redox reactions occurred due to the presence of the redox materials in the converting droplets (ii). **b**, Measuring the current with gold electrodes by applying 500 mV input voltage. The redox materials can produce more ion flux and thus provide a higher current by comparison with pure electrodes. Although KI/ I_2 (Lugol solution, Sigma-Aldrich) could conduct a redox reaction, the large solubility of I_2 in oil limits its applicable time. Therefore, we used PEDOT:PSS for converting.

Fig. 54 – Example 2 Supplementary Fig. 12 Schematic to illustrate the two different stimulation approaches powered by LiDBs.

Fig. 55 – Example 2 Supplementary Fig. 13 Comparison of induced beating intervals of LiDBs with different droplet volumes. Control group stands for fully discharged LiDBs (intrinsic heartbeats). Data are mean values $\pm$ s.d. (n = 5).

Fig. 56 – Example 2 Supplementary Fig. 14 ECG traces of hearts at the times of LiDB attachment and detachment. Different extents of electrical stimulation were produced by using LiDBs with droplet volumes of 0.2 (a and b), 1 (c and d), and 3 μ L (e and f).

Fig. 57 – Example 2 Supplementary Fig. 15 ECG traces of hearts at the beginning and ending times of constant direct current stimulation through wired electrodes. Different extents of electrical stimulation were produced by applying currents of 15 (a and b), 30 (c and d), and 45 μ A (e and f).

Fig. 58 – Example 2 Supplementary Fig. 16 ECG traces of hearts before and after LiDB-enabled defibrillation. a and b, ECG traces of hearts during ventricular tachycardia (a) and after LiDB-enabled defibrillation (b). c and d, ECG traces of hearts during ventricular fibrillation (c) and after LiDB-enabled defibrillation (d).

Fig. 59 – Example 2 Supplementary Fig. 17 Cyclic voltammograms of the silk hydrogel without (grey) and with Ni-particles (black) at a scan rate of 10 mV s⁻¹.

Fig. 60 – Example 2 Supplementary Fig. 18 Images of the maze filled with oil (a) and the double-deck well filled with oil and aqueous solution with blue dye (b).

Scale bars, 2 cm.

Fig. 61 – Example 2 Supplementary Fig. 19 The 1st (a) and 10th (b) charging cycle of a 2 mF capacitor by the magnetically driven LiDB. The capacitor was connected to the target electrodes in the maze to collect the delivered energy of each cycle.

Fig. 62 – Example 2 Supplementary Fig. 20 Organogel encapsulation enabled preservation of LiDBs in physiological environments. Left, Schematic showing droplets without (i) and with (ii) poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) triblock copolymer encapsulation. Right, cyclic performance of LiDBs at a charging-discharging current of 1 μ A. C_0 corresponds to the battery capacity before immersion in phosphate-buffered saline (pH 7.4, Gibco). C corresponds to the capacities after the charging-discharging cycle. Data are mean values $\pm$ s.d. ($n = 3$).

Fig. 63 – Example 3 Fig. 1 The chemistry occurring in the enzyme-enabled droplet biobattery. (a), A droplet biobattery is created by separating oxidation and reduction reactions in a droplet pair. In the cathode droplet (green), Lac catalyzes oxygen reduction, consuming electrons. In the anode droplet, NADH undergoes oxidation, generating electrons. Electron transfer between gold electrodes and the aqueous phase is facilitated by ABTS in the cathode droplet and AQDS in the anode droplet, which serve as electron shuttles. The redox reaction drives electron flow in an external circuit, which is accompanied by the transport of monocations in the aqueous droplets, such as sodium ions (Na^+), and protons (H^+), across the DIB through monocation-selective gA channels to maintain charge balance. (b) Photograph of a droplet biobattery. Scale bar, 200 μm . (c) Electrochemical reactions occurring in the anode and cathode droplets. (d) Short-circuit current and open-circuit voltage traces of a droplet biobattery recorded over 1h with a patch-clamp amplifier. Data are presented as mean values $\pm$ standard deviations (s.d.), $n=5$.

Detailed description

The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. Any reference signs in the claims shall not be construed as limiting the scope. Of course, it is to be understood that not necessarily all aspects or advantages may be achieved

in accordance with any particular embodiment of the invention. Thus, for example those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other aspects or advantages as may be taught or suggested
5 herein.

The invention, both as to organization and method of operation, together with features and advantages thereof, may best be understood by reference to the following detailed description when read in conjunction with the accompanying drawings. The aspects and advantages of the invention will be apparent from and elucidated with
10 reference to the embodiment(s) described hereinafter. Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not
15 necessarily all referring to the same embodiment, but may. Similarly, it should be appreciated that in the description of exemplary embodiments of the invention, various features of the invention are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of one or more of the various inventive aspects. This method of disclosure,
20 however, is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment.

It should be appreciated that "embodiments" of the disclosure can be specifically combined
25 together unless the context indicates otherwise. The specific combinations of all disclosed embodiments (unless implied otherwise by the context) are further disclosed embodiments of the claimed invention.

In addition as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. Thus,
30 for example, reference to "a droplet" includes two or more droplets, reference to "a motor protein" includes two or more such proteins, reference to "a salt" includes two or more

salts, reference to “a monomer” refers to two or more monomers, reference to “an amphipathic molecule” includes two or more amphipathic molecules and the like. All publications, patents and patent applications cited herein, whether supra or infra, are hereby incorporated by reference in their entirety.

5

Definitions

Where an indefinite or definite article is used when referring to a singular noun e.g. “a” or “an”, “the”, this includes a plural of that noun unless something else is specifically stated. Where the term "comprising" is used in the present description and claims, it does not exclude other elements or steps. Furthermore, the terms first and second and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order.

“About” as used herein when referring to a measurable value such as an amount and the like, is meant to encompass variations of $\pm 20\%$ or $\pm 10\%$, more preferably $\pm 5\%$, even more preferably $\pm 1\%$, and still more preferably $\pm 0.1\%$ from the specified value, as such variations are appropriate to perform the disclosed methods.

Where a droplet is described as “separated from its one or more neighbouring droplets” this means that there is no, or substantially no, diffusion of any chemical matter (for instance, anions, cations, and/or a solvent, such as water) between the contents of the droplet and the contents of its one or more neighbouring droplets. Said another way, the droplets are not diffusively continuous with one another.

Where a compartment is described as “diffusively continuous with its one or more neighbouring compartments” this means that at least some chemical matter (for instance, at least anions, cations, and/or a solvent, such as water) is able to diffuse from one compartment into another.

Power unit (1)

As discussed above, the power unit of the invention is a power unit comprising a series of droplets, wherein said series of droplets comprises:
one or more first droplets, and
one or more second droplets,

wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein

each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

5 The power unit of the invention is thus a form of battery in an inactive state - it contains a potential energy difference across a barrier that can be made selectively permeable. In one embodiment, the barrier is an amphiphilic between a first droplet and second droplet. However, in a preferred embodiment, the barrier is a separator droplet. Thus, in a preferred embodiment of the invention, the power unit is a power unit
10 comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more first droplets,
- (b) one or more separator droplets, and
- (c) one or more second droplets,

15 wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

The skilled person would be aware that any battery chemistry can in principle be
20 employed within the power unit of the invention to provide a potential energy difference between the one or more first droplets and the one or more second droplets. However, in a preferred embodiment of the invention, the potential energy difference is an ionic gradient (i.e. a difference in salt concentration across the barrier). This potential energy difference can be converted into an electromotive force across the barrier when the barrier is made
25 selectively permeable to the either the cationic portion of the salt or the anionic portion of the salt (for instance, by the introduction of ion-selective channels in the amphiphilic membrane, or by the use of an anionic or cationic polymer within the separator droplets). Thus, in a preferred embodiment, the first droplets are droplets of high salt fluids and the second droplets are droplets of salt diffusion target fluids (wherein the “high salt fluid”
30 contains one or more salts in a concentration higher than that of the “salt diffusion target fluid” such that there is a driving force for an anion or cation of the salt to diffuse across the anion or cation-selective permeable barrier to the “salt diffusion target fluid”).

Accordingly, it is preferred that the power unit of the invention is a power unit comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more high salt fluids,
- 5 (b) one or more droplets of one or more cation selective fluids or one or more droplets of one or more anion selective fluids, and
- (c) one or more droplets of one or more salt diffusion target fluids, and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

10 In this case, the above droplets of one or more cation selective fluids/droplets of one or more anion selective fluids are separator droplets.

Suitably, an increased current may be obtained in the power unit of the invention by arranging a number of series of droplets in parallel. Thus, it is preferred that the power unit comprises a plurality of series of droplets, wherein the plurality of series of droplets
15 are arranged in parallel such that droplets of the same type within each series of droplets are positioned adjacent to one another.

As discussed above, in a particularly preferred embodiment the present invention provides a power unit comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- 20 (a) one or more droplets of one or more high salt fluids,
- (b) one or more droplets of one or more cation selective fluids,
- (c) one or more droplets of one or more salt diffusion target fluids,
- (d) one or more droplets of one or more anion selective fluids, and
- (e) one or more droplets of one or more high salt fluids;
- 25 wherein the one or more droplets of the above (a) may be the same one or more droplets as the one or more droplets of the above (e), and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

Where the one or more droplets of the above (a) are the same one or more droplets
30 as the one or more droplets of the above (e), the power unit is present in a circular form, wherein the cations and anions from the high salt fluids move in different directions around the circle.

Thus, this particularly preferred embodiment of the invention contains two droplets as barriers, wherein one barrier can be made selectively permeable to the cationic portion of the salt in the one or more droplets of the above (a) and the other barrier can be made selectively permeable to the anionic portion of the salt in the one of droplets of the above (e) (such that cations from the one or more droplets of the above (a) and anions from the one or more droplets of the above (e) will be able to diffuse into the one or more droplets of the above (c)). Thus, when the barriers are made permeable, an electromotive force is created across the one or more droplets of (a) and the one of more droplets of the above (e).

10 This embodiment of the invention is particularly preferred as it allows for the voltage of the power unit of the invention to be conveniently increased by placing the series of droplets (a) to (e) in a series arrangement in order to increase the overall voltage of the power unit. Thus, it is preferred that the series of droplets of the particularly preferred embodiment further comprises, between the one or more droplets of the above (a) and the one or more droplets of the above (b), an optionally repeating sub-series of droplets comprising, in this order:

- (i) one or more droplets of one or more cation selective fluids,
- (ii) one or more droplets of one or more salt diffusion target fluids,
- (iii) one or more droplets of more or more anion selective fluids, and
- 20 (iv) one or more droplets of one or more high salt fluids.

In the broader embodiments of the power source of the invention, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids. More preferably, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids that are each solutions or suspensions in a droplet medium, wherein solutions in a droplet medium are most preferred.

Similarly, the one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids, and one or more anion selective fluids are each solutions or suspensions in a droplet medium, wherein solutions in a droplet medium are most preferred.

The droplet medium may be any liquid medium that is immiscible with one or more other liquid media and so may be a fluorinated solvent, an organic solvent, oil (for

example, one or more of a mineral oil, a vegetable oil (such as olive oil, canola oil, peanut oil, avocado oil or sunflower oil) or a synthetic oil (such as a polyalphaolefin or silicone oil), preferably a hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), more preferably still hexadecane, undecane and/or polyphenylmethylsiloxane, most preferably undecane and/or polyphenylmethylsiloxane), or water. Suitably, the droplet medium is oil or water. The droplet medium is most preferably water.

Preferably, the power unit of the invention is suspended in a suspension medium that is immiscible with the droplet medium, and so may also be any liquid medium that is immiscible with one or more other liquid media and so may be a fluorinated solvent, an organic solvent, oil (for example, one or more of a mineral oil, a vegetable oil (such as olive oil, canola oil, peanut oil, avocado oil or sunflower oil) or a synthetic oil (such as a polyalphaolefin or silicone oil), preferably a hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), more preferably still hexadecane, undecane and/or polyphenylmethylsiloxane, most preferably undecane and/or polyphenylmethylsiloxane), or water. Suitably, the suspension medium is oil or water. The suspension medium is preferably oil.

Thus, in a preferred embodiment, the droplet medium is water, and the suspension medium is a hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), preferably undecane and/or polyphenylmethylsiloxane.

In the broader embodiments of the power source of the invention, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets preferably each contain one or more gelling agents. More preferably, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets each contain the same one or more gelling agents. More preferably still, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets each contain one gelling agent, most preferably the same one gelling agent.

Similarly, the one or more high salt fluids, one or more cation selective fluids, one or more low salt fluids, and one or more anion selective fluids each contain one or more gelling agents. More preferably, the one or more high salt fluids, one or more cation selective fluids, one or more low salt fluids, and one or more anion selective fluids each contain the same one or more gelling agents. More preferably still, the one or more high salt fluids, one or more cation selective fluids, one or more low salt fluids, and one or more anion selective fluids each contain one gelling agent, most preferably the same one gelling agent.

Preferably, each gelling agent is a polymer or a polymerizable monomer or oligomer. As the droplet medium is most preferably water, the gelling agent is preferably a hydrogel gelling agent.

Typically, the polymer gelling agent is selected from a polysaccharide (such as agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (such as DNA and RNA), a polyamide (such as collagen, gelatin, and silk fibroin, most preferably silk fibroin), a polyphenol (such as ligin), a polyester (such as polycaprolactone and polylactic acid), a polyether (such as polyethyleneglycol), a vinyl polymer (such as polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (such as polyacrylic acid), an acrylamide polymer (such as polyacrylamide). The polymer gelling agent may also be a copolymer or a grafted form of one or more of the previously-recited polymers, and may contain functional groups that permit the polymer to be crosslinked (such as acryloyl groups). Preferably, the polymer gelling agent is a polysaccharide, a polynucleic acid, a polyamide, or a polyphenol. More preferably, the polymer gelling agent is a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably agarose. Polysaccharides and polyamides (such as agarose and silk fibroin) are particularly preferred owing to their ease of digestibility, for instance by agarases and peptidases (respectively). This provides the power source of the invention with advantageous degradability, specifically biodegradability.

Typically, the polymerizable monomer or oligomer gelling agent is a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde

group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group. More preferably, the polymerizable monomer or oligomer gelling agent is a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group),
5 particularly preferably methyl acrylate, methyl methacrylate and acrylamide, most preferably acrylamide.

Most preferably, the gelling agent is a polymer gelling agent.

The gelling agent may be gelled by any means known to a person skilled in the art.

For instance, the polymer gelling agents may be gelled by heating, cooling,
10 crosslinking (using chemical agents (such as glutaraldehyde and N,N'-methylene-bis-acrylamide) and/or by ultraviolet light). In one embodiment, the polymer gelling agent is agarose, and the agarose is gelled by cooling (for instance to below 37 °C, preferably below 25 °C, more preferably below 10 °C, preferably around 4 °C). In another embodiment, the polymer gelling agent is silk fibroin, and the silk fibroin is gelled with
15 UV light. In one embodiment, the silk fibroin is gelled by crosslinking tyrosine residues within the silk fibroin protein backbones with UV light (i.e. light having a wavelength of from 100 to 400 nm, preferably 200 to 400 nm, more preferably 300 to 400 nm, more preferably still 350 to 400 nm, most preferably around 365 nm) by use of a photocatalyst (preferably a homogeneous photocatalyst, preferably an iridium or ruthenium
20 photocatalyst, most preferably $\text{Ru(II)(bpy)}_3^{2+}$) the presence of an oxidant (preferably a perchlorate or persulfate oxidant, preferably a persulfate oxidant, most preferably sodium persulfate). It will be appreciated that many gelling agents, particularly polyamide gelling agents, may be modified to have groups (like tyrosine) which are capable of undergoing UV crosslinking as discussed above.

25 Thus, typically, when the gelling agent is a gelling agent susceptible to crosslinking under UV light, the fluids containing the gelling agent contain both a photocatalyst (as defined above) and an oxidant (as defined above). Typically, the photocatalyst is present in the fluids containing the gelling agent in an amount of from 0.05 to 20 mM, preferably 0.1 to 10 mM, more preferably 0.5 to 5 mM, more preferably still 0.7 to 2 mM, most
30 preferably around 1 mM. Analogously, the oxidant is present in the fluids containing the gelling agent in an amount of from 0.2 to 50 mM, preferably 0.5 to 20 mM, more preferably 1 to 10 mM, more preferably still 3 to 7 mM, most preferably around 5 mM.

The use of gelling agents susceptible to crosslinking under UV light (such as silk fibroin) is particularly advantageous in that it enables the remote control of gelling. This is particularly advantageous in the context of the remote activation of the power sources of the invention, where crosslinking can rupture the amphiphilic membranes of the power sources of the invention (as discussed further below). In principle, any number of gelling agents may be made susceptible to crosslinking under UV light by the addition of UV-crosslinking groups known to the person skilled in the art (i.e. by the modification of gelling agents with groups such as alkenes (optionally conjugated to an electron-withdrawing group, such as a carbonyl or nitrile group) or with phenolic moieties (like those of tyrosine).

Silk fibroin is further preferable in that it has a number of physicochemical properties that renders it particularly suitable for use as a matrix material for the power unit of the invention. Thus, silk fibroin (when gelled) has elastic behaviour, providing flexibility and compressibility with a modulus of ~10 kPa at 80% compression. It is, further, biocompatible, biodegradable (as discussed further above), and strongly adhesive towards tissues, properties which are advantageous for biological use.

Typically, the polymerizable monomer or oligomer gelling agent is gelled by polymerisation, optionally in the presence of a crosslinker (for instance a carbodiimide or similar, or a bis-acrylamide (such as N,N'-methylene-bis-acrylamide) or similar). The polymerization may be any form of polymerisation (e.g. acid catalysed or base catalysed polymerisation, or radical polymerisation). However, typically, the polymerisation is radical polymerisation. In one embodiment, the polymerizable monomer or oligomer gelling agent is acrylamide and the acrylamide is gelled with UV light (with a photoinitiator) in the presence of N,N'-methylene-bis-acrylamide.

The gelling agent may be present in the droplets (in the fluids) in any concentration that is suitable for providing a gel. For instance, the polymer gelling agent may be present in an amount of from 0.1 to 50% w/v, preferably from 0.5 to 25% w/v, more preferably from 1 to 10% w/v, more preferably still from 1.5 to 5% w/v, most preferably around 2% w/v. The polymerizable monomer or oligomer gelling agent may be present in an amount of from 1 to 70% w/v, preferably 5 to 60% w/v, more preferably 20 to 50% w/v, most preferably around 40% w/v.

For the avoidance of doubt, where the droplets contain a gelling agent, the gelling agent is preferably not gelled or is only partly gelled (for instance to provide not more than 10%, not more than 20%, or not more than 50% of the strength of the fully-gelled form).

Said one or more high salt fluids each contain one or more salts. Preferably, the
 5 total concentration of the one or more salts in each of the one or more high salt fluids is independently from 10 M to 0.2 M, preferably from 5 M to 0.5 M, more preferably from 4 M to 1 M, even more preferably from 2.5 to 1.5 M. Most preferably, the total concentration of the one or more salts in each of the one or more high salt fluids is around 2 M.

10 Said one or more salt diffusion target fluids each contain no salt or contain one or more salts. Thus, in one embodiment, said one or more salt diffusion target fluids each contain no salt. In another embodiment, said one or more salt diffusion target fluids each contain one or more salts.

Where one or more salt diffusion target fluids contain one or more salts, the total
 15 concentration of the one or more salts in the one or more salt diffusion target fluids is independently from 0.05 M to 0.001 M, preferably from 0.03 M to 0.002 M, more preferably from 0.02 M to 0.005 M, even more preferably from 0.015 to 0.005 M. Most preferably, the total concentration of the one or more salts in the one or more salt diffusion target fluids is around 0.01 M.

20 Additionally, or alternatively, where one or more salt diffusion target fluids contain one or more salts, the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 2000 to 1.1 times, preferably 1000 to 10 times, preferably from 800 to 50 times, more preferably from 500 to 100 times, even more preferably from 300 to 150 times, higher than the total concentration of the one or more
 25 salts in the salt diffusion target fluids. Most preferably, the total concentration of the one or more salts in each of the one or more high salt fluids is around 200 times higher than the total concentration of the one or more salts in the salt diffusion target fluids.

Typically, the one or more salts (i.e. contained within the one or more high salt fluids and within one or more salt diffusion target fluids when the one or more salt
 30 diffusion target fluids contain one or more salts) are each independently salts of the formula $A^{p+}_n X^{q-}_m$, wherein:

A is selected from metal cations and organic cations;

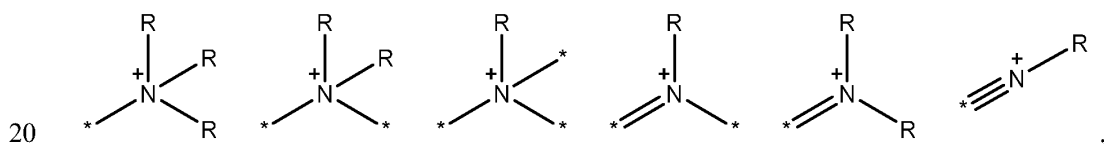
X is selected from halogen anions, inorganic anions, and organic anions; and

p, q, n and m are each integers from 1 to 4, wherein $p \times n = q \times m$.

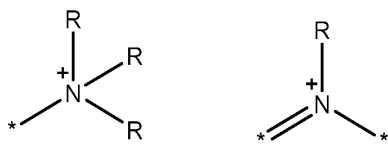
Typically, the salts are salts that are soluble in the droplet medium. Accordingly, preferably, the salts are salts that are soluble in water.

- 5 Preferably, the metal cations are cations of the metals of groups I to XV of the periodic table. More preferably, the metal cations are cations of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Y, Lu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi and P. More preferably still, the metal cations are cations of Li, Na, K, Rb, Be, Mg, Ca, Sr, Sc, Y, Ti, 10 Zr, V, Nb, Cr, Mo, Mn, Tc, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ga, In, Ge, Sn and Sb. Even more preferably, the metal cations are cations of Li, Na, K, Be, Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga and Ge. Even more preferably, the metal cations are cations of Li, Na, K, and Ca. In a most preferred embodiment, the metal cation is a cation of Ca (i.e. Ca^{2+}).

- 15 Preferably, the organic cations are organic cations of carbon-based molecules (preferably carbon-based molecules having a molecular weight of less than 500 g/mol, more preferably less than 400 g/mol, most preferably less than 300 g/mol). Preferably, the organic cations of carbon-based molecules are molecules having at least one of the following cationic groups:



and more preferably one of the following cationic groups



- wherein * denotes a point of attachment to the remainder of the molecule, and each R is independently selected from H or C_{1-6} alkyl (preferably C_{1-3} alkyl, more 25 preferably methyl), most preferably methyl.

Preferably, each * independently indicates a point of attachment to a group selected from the list consisting of an optionally substituted C_{1-6} alkyl group, an optionally

substituted C₃₋₁₄ carbocyclic group, or an optionally substituted 5-14 membered heterocyclic group having from 1 to 4 heteroatoms selected from O, N and S, or

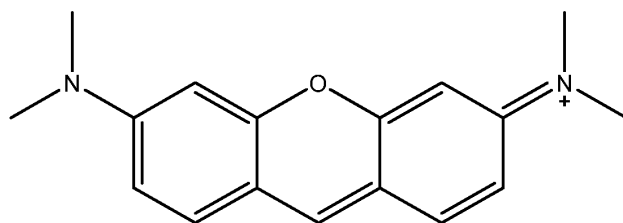
two * indicate points of attachment within an optionally substituted 5-14 membered heterocyclic group having from 1 to 4 heteroatoms selected from O, N and S, wherein at

5 least one heteroatom is N.

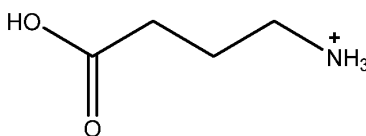
Typically, there may be 1 or 2 optional substituents on each of the above optionally substituted groups. More typically, there is 1 substituent on each of the above groups.

Preferably, the substituents are independently selected from the group consisting of one of the cationic groups as defined above, halogen, C₁₋₆ alkyl, OH, OC₁₋₆ alkyl, -NH₂,
 10 NHC₁₋₆ alkyl, N(C₁₋₆ alkyl)₂, CN, NO₂, COOH, COOC₁₋₆ alkyl, CONH₂, CONHC₁₋₆ alkyl, CON(C₁₋₆ alkyl)₂, SO₂NH₂, SO₂NHC₁₋₆ alkyl and SO₂N(C₁₋₆ alkyl)₂, wherein, preferably, each C₁₋₆ alkyl is C₁₋₃ alkyl. More preferably, the substituents are independently selected from the group consisting of one of the cationic groups as defined above, halogen, C₁₋₃ alkyl, OH, OC₁₋₃ alkyl, -NH₂, NHC₁₋₃ alkyl, N(C₁₋₃ alkyl)₂, CN, COOH, and COOC₁₋₃
 15 alkyl.

Most preferably, the organic cations are cations selected from the ammonium cation, the tetramethylammonium cation, the pyronine Y cation, i.e.



or the gaba cation, i.e.



20

A is most preferably selected from metal cations.

Preferably, the halogen anions are selected from fluoride, chloride, bromide and iodide. More preferably, the halogen anions are selected from fluoride, chloride and bromide. Most preferably, the halogen anion is chloride.

25 Preferably, the inorganic anions are anions selected from the group consisting of ClO₄⁻, BF₄⁻, NO₃⁻, NO₂⁻, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, NCS⁻, PF₆⁻, SiF₆⁻, SbF₆⁻, CN⁻, CF₃SO₃⁻,

SO_4^{2-} and N_3^- . More preferably, the inorganic anions are anions selected from the group consisting of BF_4^- , NO_3^- , NO_2^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , PF_6^- , SiF_6^- , CF_3SO_3^- and SO_4^{2-} .

Preferably, the organic anions are anions of the formula RSO_3^- , as will be well known to the person skilled in the art. Typically, however, R is C_{1-3} alkyl or optionally substituted phenyl. Preferably, R is methyl or optionally substituted phenyl. The optional substituents of the phenyl group may 1 or 2 substituents selected from halogen (preferably fluorine, chloride, bromine or iodine), NO_2 , or C_{1-3} alkyl (preferably methyl), most preferably one methyl substituent. Most preferably the organic anions are selected from mesylate, tosylate and nosylate.

10 X is most preferably selected from halogen anions.

The one or more salts may advantageously each be independently selected from lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride. More preferably, the one or more salts are each independently selected from lithium chloride, sodium chloride, potassium chloride and calcium chloride.

15 Most preferably, only one salt is used and the salt used is calcium chloride.

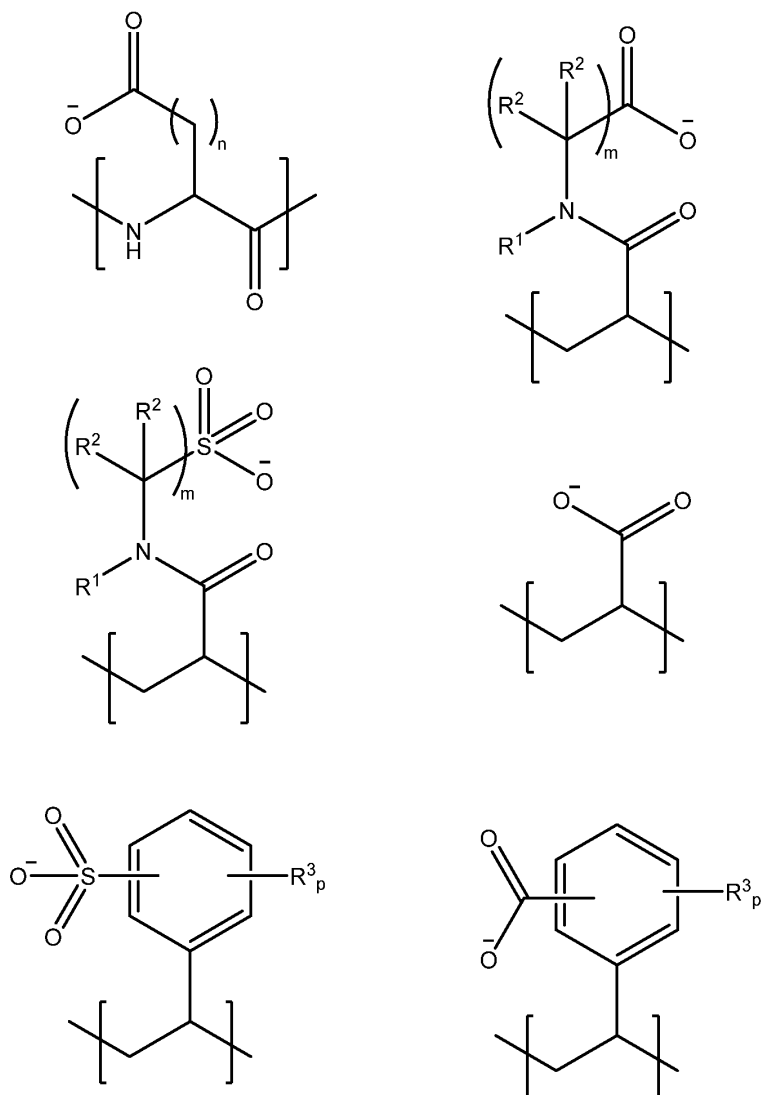
Preferably, the cation-selective fluids contain one or more polymers having anionic groups attached to, or forming part of, the polymer backbone, also known herein as anionic polymers. Any anionic polymer may in principle be used in the present invention. The anionic polymer may be a homopolymer or a copolymer. The anionic groups within the anionic polymer may be introduced into the polymer either through direct polymerisation of anionic monomers, or by post-treatment of a neutral polymer.

Preferably, at least 10% (such as at least 20%, at least 30 %, at least 40% or at least 50%) of the monomeric units within the anionic polymer contains an anionic group. More preferably, at least 70% of the monomeric units within the anionic polymer contains an anionic group. More preferably still, at least 90% of the monomeric units within the anionic polymer contains an anionic group. Most preferably, all of the monomeric units within the anionic polymer contain an anionic group.

The anionic groups within the monomeric units are preferably carboxylate or sulfonate groups, most preferably sulfonate.

30 Suitable monomeric units containing an anionic group are, for instance, polystyrene monomeric units containing a sulfonate or carboxylate group on the benzene ring, polypeptide monomeric units having a carboxylate group (i.e. an aspartate monomeric unit

or a glutamate monomeric unit), polyacrylamide monomeric units having a sulfonate or carboxylate group, and polyacrylate monomeric units. Thus, typical monomeric units are units of the following formulae:



5

wherein

n is an integer from 0 to 3 (preferably 1 or 2),

m is an integer from 1 to 4 (preferably 2 or 3),

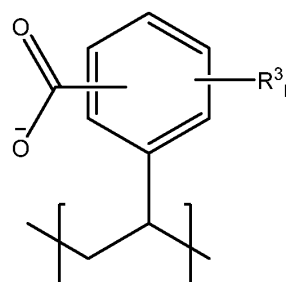
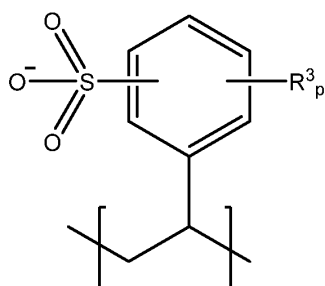
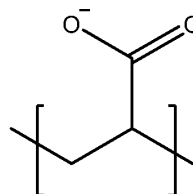
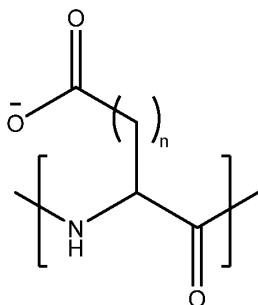
p is an integer from 0 to 2 (preferably 0),

*R*¹ and *R*² are each independently selected from H or C₁₋₃ alkyl (preferably methyl),

10 and

R^3 is each independently selected from halogen (preferably Cl or Br) and C_{1-3} alkyl (preferably methyl).

Preferred monomeric units are units of the following formulae:



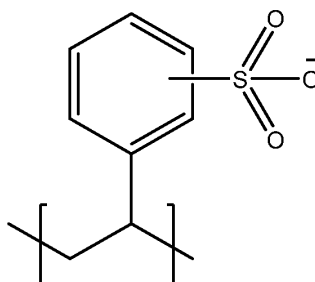
5

wherein

n is an integer from 0 to 3 (preferably 1 or 2), and

R^3 is each independently selected from halogen (preferably Cl or Br) and C_{1-3} alkyl (preferably methyl).

Particularly preferred monomeric units are units of the following formula:



10

Typically, the anionic groups have one or more associated cations in order to maintain charge neutrality. The cations may be any cation as defined above in connection with the one or more salts. However, preferably, the cations are metal cations (most

preferably Li^+ , Na^+ , or K^+) or ammonium cations (i.e. NR_4^+ , wherein each R is independently H or C_{1-6} alkyl, preferably H or C_{1-3} alkyl, most preferably H or methyl).

Particularly preferred anionic polymers (i.e. polymers having anionic groups attached to, or forming part of, the polymer backbone) are poly(sodium 4-
 5 styrenesulfonate), poly(sodium 3-styrenesulfonate), poly(sodium 2-styrenesulfonate), poly-L-glutamic acid sodium, poly-L-aspartic acid sodium, poly(sodium 2-acrylamino-2-methylpropane sulfonate), poly(sodium acrylate), poly(potassium 4-styrenesulfonate), poly(potassium 3-styrenesulfonate), poly(potassium 2-styrenesulfonate), poly-L-glutamic acid potassium, poly-L-aspartic acid potassium, poly(potassium 2-acrylamino-2-
 10 methylpropane sulfonate), poly(sodium 2-acrylamino-2-methylpropane sulfonate), poly(potassium acrylate), poly(ammonium 4-styrenesulfonate), poly(ammonium 3-styrenesulfonate), poly(ammonium 2-styrenesulfonate), poly-L-glutamic acid ammonium, poly-L-aspartic acid ammonium, poly(ammonium 2-acrylamino-2-methylpropane sulfonate), poly(ammonium 2-acrylamino-2-methylpropane sulfonate), poly(ammonium
 15 acrylate). More preferably, the anionic polymers (i.e. polymers having anionic groups attached to, or forming part of, the polymer backbone) are poly(sodium 4-styrenesulfonate), poly(sodium 3-styrenesulfonate), poly(sodium 2-styrenesulfonate), poly-L-glutamic acid sodium, poly-L-aspartic acid sodium, poly(sodium acrylate), poly(potassium 4-styrenesulfonate), poly(potassium 3-styrenesulfonate), poly(potassium 2-
 20 styrenesulfonate), poly-L-glutamic acid potassium, poly-L-aspartic acid potassium, poly(potassium acrylate), poly(ammonium 4-styrenesulfonate), poly(ammonium 3-styrenesulfonate), poly(ammonium 2-styrenesulfonate), poly-L-glutamic acid ammonium, poly-L-aspartic acid ammonium, poly(ammonium acrylate). Particularly preferably, the anionic polymers (i.e. polymers having anionic groups attached to, or forming part of, the
 25 polymer backbone) are poly(sodium 4-styrenesulfonate), poly(potassium 4-styrenesulfonate) and poly(ammonium 4-styrenesulfonate). Most preferably, only one anionic polymer is used, and the anionic polymer is poly(sodium 4-styrenesulfonate).

The concentration of the one or more polymers having anionic groups attached to, or forming part of, the polymer backbone within the cation-selective fluids is unrestricted.
 30 However, typically, the anionic polymer is present in a concentration of from 1 to 50% w/v, preferably 5 to 40% w/v, more preferably 10 to 30% w/v, most preferably around 20% w/v.

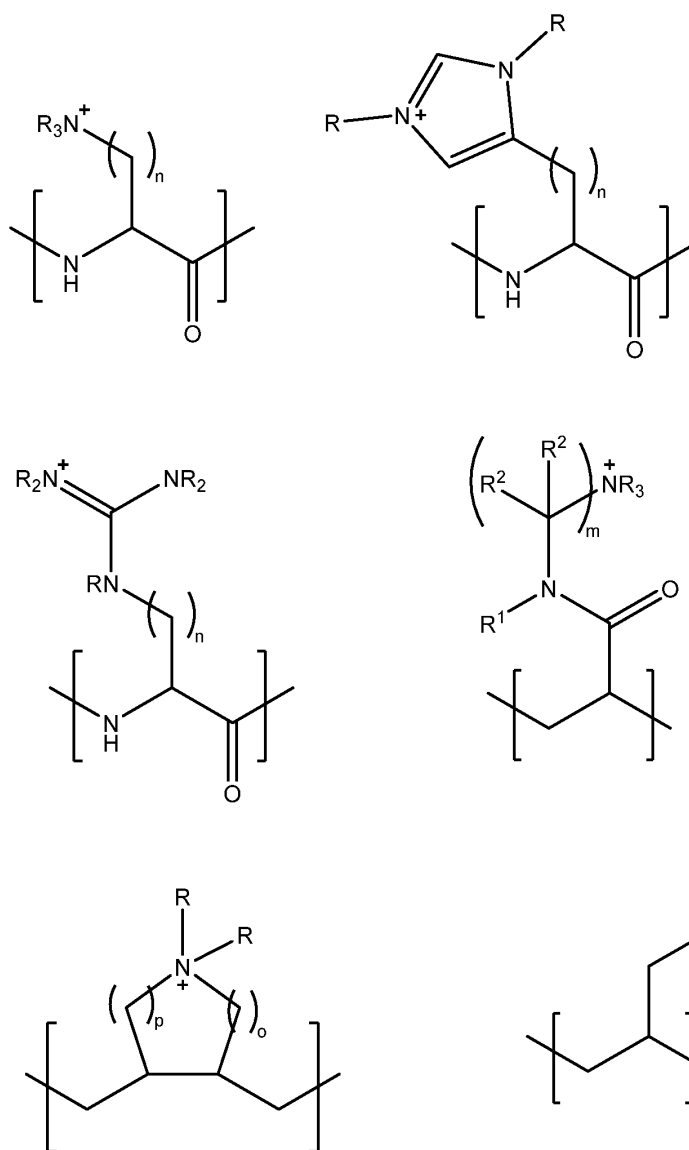
The molecular weight of the one of the one or more polymers having anionic groups attached to, or forming part of, the polymer backbone within the cation-selective fluids is unrestricted. However, typically, the anionic polymer has a weight average molecular weight of around 10,000 to 200,000 g/mol, preferably around 20,000 to 150,000 g/mol, more preferably around 30,000 to 100,00 g/mol, most preferably around 40,000 to 80,000 g/mol.

Preferably, the anion-selective fluids contain one or more polymers having cationic groups attached to, or forming part of, the polymer backbone, also known herein as cationic polymers. Any cationic polymer may in principle be used in the present invention, including those discussed in Chem. Soc. Rev., 2012, 41, 7147-7194. The cationic polymer may be a homopolymer or a copolymer. The cationic groups within the cationic polymer may be introduced into the polymer either through direct polymerisation of cationic monomers, or by post-treatment of a neutral polymer.

Preferably, at least 10% (such as at least 20%, at least 30 %, at least 40% or at least 50%) of the monomeric units within the cationic polymer contains a cationic group. More preferably, at least 70% of the monomeric units within the cationic polymer contains a cationic group. More preferably still, at least 90% of the cationic units within the cationic polymer contains a cationic group. Most preferably, all of the monomeric units within the cationic polymer contain a cationic group.

The cationic groups within the monomeric units are preferably imidazolium groups ammonium groups or guanidium groups, most preferably ammonium groups.

Suitable monomeric units containing a cationic group are, for instance, polypeptide monomeric units having an imidazolium, ammonium or guanidium group (i.e. an histidine monomeric unit, a lysine monomeric unit or an arginine monomeric unit), polyacrylamide monomeric units having an ammonium group, a cyclic ammonium monomeric unit, and allylammonium monomeric units. Thus, typical monomeric units are units of the following formulae:



wherein

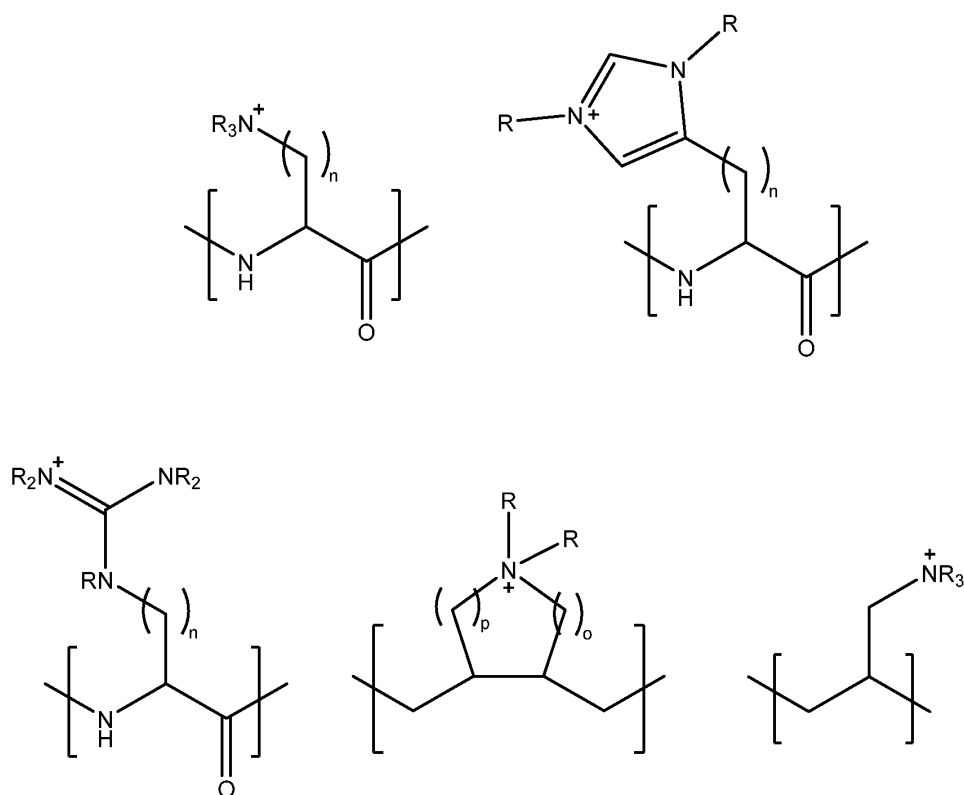
n is an integer from 1 to 4,

m is an integer from 1 to 4 (preferably 2 or 3),

5 p and o are each an integer from 0 to 2, with the proviso that $p+o$ is at least 2 (wherein preferably p and o are each 1),

R , R^1 and R^2 are each independently selected from H or C_{1-3} alkyl (preferably methyl).

Preferred monomeric units are units of the following formulae:



wherein

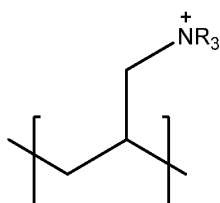
n is an integer from 1 to 4,

p and o are each an integer from 0 to 2, with the proviso that p+o is at least 2

5 (wherein preferably p and o are each 1),

R are each independently selected from H or C₁₋₃ alkyl (preferably methyl).

Particularly preferred monomeric units are units of the following formula:



Typically, the cationic groups have one or more associated anions in order to
 10 maintain charge neutrality. The anion may be any anion as defined above in connection
 with the one or more salts. However, preferably, the anions are halogen anions or

inorganic anions. Particularly preferably, the anions are halogen anions, most preferably chloride or bromide.

Particularly preferred cationic polymers (i.e. polymers having cationic groups attached to, or forming part of, the polymer backbone) are poly-L-lysine hydrochloride, poly-L-histidine hydrochloride, poly-L-arginine hydrochloride, poly (3-
 5 acrylamidopropyltrimethylammonium chloride, poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), poly-L-lysine hydrobromide, poly-L-histidine hydrobromide, poly-L-arginine hydrobromide, poly (3-
 acrylamidopropyltrimethylammonium bromide, poly(diallyldimethylammonium bromide),
 10 and poly(allylamine hydrobromide). More preferably, the cationic polymers are poly-L-lysine hydrochloride, poly-L-histidine hydrochloride, poly-L-arginine hydrochloride, poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), poly-L-lysine hydrobromide, poly-L-histidine hydrobromide, poly-L-arginine hydrobromide, poly(diallyldimethylammonium bromide), and poly(allylamine hydrobromide).
 15 Particularly preferably, the cationic polymers (i.e. polymers having cationic groups attached to, or forming part of, the polymer backbone) are poly(allylamine hydrochloride) and poly(allylamine hydrobromide). Most preferably, only one cationic polymer is used, and the cationic polymer is poly(allylamine hydrochloride).

The concentration of the one or more polymers having cationic groups attached to, or forming part of, the polymer backbone within the anion-selective fluids is unrestricted.
 20 However, typically, the cationic polymer is present in a concentration of from 1 to 50% w/v, preferably 5 to 40% w/v, more preferably 10 to 30% w/v, most preferably around 20% w/v.

The molecular weight of the one of the one or more polymers having cationic groups attached to, or forming part of, the polymer backbone within the anion-selective fluids is unrestricted. However, typically, the cationic polymer has a weight average molecular weight of around 10,000 to 200,000 g/mol, preferably around 20,000 to 150,000 g/mol, more preferably around 30,000 to 100,00 g/mol, most preferably around 40,000 to 80,000 g/mol.

30 Preferably, the droplets of the power units of the invention are biocompatible droplets. Suitably, biocompatible droplets are droplets in which:

(a) the droplet medium is water,

(b) the one or more gelling agents (if present) are each a polymer gelling agent as defined above (wherein, preferably, the polymer gelling agent is a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably agarose),

(c) the one or more salts are non-toxic (and are preferably lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride; more preferably, the one or more salts are each independently selected from lithium chloride, sodium chloride, potassium chloride and calcium chloride; most preferably, only one salt is used and the salt used is calcium chloride); and

(d) the cationic and anionic polymers are not polymers having polyacrylamide monomeric units (and, preferably, the cationic polymers are poly-L-lysine hydrochloride, poly-L-histidine hydrochloride, poly-L-arginine hydrochloride, poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), poly-L-lysine hydrobromide, poly-L-histidine hydrobromide, poly-L-arginine hydrobromide, poly(diallyldimethylammonium bromide), and poly(allylamine hydrobromide); and, preferably, the anionic polymer is poly(sodium 4-styrenesulfonate), poly(sodium 3-styrenesulfonate), poly(sodium 2-styrenesulfonate), poly-L-glutamic acid sodium, poly-L-aspartic acid sodium, poly(sodium acrylate), poly(potassium 4-styrenesulfonate), poly(potassium 3-styrenesulfonate), poly(potassium 2-styrenesulfonate), poly-L-glutamic acid potassium, poly-L-aspartic acid potassium, poly(potassium acrylate), poly(ammonium 4-styrenesulfonate), poly(ammonium 3-styrenesulfonate), poly(ammonium 2-styrenesulfonate), poly-L-glutamic acid ammonium, poly-L-aspartic acid ammonium, and poly(ammonium acrylate).

Typically, the amphipathic membrane is a layer formed from amphiphilic molecules, which have both at least one hydrophilic portion and at least one lipophilic or hydrophobic portion. The amphiphilic layer may be a monolayer or a bilayer, and is typically a bilayer. The amphiphilic molecules may be synthetic or naturally occurring, and are typically lipids, surfactants, and block copolymer amphiphiles. Preferably, the amphiphilic molecules are lipids or block copolymer amphiphiles, more preferably lipids, most preferably phospholipids.

Non-naturally occurring amphiphiles and amphiphiles which form a monolayer are known in the art and include, for example, block copolymers (Gonzalez-Perez et al., Langmuir, 2009, 25, 10447-10450).

In some embodiments the membrane comprises one or more archaebacterial bipolar tetraether lipids or mimics thereof. Such lipids are generally found in extremophiles such as that survive in harsh biological environments, thermophiles, halophiles and acidophiles. Their stability is believed to derive from the fused nature of the final bilayer. It is
5 straightforward to construct block copolymer materials that mimic these biological entities by creating a triblock polymer that has the general motif hydrophilic-hydrophobic-hydrophilic. This material may form monomeric membranes that behave similarly to lipid bilayers and encompass a range of phase behaviours from vesicles through to laminar membranes.

10 Block copolymers are polymeric materials in which two or more monomer sub-units polymerized together create a single polymer chain. Block copolymers typically have properties that are contributed by each monomer sub-unit. However, a block copolymer may have unique properties that polymers formed from the individual sub-units do not possess. Block copolymers can be engineered such that one of the monomer sub-
15 units is hydrophobic (i.e. lipophilic), whilst the other sub-unit(s) are hydrophilic whilst in aqueous media. In this case, the block copolymer may possess amphiphilic properties and may form a structure that mimics a biological membrane. The block copolymer may be a diblock (consisting of two monomer sub-units), but may also be constructed from more than two monomer sub-units to form more complex arrangements that behave as
20 amphiphiles. The copolymer may be a triblock, tetrablock or pentablock copolymer. Typically the copolymer is a triblock copolymer comprising two monomer subunits A and B in an A-B-A pattern; typically the A monomer subunit is hydrophilic and the B subunit is hydrophobic.

The amphiphilic layer is typically a planar lipid bilayer or a supported bilayer.
25 The amphiphilic layer is typically a lipid bilayer. Lipid bilayers are models of cell membranes and serve as excellent platforms for a range of experimental studies. For example, lipid bilayers can be used for *in vitro* investigation of membrane proteins by single-channel recording. Alternatively, lipid bilayers can be used as biosensors to detect the presence of a range of substances. The lipid bilayer may be any lipid bilayer. Suitable
30 lipid bilayers include, but are not limited to, a planar lipid bilayer, a supported bilayer or a liposome. The lipid bilayer is usually a planar lipid bilayer. Suitable lipid bilayers are disclosed in WO 2008/102121, WO 2009/077734 and WO 2006/100484).

Any lipid composition that forms a lipid bilayer may be used. Lipids typically comprise a head group, an interfacial moiety and two hydrophobic tail groups which may be the same or different. Suitable head groups include, but are not limited to, neutral head groups, such as diacylglycerides (DG) and ceramides (CM); zwitterionic head groups, such as

5 phosphatidylcholine (PC), phosphatidylethanolamine (PE) and sphingomyelin (SM); negatively charged head groups, such as phosphatidylglycerol (PG); phosphatidylserine (PS), phosphatidylinositol (PI), phosphatic acid (PA) and cardiolipin (CA); and positively charged headgroups, such as trimethylammonium-Propane (TAP). Suitable interfacial moieties include, but are not limited to, naturally-occurring interfacial moieties, such as

10 glycerol-based or ceramide-based moieties. Suitable hydrophobic tail groups include, but are not limited to, saturated hydrocarbon chains, such as lauric acid (*n*-Dodecanolic acid), myristic acid (*n*-Tetradecanoic acid), palmitic acid (*n*-Hexadecanoic acid), stearic acid (*n*-Octadecanoic) and arachidic (*n*-Eicosanoic); unsaturated hydrocarbon chains, such as oleic acid (*cis*-9-Octadecanoic); and branched hydrocarbon chains, such as phytanoyl. The

15 length of the chain and the position and number of the double bonds in the unsaturated hydrocarbon chains can vary. The length of the chains and the position and number of the branches, such as methyl groups, in the branched hydrocarbon chains can vary. The hydrophobic tail groups can be linked to the interfacial moiety as an ether or an ester. The lipids may be mycolic acid. In the present invention, the lipids are particularly preferably

20 phospholipids, most preferably 2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC).

The lipids can also be chemically-modified. The head group or the tail group of the lipids may be chemically-modified. Suitable lipids whose head groups have been chemically-modified include, but are not limited to, PEG-modified lipids, such as 1,2-Diacyl-sn-

25 Glycero-3-Phosphoethanolamine-N-[Methoxy(Polyethylene glycol)-2000]; functionalised PEG Lipids, such as 1,2-Distearoyl-sn-Glycero-3 Phosphoethanolamine-N-[Biotinyl(Polyethylene Glycol)2000]; and lipids modified for conjugation, such as 1,2-Dioleoyl-sn-Glycero-3-Phosphoethanolamine-N-(succinyl) and 1,2-Dipalmitoyl-sn-Glycero-3-Phosphoethanolamine-N-(Biotinyl). Suitable lipids whose tail groups have

30 been chemically-modified include, but are not limited to, polymerisable lipids, such as 1,2-bis(10,12-tricosadiynoyl)-sn-Glycero-3-Phosphocholine; fluorinated lipids, such as 1-Palmitoyl-2-(16-Fluoropalmitoyl)-sn-Glycero-3-Phosphocholine; deuterated lipids, such as

1,2-Dipalmitoyl-D62-sn-Glycero-3-Phosphocholine; and ether linked lipids, such as 1,2-Di-O-phytanyl-sn-Glycero-3-Phosphocholine. The lipids may be chemically-modified or functionalised to facilitate coupling of the polynucleotide.

Other components that affect the properties of the amphiphilic layer may be incorporated,
5 such as fatty acids, such as palmitic acid, myristic acid and oleic acid; fatty alcohols, such as palmitic alcohol, myristic alcohol and oleic alcohol; sterols, such as cholesterol, ergosterol, lanosterol, sitosterol and stigmasterol; lysophospholipids, such as 1-Acyl-2-Hydroxy-sn- Glycero-3-Phosphocholine; and ceramides.

Methods for forming lipid bilayers are known in the art. Suitable methods are
10 disclosed in the Example. Lipid bilayers are commonly formed by the method of Montal and Mueller (Proc. Natl. Acad. Sci. USA., 1972; 69: 3561-3566), in which a lipid monolayer is carried on aqueous solution/air interface past either side of an aperture which is perpendicular to that interface. The method of Montal & Mueller is popular because it is a cost-effective and relatively straightforward method of forming good quality lipid
15 bilayers that are suitable for protein pore insertion. Other common methods of bilayer formation include tip-dipping, painting bilayers and patch-clamping of liposome bilayers. The lipid bilayer may be formed as described in WO 2009/077734. A lipid bilayer may also be a droplet interface bilayer formed between two or more aqueous droplets each comprising a lipid shell such that when the droplets are contacted a lipid bilayer is formed
20 at the interface of the droplets.

Any of the amphiphilic membranes, compounds or layers discussed above may be used in the invention.

The volume of each droplet in the power unit of the invention is typically from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL,
25 more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL. In a particularly preferred embodiment, each droplet has a volume of around 1.84 nL.

Preferably, at least one droplet within the power unit of the invention comprises magnet particles. More preferably, all droplets within the power unit of the invention
30 comprises magnetic particles. The magnetic particles are, for example, iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3) or nickel (Ni) particles. In one embodiment, the magnetic particles are iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3). In order embodiment, the

magnetic particles are nickel (Ni) particles. These magnetic particles advantageously permit the power unit of the invention to be moved remotely using magnetic fields.

Power unit (2)

As discussed above, the power unit of the invention is a power unit comprising a
5 series of droplets, wherein said series of droplets comprises:
one or more first droplets, and
one or more second droplets,
wherein there is a potential energy difference between the one or more first droplets
and the one or more second droplets, and wherein
10 each droplet is separated from its one or more neighbouring droplets by an
amphiphilic membrane.

The power unit of the invention is thus a form of battery in an inactive state - it
contains a potential energy difference across a barrier that can be made selectively
permeable. In one embodiment, the barrier is an amphiphilic between a first droplet and
15 second droplet. However, in a preferred embodiment, the barrier is a separator droplet.
Thus, in a preferred embodiment of the invention, the power unit is a power unit
comprising a series of droplets, wherein said series of droplets comprises, in this order or
the reverse thereof:

(a) one or more first droplets,
20 (b) one or more separator droplets, and
(c) one or more second droplets,
wherein there is a potential energy difference between the one or more first droplets
and the one or more second droplets, and wherein
each droplet is separated from its one or more neighbouring droplets by an
25 amphiphilic membrane.

As discussed above, the skilled person would be aware that any battery chemistry
can in principle be employed within the power unit of the invention to provide a potential
energy difference between the one or more first droplets and the one or more second
droplets. In another preferred embodiment of the invention, the potential energy difference
30 is the relative stability of ions within different ion donor/acceptor materials (i.e. a
difference in chemical potential energy when an ion is present in one ion donor/acceptor
material relative to its presence in another ion donor/acceptor material, as in a “rocking

chair” system). This potential energy difference can be converted into an electromotive force across the barrier when the barrier is made permeable to the ion (for instance, by the introduction of channels in the amphiphilic membrane, or by the use of ion-permeable separator droplets). Thus, in a preferred embodiment, the first droplets are droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material and the second droplets are droplets of discharge anodic fluids containing a second ion donor/acceptor material (wherein the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions, one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material, and one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material). Thus, there is a driving force for the ion to diffuse out of the discharge ion donor material (i.e. the material in which the ion is in a higher chemical potential environment), across the barrier, and into the discharge ion acceptor material (i.e. the material in which the ion is in a lower chemical potential environment).

It is to be noted that the “discharge cathodic fluids” and “discharge anodic fluids” are termed as such because they are fluids that act as cathodes and anodes respectively during discharge. It will be understood, therefore, that the discharge cathodic fluid will act as an anode (i.e. as an anodic fluid) during re-charge. Similarly, it will be understood that the discharge anodic fluid will act as a cathode (i.e. as a cathodic fluid) during re-charge.

The nature of the fluids to alternate as cathodes and anodes during discharge and re-charge is also why the first ion donor/acceptor materials and second ion/donor acceptor materials are termed as such and are assigned as discharge ion acceptor materials and discharge ion donor materials. During discharge, one of the first and second ion/donor acceptor materials acts as ion acceptor material (typically — i.e. when the ions of the ion donor/acceptor materials are cations — this will be the first ion donor/acceptor material, the ion donor/acceptor material within the discharge cathodic fluid) and the other acts as ion donor material (typically — i.e. when the ions of the ion donor/acceptor materials are cations — this will be the second ion donor/acceptor material, the ion donor/acceptor material within the discharge anodic fluid). However, in re-charge, the first ion/donor materials swap roles (thus, typically — i.e. when the ions of the ion donor/acceptor materials are cations — the first ion donor/acceptor material (in the discharge cathodic

fluid) will act as ion donor and the second ion donor/acceptor material (in the discharge anodic fluid) will act as ion acceptor).

Accordingly, it is preferred that the power unit of the invention is a power unit comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
- (b) one or more droplets of one or more separator fluids, and
- (c) one or more droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

In this case, the above one or more droplets of one or more separator fluids are separator droplets.

In one embodiment, the power unit may be arranged into a circular form. In this embodiment said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
- (b) one or more droplets of one or more separator fluids,
- (c) one or more droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material, and
- (d) one or more droplets of one or more separator fluids, wherein at least one of the one or more or more droplets of the above (d) is in contact with the one or more droplets of the above (a); and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

Suitably, an increased current may be obtained in the power unit of the invention by arranging a number of series of droplets in parallel. Thus, it is preferred that the power unit comprises a plurality of series of droplets, wherein the plurality of series of droplets are arranged in parallel such that droplets of the same type within each series of droplets
5 are positioned adjacent to one another.

Similarly, to increase the voltage of the power unit, the series of droplets may be presented in a series arrangement. Specifically, in one embodiment, said series of droplets further comprises, between the one or more droplets of the above (a) and the one or more droplets of the above (b), an optionally repeating sub-series of droplets comprising, in this
10 order:

- (i) one or more droplets of one or more separator fluids,
- (ii) one or more droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material,
- (iii) one or more droplets of one or more separator fluids,
- 15 (iv) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material.

As discussed above, in the broader embodiments of the power source of the invention, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids. More preferably, the
20 one of more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids that are each solutions or suspensions in a droplet medium, wherein solutions in a droplet medium are most preferred.

Similarly, the one or more discharge cathodic fluids, one or more separator fluids,
25 and one or more discharge anodic fluids are each solutions or suspensions in a droplet medium.

As above, the droplet medium may be any liquid medium that is immiscible with one or more other liquid media and so may be a fluorinated solvent, an organic solvent, oil (for example, one or more or a mineral oil, a vegetable oil (such as olive oil, canola oil,
30 peanut oil, avocado oil or sunflower oil) or a synthetic oil (such as a polyalphaolefin or silicone oil), preferably a hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a

polyphenyl(C₁₋₆ alkyl)siloxane), most preferably undecane and/or polyphenylmethylsiloxane), or water. Suitably, the droplet medium is oil or water. The droplet medium is most preferably water.

Preferably, the power unit of the invention is suspended in a suspension medium
5 that is immiscible with the droplet medium, and so may also be any liquid medium that is immiscible with one or more other liquid media and so may be a fluorinated solvent, an organic solvent, oil (for example, one or more or a mineral oil, a vegetable oil (such as olive oil, canola oil, peanut oil, avocado oil or sunflower oil) or a synthetic oil (such as a polyalphaolefin or silicone oil), preferably a hydrocarbon oil (preferably C₈₋₃₀
10 hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), more preferably still hexadecane, undecane and/or polyphenylmethylsiloxane, most preferably hexadecane), or water. Suitably, the suspension medium is oil or water. The suspension medium is preferably oil.

15 Thus, in a preferred embodiment, the droplet medium is water, and the suspension medium is a hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), more preferably still hexadecane, undecane and/or polyphenylmethylsiloxane, most preferably hexadecane.

20 As discussed above, in the broader embodiments of the power source of the invention, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets preferably each contain one or more gelling agents. More preferably, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets each contain the same one or more gelling agents. More
25 preferably still, the one of more first droplets, the one or more second droplets, and the optional one or more separator droplets each contain one gelling agent, most preferably the same one gelling agent.

Similarly, the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids preferably each contain one or more gelling
30 agents. More preferably, the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain one or more gelling agents each contain the same one or more gelling agents. More preferably still, the one or more

discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain one or more gelling agents each contain one gelling agent, most preferably the same one gelling agent.

Preferably, each gelling agent is a polymer or a polymerizable monomer or
5 oligomer. As the droplet medium is most preferably water, the gelling agent is preferably a hydrogel gelling agent.

Typically, the polymer gelling agent is selected from a polysaccharide (such as agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most
10 preferably agarose), a polynucleic acid (such as DNA and RNA), a polyamide (such as collagen, gelatin, and silk fibroin, most preferably silk fibroin), a polyphenol (such as ligin), a polyester (such as polycaprolactone and polylactic acid), a polyether (such as polyethyleneglycol), a vinyl polymer (such as polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (such as polyacrylic acid), an acrylamide polymer
15 (such as polyacrylamide). The polymer gelling agent may also be a copolymer or a grafted form of one or more of the previously-recited polymers, and may contain functional groups that permit the polymer to be crosslinked (such as acryloyl groups). Preferably, the polymer gelling agent is a polysaccharide, a polynucleic acid, a polyamide, or a polyphenol. More preferably, the polymer gelling agent is a polysaccharide or polyamide,
20 particularly preferably agarose or silk fibroin, most preferably silk fibroin. Polysaccharides and polyamides (such as agarose and silk fibroin) are particularly preferred owing to their ease of digestibility, for instance by agarases and peptidases (respectively). This provides the power source of the invention with advantageous degradability, specifically biodegradability.

25 Typically, the polymerizable monomer or oligomer gelling agent is a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group. More preferably, the polymerizable monomer or oligomer gelling agent is
30 a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group),

particularly preferably methyl acrylate, methyl methacrylate and acrylamide, most preferably acrylamide.

Most preferably, the gelling agent is a polymer gelling agent.

The gelling agent may be gelled by any means known to a person skilled in the art.

- 5 For instance, the polymer gelling agents may be gelled by heating, cooling, crosslinking (using chemical agents (such as glutaraldehyde and N,N'-methylene-bis-acrylamide) and/or by ultraviolet light). In one embodiment, the polymer gelling agent is agarose, and the agarose is gelled by cooling (for instance to below 37 °C, preferably below 25 °C, more preferably below 10 °C, preferably around 4 °C). In another
- 10 embodiment, the polymer gelling agent is silk fibroin, and the silk fibroin is gelled with UV light. In one embodiment, the silk fibroin is gelled by crosslinking tyrosine residues within the silk fibroin protein backbones with UV light (i.e. light having a wavelength of from 100 to 400 nm, preferably 200 to 400 nm, more preferably 300 to 400 nm, more preferably still 350 to 400 nm, most preferably around 365 nm) by use of a photocatalyst
- 15 (preferably a homogeneous photocatalyst, preferably an iridium or ruthenium photocatalyst, most preferably $\text{Ru(II)(bpy)}_3^{2+}$) the presence of an oxidant (preferably a perchlorate or persulfate oxidant, preferably a persulfate oxidant, most preferably sodium persulfate). It will be appreciated that many gelling agents, particularly polyamide gelling agents, may be modified to have groups (like tyrosine) which are capable of undergoing
- 20 UV crosslinking as discussed above.

- Thus, typically, when the gelling agent is a gelling agent susceptible to crosslinking under UV light, the fluids containing the gelling agent contain both a photocatalyst (as defined above) and an oxidant (as defined above). Typically, the photocatalyst is present in the fluids containing the gelling agent in an amount of from 0.05 to 20 mM, preferably
- 25 0.1 to 10 mM, more preferably 0.5 to 5 mM, more preferably still 0.7 to 2 mM, most preferably around 1 mM. Analogously, the oxidant is present in the fluids containing the gelling agent in an amount of from 0.2 to 50 mM, preferably 0.5 to 20 mM, more preferably 1 to 10 mM, more preferably still 3 to 7 mM, most preferably around 5 mM.

- The use of gelling agents susceptible to crosslinking under UV light (such as silk
- 30 fibroin) is particularly advantageous in that it enables the remote control of gelling. This is particularly advantageous in the context of the remote activation of the power sources of the invention, where crosslinking can rupture the amphiphilic membranes of the power

sources of the invention (as discussed further below). In principle, any number of gelling agents may be made susceptible to crosslinking under UV light by the addition of UV-crosslinking groups known to the person skilled in the art (i.e. by the modification of gelling agents with groups such as alkenes (optionally conjugated to an electron-withdrawing group, such as a carbonyl or nitrile group) or with phenolic moieties (like those of tyrosine).

Silk fibroin is further preferable in that it has a number of physicochemical properties that renders it particularly suitable for use as a matrix material for the power unit of the invention. Thus, silk fibroin (when gelled) has elastic behaviour, providing flexibility and compressibility with a modulus of ~10 kPa at 80% compression. It is, further, biocompatible, biodegradable (as discussed further above), and strongly adhesive towards tissues, properties which are advantageous for biological use. Further, crosslinked silk fibroin provides for stable support of particulate matter such as the first/second ion donor/acceptor materials and/or electron-conducting materials (as discussed further below). Crosslinked silk fibroin also demonstrates enhanced cation selectivity, by its negatively-charged amino acids (an average zeta potential of -20.2 mV), making it a particularly useful matrix material when the battery chemistry is based on the relative stability of ions within different ion donor/acceptor materials, and said ions are cations.

Typically, the polymerizable monomer or oligomer gelling agent is gelled by polymerisation, optionally in the presence of a crosslinker (for instance a carbodiimide or similar, or a bis-acrylamide (such as N,N'-methylene-bis-acrylamide) or similar). The polymerization may be any form of polymerisation (e.g. acid catalysed or base catalysed polymerisation, or radical polymerisation). However, typically, the polymerisation is radical polymerisation. In one embodiment, the polymerizable monomer or oligomer gelling agent is acrylamide and the acrylamide is gelled with UV light (with a photoinitiator) in the presence of N,N'-methylene-bis-acrylamide.

The gelling agent may be present in the droplets (in the fluids) in any concentration that is suitable for providing a gel. For instance, the polymer gelling agent may be present in an amount of from 0.1 to 50% w/v, preferably from 0.5 to 25% w/v, more preferably from 1 to 10% w/v, more preferably still from 1.5 to 7% w/v, most preferably around 5% w/v. The polymerizable monomer or oligomer gelling agent may be present in an amount of

from 1 to 70% w/v, preferably 5 to 60% w/v, more preferably 20 to 50% w/v, most preferably around 40% w/v.

For the avoidance of doubt, where the droplets contain a gelling agent, the gelling agent is preferably not gelled or is only partly gelled (for instance to provide not more than 5 10%, not more than 20%, or not more than 50% of the strength of the fully-gelled form).

The one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids may each contain a viscosity increasing agent. Preferably, the viscosity increasing agent is polyethylene glycol, typically polyethylene glycol having an average molecular weight of from 200 to 600 g/mol, preferably from 300 to 500 g/mol, 10 more preferably around 400 g/mol.

Typically, the viscosity increasing agent is present in the fluids an amount of from 0.5 to 40 v/v%, preferably from 1 to 30 v/v%, more preferably 5 to 20 v/v%, most preferably around 10 v/v%.

The one or more discharge cathodic fluids, one or more separator fluids, and one or 15 more discharge anodic fluids at low temperatures, may each include a surfactant. Preferably the surfactant is a non-ionic surfactant, such as a polyol surfactant, for example Pluronic F-68.

Typically, the surfactant is present in the fluids in an amount of from 0.05 to 5 w/v%, preferably from 0.1 to 2 w/v%, more preferably 0.2 to 1 w/v%, most preferably 20 around 0.5 w/v%.

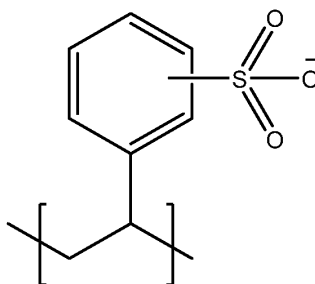
In order to facilitate the movement of electrons throughout the discharge cathodic fluids and discharge anodic fluids, the said one or more discharge cathodic fluids and said one or more discharge anodic fluids each contain one or more electron-conducting materials. Preferably, the said one or more discharge cathodic fluids and said one or more 25 discharge anodic fluids each contain one electron-conducting material. More preferably, the said one or more discharge cathodic fluids and said one or more discharge anodic fluids each contain the same one electron-conducting material.

Typically, each electron-conducting material is selected from a carbon nanomaterial (such as carbon nanotubes, graphene, carbon nanodiamonds, carbon 30 nanohorns, carbon nanofibers, preferably carbon nanotubes), nanowires (such as nickel, platinum, gold and silver nanowires, preferably silver nanowires) or a conductive polymer (such as poly(acetylene), poly(p-phenylenevinylene), poly(pyrrole), poly(aniline),

poly(thiophene), poly(3,4-ethylenedioxythiophene), and poly(p-phenylene sulfide), preferably poly(3,4-ethylenedioxythiophene). Preferably, the electron-conducting material is a carbon nanomaterial or a conductive polymer. More preferably, the electron-conducting material is a carbon nanomaterial, most preferably carbon nanotubes.

5 When the electron-conducting material is a conductive polymer, the conductive polymer may be modified in order to increase solubility in water. For instance, the conductive polymer may be modified with acid groups (such as carboxylic acid groups or sulfuric acid groups) or basic groups (such as amine groups) in order to increase solubility in water.

10 Alternatively, when the electron-conducting material is a conductive polymer, the conductive polymer may be present as a mixture with a second polymer having good solubility in water. Advantageously, as the conductive polymer is partially oxidised in order to provide conducting properties, the second polymer typically has anionic groups. Typically, therefore, the second polymer is a polymer having anionic groups attached to, or
15 forming part of, the polymer backbone as defined above (wherein at least some of the associated cations are displaced in favour of the cationic behaviour of the partially oxidised conductive polymer). Most preferably, the second polymer is a poly 2-styrene sulfonate, i.e. a polymer having monomeric units of the following formula:



20 Preferably, when the electron-conducting material is a conductive polymer, the conductive polymer is poly(3,4-ethylenedioxythiophene mixed with poly 2-styrene sulfonate (i.e. PEDOT:PSS).

Typically, the electron-conducting material is present in the droplets in which it is contained in an amount of from 5 to 60 v/v%, preferably from 10 to 50 v/v%, more
25 preferably 20 to 40 v/v%, most preferably around 30 v/v%.

In order to facilitate the movement of ions in the discharge cathodic fluids, separator fluid and discharge anodic fluids (so, when the power source is active, facilitating the ions to diffuse out of the discharge ion donor material, across the barrier (separator), and into the discharge ion acceptor material), the one or more discharge
 5 cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids may each contain mobile ions, wherein the mobile ions are the same ions as are donated/accepted by the first ion donor/acceptor material and the second ion donor/acceptor material. Preferably, all of the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids contain mobile ions,
 10 wherein the mobile ions are the same ions as are donated/accepted by the first ion donor/acceptor material and the second ion donor/acceptor material.

Thus, the mobile ions are capable of freely diffusing throughout the fluids in which they are contained. The specific type of ions depends on the nature of battery chemistry, however, as discussed further below, the ions may be cations (such as Al ions (Al^{3+} ions),
 15 Ca ions (Ca^{2+} ions), Li ions (Li^{+} ions), Mg ions (Mg^{2+} ions), K ions (K^{+} ions), Na ions (Na^{+} ions) and Zn ions (Zn^{2+} ions), preferably Li ions (Li^{+} ions), Mg ions (Mg^{2+} ions), K ions (K^{+} ions), Na ions (Na^{+} ions) and Zn ions (Zn^{2+} ions), most preferably Li ions (Li^{+} ions)); or the ions may be anions (such as F ions (F^{-} ions), Cl ions (Cl^{-} ions), Br ions (Br^{-} ions), I
 20 ions (I^{-} ions), PF_6^{-} , BF_4^{-} , FSI^{-} , FTFSI^{-} , TFSI^{-} , FSA^{-} , BETI^{-} , HSO_4^{-} , ClO_4^{-} , AlCl_4^{-} , NO_3^{-} , and $[\text{ZnCl}_4]^{2-}$, preferably F ions (F^{-} ions), Cl ions (Cl^{-} ions), Br ions (Br^{-} ions), most preferably F ions (F^{-} ions)).

Typically, the mobile ions are present in the fluids in the form of a salt with an appropriate counterion. One or more counterions may be used, and each fluid may contain different counterions. Typically, however, the counterions are the same in all fluids,
 25 typically the same one counterion.

In an embodiment, the mobile ions are present in the form of salts with polymers having anionic (where the mobile ions are cations) or cationic (where the mobile ions are anions) groups attached thereto. Accordingly, in one embodiment, when the mobile ions are cations, the mobile ions are present in the form of salts with polymers having anionic
 30 groups attached to, or forming part of, the polymer backbone as defined above. In another embodiment, when the mobile ions are anions, the mobile ions are present in the form of

salts with polymers having cationic groups attached to, or forming part of, the polymer backbone as defined above.

However, more typically, the mobile ions are present in the form a soluble salt of the mobile ion with a mobile counterion (i.e. both the ion and the counterion may freely
5 diffuse . Thus, when the mobile ions are cations, the mobile counterions are anions, such as halogen anions, inorganic anions, and organic anions, preferably halogen anions or inorganic anions, most preferably halogen anions. When the mobile ions are anions, the mobile counterions are cations, such as metal cations and organic cations, most preferably metal cations.

10 Typically, the halogen anions, inorganic anions and organic anions are as defined above. Thus:

Preferably, the halogen anions are selected from fluoride, chloride, bromide and iodide. More preferably, the halogen anions are selected from fluoride, chloride and bromide. Most preferably, the halogen anion is chloride.

15 Preferably, the inorganic anions are anions selected from the group consisting of ClO_4^- , BF_4^- , NO_3^- , NO_2^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , NCS^- , PF_6^- , SiF_6^- , SbF_6^- , CN^- , CF_3SO_3^- , SO_4^{2-} and N_3^- . More preferably, the inorganic anions are anions selected from the group consisting of ClO_4^- , BF_4^- , NO_3^- , NO_2^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , PF_6^- , SiF_6^- , CF_3SO_3^- and SO_4^{2-} . Most preferably, the inorganic anions are ClO_4^- , BF_4^- , and PF_6^- .

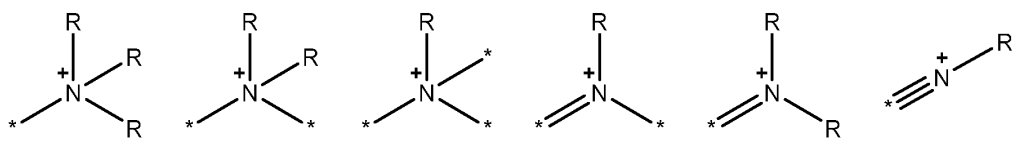
20 Preferably, the organic anions are anions of the formula RSO_3^- , as will be well known to the person skilled in the art. Typically, however, R is C_{1-3} alkyl or optionally substituted phenyl. Preferably, R is methyl or optionally substituted phenyl. The optional substituents of the phenyl group may 1 or 2 substituents selected from halogen (preferably fluorine, chloride, bromine or iodine), NO_2 , or C_{1-3} alkyl (preferably methyl), most
25 preferably one methyl substituent. Most preferably the organic anions are selected from mesylate, tosylate and nosylate.

Typically, the metal cations and organic cations are as defined above. Thus:

Preferably, the metal cations are cations of the metals of groups I to XV of the periodic table. More preferably, the metal cations are cations of Li, Na, K, Rb, Cs, Be,
30 Mg, Ca, Sr, Ba, Sc, Y, Lu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi and P. More preferably still, the metal cations are cations of Li, Na, K, Rb, Be, Mg, Ca, Sr, Sc, Y, Ti,

Zr, V, Nb, Cr, Mo, Mn, Tc, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ga, In, Ge, Sn and Sb. Even more preferably, the metal cations are cations of Li, Na, K, Be, Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga and Ge. Even more preferably, the metal cations are cations of Li, Na, K, and Ca. In a most preferred embodiment, the metal cation is a cation of Na (i.e. Na^+).

Preferably, the organic cations are organic cations of carbon-based molecules (preferably carbon-based molecules having a molecular weight of less than 500 g/mol, more preferably less than 400 g/mol, most preferably less than 300 g/mol). Preferably, the organic cations of carbon-based molecules are molecules having at least one of the following cationic groups:



and more preferably one of the following cationic groups.



wherein * denotes a point of attachment to the remainder of the molecule, and each R is independently selected from H or C_{1-6} alkyl (preferably C_{1-3} alkyl, more preferably methyl), most preferably methyl.

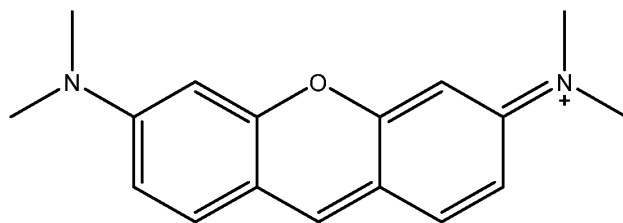
Preferably, each * independently indicates a point of attachment to a group selected from the list consisting of an optionally substituted C_{1-6} alkyl group, an optionally substituted C_{3-14} carbocyclic group, or an optionally substituted 5-14 membered heterocyclic group having from 1 to 4 heteroatoms selected from O, N and S, or

two * indicate points of attachment within an optionally substituted 5-14 membered heterocyclic group having from 1 to 4 heteroatoms selected from O, N and S, wherein at least one heteroatom is N.

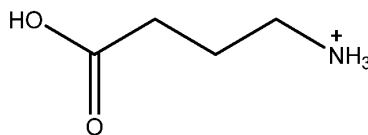
Typically, there may be 1 or 2 optional substituents on each of the above optionally substituted groups. More typically, there is 1 substituent on each of the above groups.

Preferably, the substituents are independently selected from the group consisting of one of the cationic groups as defined above, halogen, C₁₋₆ alkyl, OH, OC₁₋₆ alkyl, -NH₂, NHC₁₋₆ alkyl, N(C₁₋₆ alkyl)₂, CN, NO₂, COOH, COOC₁₋₆ alkyl, CONH₂, CONHC₁₋₆ alkyl, CON(C₁₋₆ alkyl)₂, SO₂NH₂, SO₂NHC₁₋₆ alkyl and SO₂N(C₁₋₆ alkyl)₂, wherein, preferably, each C₁₋₆ alkyl is C₁₋₃ alkyl. More preferably, the substituents are independently selected from the group consisting of one of the cationic groups as defined above, halogen, C₁₋₃ alkyl, OH, OC₁₋₃ alkyl, -NH₂, NHC₁₋₃ alkyl, N(C₁₋₃ alkyl)₂, CN, COOH, and COOC₁₋₃ alkyl.

Most preferably, the organic cations are cations selected from the ammonium cation, the tetramethylammonium cation, the pyronine Y cation, i.e.



or the gaba cation, i.e.



In another embodiment, when the mobile ions are cations, the mobile counterions are anions as defined in the “ions useful as ions donated/accepted by the first ion/donor acceptor material and second ion donor/acceptor material” section further below. Similarly, when the mobile ions are anions, the mobile counterions are cations as defined in the “cations useful as ions donated/accepted by the first ion/donor acceptor material and second ion donor/acceptor material” section further below.

By way of example, when the mobile ions are Al ions (Al³⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be AlCl₃, AlBr₃, Al(PF₆)₃, Al(BF₄)₃, Al(ClO₄)₃, Al₂(SO₄)₃ and Al(NO₃)₃, preferably AlCl₃, AlBr₃, Al₂(SO₄)₃ and Al(NO₃)₃, most preferably AlCl₃.

By way of example, when the mobile ions are Ca ions (Ca²⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be CaCl₂, CaBr₂, Ca(PF₆)₂, Ca(BF₄)₂,

Ca(ClO₄)₂, CaSO₄ and Ca(NO₃)₂, preferably CaCl₂, CaBr₂, CaSO₄ and Ca(NO₃)₂, most preferably CaCl₂.

By way of example, when the mobile ions are Mg ions (Mg²⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be MgCl₂, MgBr₂, Mg(PF₆)₂, Mg(BF₄)₂,
 5 Mg(ClO₄)₂, MgSO₄ and Mg(NO₃)₂, preferably MgCl₂, MgBr₂, MgSO₄ and Mg(NO₃)₂, most preferably MgCl₂.

By way of example, when the mobile ions are Zn ions (Zn²⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be ZnCl₂, ZnBr₂, Zn(PF₆)₂, Zn(BF₄)₂,
 Zn(ClO₄)₂, ZnSO₄ and Zn(NO₃)₂, preferably ZnCl₂, ZnBr₂, ZnSO₄ and Zn(NO₃)₂, most
 10 preferably ZnCl₂.

By way of example, when the mobile ions are K ions (K⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be KCl, KBr, KPF₆, KBF₄, KClO₄, K₂SO₄ and KNO₃, preferably KCl, KBr, K₂SO₄ and KNO₃, most preferably KCl.

By way of example, when the mobile ions are Na ions (Na⁺ ions), the soluble salt of
 15 the mobile ion with a mobile counterion may be NaCl, NaBr, NaPF₆, NaBF₄, NaClO₄, Na₂SO₄ and NaNO₃, preferably NaCl, NaBr, Na₂SO₄ and NaNO₃, most preferably NaCl.

By way of example, when the mobile ions are Li ions (Li⁺ ions), the soluble salt of the mobile ion with a mobile counterion may be LiCl, LiBr, LiPF₆, LiBF₄, LiClO₄, Li₂SO₄ and LiNO₃, preferably LiCl, LiBr, Li₂SO₄ and LiNO₃, most preferably LiCl.

Typically, the concentration of the mobile ions in each of the one or more discharge
 20 cathodic fluids, one or more separator fluids, and one or more discharge anodic is independently from 10 M to 0.1 M, preferably from 5 M to 0.2 M, more preferably from 4 M to 0.5 M, even more preferably from 2 to 0.5 M. Most preferably, the concentration of the mobile ions in each of the one or more discharge cathodic fluids, one or more separator
 25 fluids, and one or more discharge anodic is around 1 M.

As discussed above, the first and second ion donor/acceptor materials are defined in that:

- the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
- 30 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,

- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material.

As discussed above, the ions donated/accepted by the first ion/donor acceptor material and second ion donor/acceptor material (being the same ions as the mobile ions discussed above) depend on the nature of battery chemistry. The battery chemistry may be such that the charge carriers (i.e. the ions) are cations. In this embodiment, the first ion donor/acceptor material is a discharge ion acceptor material, and the second ion donor/acceptor material is a discharge ion donor material. Alternatively, the battery chemistry may be such that the charge carriers (i.e. the ions) are anions. In this embodiment, the first ion donor/acceptor material is a discharge ion donor material, and the second ion donor/acceptor material is a discharge ion acceptor material.

Specific examples of cations useful as ions donated/accepted by the first ion/donor acceptor material and second ion donor/acceptor material include Al ions (Al^{3+} ions), Ca ions (Ca^{2+} ions), Li ions (Li^{+} ions), Mg ions (Mg^{2+} ions), K ions (K^{+} ions), Na ions (Na^{+} ions) and Zn ions (Zn^{2+} ions). Preferably the cations are Li ions (Li^{+} ions), Mg ions (Mg^{2+} ions), K ions (K^{+} ions), Na ions (Na^{+} ions) and Zn ions (Zn^{2+} ions), most preferably the cations are Li ions (Li^{+} ions).

Specific examples of anions useful as ions donated/accepted by the first ion/donor acceptor material and second ion donor/acceptor material include F ions (F^{-} ions), Cl ions (Cl^{-} ions), Br ions (Br^{-} ions), I ions (I^{-} ions), PF_6^{-} , BF_4^{-} , FSI^{-} , FTFSI^{-} , TFSI^{-} , FSA^{-} , BETI^{-} , HSO_4^{-} , ClO_4^{-} , AlCl_4^{-} , NO_3^{-} , and $[\text{ZnCl}_4]^{2-}$. Preferably, the anions are F ions (F^{-} ions), Cl ions (Cl^{-} ions), Br ions (Br^{-} ions), most preferably the anions are F ions (F^{-} ions).

When the battery chemistry is such that the charge carriers (i.e. the ions) are anions, the discharge ion donor material (i.e. the first ion donor/acceptor material) and the discharge ion acceptor material (i.e. the second ion donor/acceptor material) may be any materials known to be cathode and anode materials in anion batteries, and so may be, for instance, any suitable pair of materials as described in Wang et al., Chem 2021, 7(8), pp 1993-2021. In one example, the anions are Cl ions (Cl^{-} ions), the discharge ion donor material is AgCl (cathode) and the discharge ion acceptor material is BiO (optionally in the form Bi + Bi_2O_3 , anode). In another example, the anions are F ions (F^{-} ions), the discharge ion donor material is F^{-} :4-hydroxy-TEMPO (cathode) and the discharge ion acceptor material is Bi (anode).

Most typically, the battery chemistry may be such that the charge carriers (i.e. the ions) are cations. In this case, the discharge ion acceptor material (i.e. the first ion donor/acceptor material) and the discharge ion donator material (i.e. the second ion donor/acceptor material) may be any materials known to be cathode and anode materials in cation batteries. The following sections detail known cathode and anode materials in cation batteries – the skilled person will appreciate, based on their common general knowledge, when the following materials are expressed in their charged form (i.e. when the anode materials are sufficiently loaded with cations, so ready to donate cation under discharge and when the cathode materials are sufficiently unloaded with cations, and so ready to accept cations under discharge) or their discharged form (i.e. the anode materials do not contain cations and so require charging prior to discharge and when the cathode materials contain cation and require the removal of cations (i.e. under charging conditions) prior to discharge.

Thus, for instance, when Al ions (Al^{3+} ions) are the ions, the discharge ion acceptor material may be spinel manganese oxide or vanadium oxide nanowire and the discharge ion donator material may be graphite or interwoven carbon fiber (with intercalated/absorbed Al ions or metal). When Ca ions (Ca^{2+} ions) are the ions, the discharge ion acceptor material may be, for example, calcium manganese oxide, calcium cobalt oxide and titanium disulfide, or hexacyanoferrates, and the discharge ion donator material may be, for example, vanadium oxide (V_2O_5), magnesium vanadium oxide (MgV_2O_5), graphite or silicon (each with intercalated/absorbed Ca ions or metal), copper-calcium alloy or metallic calcium. When Mg ions (Mg^{2+} ions) are the ions, the discharge ion acceptor material may be, for example, zirconium disulfide, cobalt(II,III) oxide, tungsten diselenide, vanadium pentoxide, vanadate, MgMn_2O_4 , MgV_2O_4 , and MgCr_2O_4 , MgFeSiO_4 and MgMnSiO_4 and the discharge ion donator material may be, for example, Mg_3Bi_2 . When K ions (K^+ ions) are the ions, the discharge ion acceptor material may be, for example, Prussian blue, $\text{K}_{0.3}\text{MnO}_2$, $\text{K}_{0.55}\text{CoO}_2$, fluorosulfates, $\text{K}_3\text{V}_2(\text{PO}_4)_3$, and KVPO_4F , and the discharge ion donator material may be, for example, graphite with intercalated/absorbed K ions or metal. When Na ions (Na^+ ions) are the ions, the discharge ion acceptor material may be, for example, sodium iron manganese oxide (such as $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$), sodium manganese nickel iron magnesium oxide (such as $\text{Na}_{0.76}\text{Mn}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$), sodium nickel sodium manganese titanium tin oxide (such

as $\text{NaNi}_{1/4}\text{Na}_{1/6}\text{Mn}_{2/12}\text{Ti}_{4/12}\text{Sn}_{1/12}\text{O}_2$), doped sodium nickel oxides (such as $\text{NaNi}_{(1-x-y-z)}\text{Mn}_x\text{Mg}_y\text{Ti}_z\text{O}_2$), sodium manganese magnesium oxides (such as $\text{Na}_{0.67}\text{Mn}_{1-x}\text{Mg}_x\text{O}_2$, for example $\text{Na}_{0.67}\text{Mn}_{0.95}\text{Mg}_{0.05}\text{O}_2$), copper-substituted sodium nickel manganese oxides (such as $\text{Na}_{0.67}\text{Ni}_{0.3-x}\text{Cu}_x\text{Mn}_{0.7}\text{O}_2$), sodium vanadium phosphate, sodium vanadium fluorophosphate, sodium-vanadium-phosphate-fluoride (such as $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$), $\text{Na}_2\text{MnFe}(\text{CN})_6$, $\text{Na}_{1.88(5)}\text{Fe}[\text{Fe}(\text{CN})_6]\cdot 0.18(9)\text{H}_2\text{O}$, and $\text{Na}_2\text{Mn}^{\text{II}}[\text{Mn}^{\text{II}}(\text{CN})_6]$, and the discharge ion donor material may be, for example, hard carbon, graphite, graphene, carbon arsenide and sodium titanates (such as $\text{Na}_2\text{Ti}_3\text{O}_7$ and NaTiO_2), each with intercalated/absorbed Na ions or metal. When Zn ions (Zn^{2+} ions) are the ions, the discharge ion acceptor material may be, for example, manganese oxides, copper hexacyanoferrate, bismuth oxide, layer sulphides, Prussian blue analogues vanadium oxides (such as $\text{Zn}_{0.25}\text{V}_2\text{O}_5$), and the discharge ion donor material may be, for example metallic zinc.

As discussed above, most typically, the battery chemistry is such that the charge carriers (i.e. the ions) are Li cations (i.e. Li^+ ions). In this embodiment, said first ion donor/acceptor material is a first Li ion donor/acceptor material and said discharge ion acceptor material is a discharge Li ion acceptor material, and said second ion donor/acceptor material is a second Li ion donor/acceptor material and said discharge ion donor material is a discharge Li ion donor material.

The discharge Li ion acceptor material may be any material known to be a cathode material in Li ion batteries. For example, the Li ion acceptor material may be selected from lithium nickel cobalt aluminium oxide (such as $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2$, for example $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$), lithium nickel manganese cobalt oxide (such as $\text{LiNi}_{(1-x-y)}\text{Mn}_x\text{Co}_y\text{O}_2$, for example $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$), lithium nickel cobalt manganese aluminium oxide (such as $\text{LiNi}_{(1-x-y-z)}\text{Co}_x\text{Mn}_y\text{Al}_z\text{O}_2$, for example $\text{LiNi}_{0.89}\text{Co}_{0.05}\text{Mn}_{0.05}\text{Al}_{0.01}\text{O}_2$), lithium manganese oxide (such as LiMn_2O_4 or Li_2MnO_3), lithium manganese nickel oxide (such as $\text{LiMn}_{(2-x)}\text{Ni}_x\text{O}_4$, for example $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$), lithium vanadium oxide (LiV_2O_4), lithium iron phosphate (LiFePO_4), lithium nickel oxide (LiNiO_2) and lithium cobalt oxide (LiCoO_2). Preferably, the Li ion acceptor material is selected from lithium manganese oxide (such as LiMn_2O_4), lithium manganese nickel oxide (such as $\text{LiMn}_{(2-x)}\text{Ni}_x\text{O}_4$, for example $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$), lithium iron phosphate (LiFePO_4), and lithium cobalt oxide

(LiCoO₂). More preferably, the Li ion acceptor material is lithium manganese oxide, most preferably LiMn₂O₄.

The discharge Li ion donor material may be any material known to be an anode material in Li ion batteries. For example, the Li ion donor material may be selected from
5 graphite, hard carbon, silicon, silicon/carbon (silicon nanowires within graphite and/or carbon-coated silicon flakes), tin/cobalt alloy, copper/tin alloy, copper/antimony alloy, manganese/tin alloy, molybdenum sulfide (such as Mo₆S₈), lithium titanate (such as Li₄Ti₅O₁₂), niobates (such as KNb₅O₁₃ and TiNb₂O₇), each having intercalated/absorbed Li ions or metal. Preferably, the Li ion donor material is selected from molybdenum sulfide
10 (such as Mo₆S₈), lithium titanate (such as Li₄Ti₅O₁₂), and niobates (such as KNb₅O₁₃ and TiNb₂O₇), more preferably molybdenum sulfide (such as Mo₆S₈) and lithium titanate (such as Li₄Ti₅O₁₂). More preferably still the Li ion donor material is lithium titanate, most preferably Li₄Ti₅O₁₂. In a particularly preferred embodiment, the Li₄Ti₅O₁₂ is carbon-coated Li₄Ti₅O₁₂.

15 Typically, the first and second discharge ion donor/acceptor materials (i.e. discharge ion acceptor materials and the discharge ion donor materials) for use in the invention are in particulate form, more preferably nanoparticulate form. For instance, the first and second discharge ion donor/acceptor materials (i.e. discharge ion acceptor materials and the discharge ion donor materials) have at least one dimension (preferably
20 two, more preferably three dimensions) in the range of from 1 to 100 nm.

Typically, the first and second discharge ion donor/acceptor materials are present in the droplets in which they are contained in an amount of from 0.5 to 40 w/v%, preferably from 1 to 30 w/v%, more preferably 5 to 20 w/v%, most preferably around 10 w/v%.

As discussed above, preferably, the droplet medium is water. Accordingly, it is
25 preferred that the first and second discharge ion donor/acceptor materials (i.e. discharge ion acceptor materials and the discharge ion donor materials) are aqueous-stable materials. The skilled person would be well aware which materials, of those listed above, are aqueous stable.

As discussed above, typically, the amphipathic membrane is a layer formed from
30 amphiphilic molecules, which have both at least one hydrophilic portion and at least one lipophilic or hydrophobic portion. The amphiphilic layer may be a monolayer or a bilayer, and is typically a bilayer. The amphiphilic molecules may be synthetic or naturally

occurring, and are typically lipids, surfactants, and block copolymer amphiphiles.

Preferably, the amphiphilic molecules are lipids or block copolymer amphiphiles, more preferably lipids, most preferably phospholipids.

Non-naturally occurring amphiphiles and amphiphiles which form a monolayer are
5 known in the art and include, for example, block copolymers (Gonzalez-Perez et al.,
Langmuir, 2009, 25, 10447-10450).

In some embodiments the membrane comprises one or more archaeobacterial bipolar
tetraether lipids or mimics thereof. Such lipids are generally found in extremophiles such
as that survive in harsh biological environments, thermophiles, halophiles and acidophiles.
10 Their stability is believed to derive from the fused nature of the final bilayer. It is
straightforward to construct block copolymer materials that mimic these biological entities
by creating a triblock polymer that has the general motif hydrophilic-hydrophobic-
hydrophilic. This material may form monomeric membranes that behave similarly to lipid
bilayers and encompass a range of phase behaviours from vesicles through to laminar
15 membranes.

Block copolymers are polymeric materials in which two or more monomer sub-
units polymerized together create a single polymer chain. Block copolymers typically
have properties that are contributed by each monomer sub-unit. However, a block
copolymer may have unique properties that polymers formed from the individual sub-units
20 do not possess. Block copolymers can be engineered such that one of the monomer sub-
units is hydrophobic (i.e. lipophilic), whilst the other sub-unit(s) are hydrophilic whilst in
aqueous media. In this case, the block copolymer may possess amphiphilic properties and
may form a structure that mimics a biological membrane. The block copolymer may be a
diblock (consisting of two monomer sub-units), but may also be constructed from more
25 than two monomer sub-units to form more complex arrangements that behave as
amphiphiles. The copolymer may be a triblock, tetrablock or pentablock copolymer.
Typically the copolymer is a triblock copolymer comprising two monomer subunits A and
B in an A-B-A pattern; typically the A monomer subunit is hydrophilic and the B subunit
is hydrophobic.

30 The amphiphilic layer is typically a planar lipid bilayer or a supported bilayer.

The amphiphilic layer is typically a lipid bilayer. Lipid bilayers are models of cell
membranes and serve as excellent platforms for a range of experimental studies. For

example, lipid bilayers can be used for *in vitro* investigation of membrane proteins by single-channel recording. Alternatively, lipid bilayers can be used as biosensors to detect the presence of a range of substances. The lipid bilayer may be any lipid bilayer. Suitable lipid bilayers include, but are not limited to, a planar lipid bilayer, a supported bilayer or a liposome. The lipid bilayer is usually a planar lipid bilayer. Suitable lipid bilayers are disclosed in WO 2008/102121, WO 2009/077734 and WO 2006/100484).

Any lipid composition that forms a lipid bilayer may be used. Lipids typically comprise a head group, an interfacial moiety and two hydrophobic tail groups which may be the same or different. Suitable head groups include, but are not limited to, neutral head groups, such as diacylglycerides (DG) and ceramides (CM); zwitterionic head groups, such as phosphatidylcholine (PC), phosphatidylethanolamine (PE) and sphingomyelin (SM); negatively charged head groups, such as phosphatidylglycerol (PG); phosphatidylserine (PS), phosphatidylinositol (PI), phosphatic acid (PA) and cardiolipin (CA); and positively charged headgroups, such as trimethylammonium-Propane (TAP). Suitable interfacial moieties include, but are not limited to, naturally-occurring interfacial moieties, such as glycerol-based or ceramide-based moieties. Suitable hydrophobic tail groups include, but are not limited to, saturated hydrocarbon chains, such as lauric acid (*n*-Dodecanoic acid), myristic acid (*n*-Tetradecanoic acid), palmitic acid (*n*-Hexadecanoic acid), stearic acid (*n*-Octadecanoic) and arachidic (*n*-Eicosanoic); unsaturated hydrocarbon chains, such as oleic acid (*cis*-9-Octadecanoic); and branched hydrocarbon chains, such as phytanoyl. The length of the chain and the position and number of the double bonds in the unsaturated hydrocarbon chains can vary. The length of the chains and the position and number of the branches, such as methyl groups, in the branched hydrocarbon chains can vary. The hydrophobic tail groups can be linked to the interfacial moiety as an ether or an ester. The lipids may be mycolic acid. In the present invention, the lipids are particularly preferably phospholipids, most preferably 2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC) and 1-palmitoyl-2-oleoylsn-glycero-3-phosphocholine (POPC).

The lipids can also be chemically-modified. The head group or the tail group of the lipids may be chemically-modified. Suitable lipids whose head groups have been chemically-modified include, but are not limited to, PEG-modified lipids, such as 1,2-Diacyl-sn-Glycero-3-Phosphoethanolamine-N-[Methoxy(Polyethylene glycol)-2000]; functionalised PEG Lipids, such as 1,2-Distearoyl-sn-Glycero-3 Phosphoethanolamine-N-

[Biotinyl(Polyethylene Glycol)2000]; and lipids modified for conjugation, such as 1,2-Dioleoyl-sn-Glycero-3-Phosphoethanolamine-N-(succinyl) and 1,2-Dipalmitoyl-sn-Glycero-3-Phosphoethanolamine-N-(Biotinyl). Suitable lipids whose tail groups have been chemically-modified include, but are not limited to, polymerisable lipids, such as 1,2-bis(10,12-tricosadiynoyl)-sn-Glycero-3-Phosphocholine; fluorinated lipids, such as 1-Palmitoyl-2-(16-Fluoropalmitoyl)-sn-Glycero-3-Phosphocholine; deuterated lipids, such as 1,2-Dipalmitoyl-D62-sn-Glycero-3-Phosphocholine; and ether linked lipids, such as 1,2-Di-O-phytanyl-sn-Glycero-3-Phosphocholine. The lipids may be chemically-modified or functionalised to facilitate coupling of the polynucleotide.

Other components that affect the properties of the amphiphilic layer may be incorporated, such as fatty acids, such as palmitic acid, myristic acid and oleic acid; fatty alcohols, such as palmitic alcohol, myristic alcohol and oleic alcohol; sterols, such as cholesterol, ergosterol, lanosterol, sitosterol and stigmasterol; lysophospholipids, such as 1-Acyl-2-Hydroxy-sn-Glycero-3-Phosphocholine; and ceramides.

Methods for forming lipid bilayers are known in the art. Suitable methods are disclosed in the Example. Lipid bilayers are commonly formed by the method of Montal and Mueller (Proc. Natl. Acad. Sci. USA., 1972; 69: 3561-3566), in which a lipid monolayer is carried on aqueous solution/air interface past either side of an aperture which is perpendicular to that interface. The method of Montal & Mueller is popular because it is a cost-effective and relatively straightforward method of forming good quality lipid bilayers that are suitable for protein pore insertion. Other common methods of bilayer formation include tip-dipping, painting bilayers and patch-clamping of liposome bilayers. The lipid bilayer may be formed as described in WO 2009/077734. A lipid bilayer may also be a droplet interface bilayer formed between two or more aqueous droplets each comprising a lipid shell such that when the droplets are contacted a lipid bilayer is formed at the interface of the droplets.

Any of the amphiphilic membranes, compounds or layers discussed above may be used in the invention.

As discussed above, The volume of each droplet in the power unit of the invention is typically from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1

nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL. In a particularly preferred embodiment, each droplet has a volume of around 1.84 nL.

Preferably, at least one droplet within the power unit of the invention comprises magnet particles. More preferably, all droplets within the power unit of the invention
5 comprises magnetic particles. The magnetic particles are, for example, iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3) or nickel (Ni) particles. In one embodiment, the magnetic particles are iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3). In order embodiment, the magnetic particles are nickel (Ni) particles. These magnetic particles advantageously permit the power unit of the invention to be moved remotely using magnetic fields.

10

Power unit (3)

As discussed above, the power unit of the invention is a power unit comprising a series of droplets, wherein said series of droplets comprises:

one or more first droplets, and
15 one or more second droplets,
wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

20 The power unit of the invention is thus a form of battery in an inactive state - it contains a potential energy difference across a barrier that can be made selectively permeable.

As discussed above, the skilled person would be aware that any battery chemistry can in principle be employed within the power unit of the invention to provide a potential
25 energy difference between the one or more first droplets and the one or more second droplets. In another embodiment, the potential energy difference is a difference in the oxidation/reduction potentials of a first reaction and a second reaction, wherein the first reaction takes place in the first droplet and the second reaction takes place in the second droplet. Accordingly, one of the first reaction and the second reaction is an oxidation
30 reaction, and the other of the first reaction and the second reaction is a reduction reaction. Typically, the first reaction and second reaction either (i) take place at electrodes placed within a first droplet and a second droplet, or (ii) are coupled to the oxidation/reduction of

an electron mediator that is capable of being oxidised/reduced at electrodes placed within a first droplet and a second droplet (in both cases when the electrodes are conductively connected). Thus, typically, the first reaction is an oxidation reaction (i.e. wherein the substrate loses electrons) and the electrons lost in the oxidation reaction move into the
5 anode electrode of the first droplet (optionally via an electron mediator) and pass to the cathode electrode of the second droplet and then are passed to the substrate of the second reaction (optionally via an electron mediator) which is then reduced. Thus, an electron motive force is generated.

Typically, when the electrodes are connected, the barrier (i.e. amphiphilic
10 membrane) is made permeable to ions to allow for charge-balancing. Typically, therefore, the oxidation reaction produces a cation in the first droplet which moves into the second droplet and is consumed in the reduction reaction.

In one particularly preferred embodiment, at least one of the substrates for the oxidation and reduction reactions is a biomolecular substrate. In one particularly preferred
15 embodiment, the substrate for the oxidation reaction is NADH, NADPH or FADH₂ (most preferably NADH). Typically, the substrate for oxidation is molecular oxygen.

Advantageously, enzymes may be introduced into the droplets in order to catalyse at least one of the first reaction and second reaction. For enzyme, when the substrate for oxidation is molecular oxygen, the enzyme is an oxidising/reducing enzyme, such as
20 laccase.

The electron mediators, where used, may be the same or different and have reduction/oxidation potentials that are appropriately set to allow for the first reaction and second reaction to take place. Examples of typical electron mediators include bisazino and quinone compounds, such as 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid,
25 (ABTS), and 9,10-anthraquinone-2,6-disulphonic acid (AQDS).

Accordingly, in one particularly preferred embodiment, the first reaction is the oxidation of NADH as is carried out in the presence of the mediator AQDS, and the second reaction is the reduction of oxygen and is carried out in the presence of the mediator ABTS and the enzyme laccase, and the electrodes are, for example, gold electrodes. Typically,
30 the barrier is the amphiphilic membrane (appropriately permeabilised with ion channels, such as gA channels). However, it will be appreciated that the barrier can also be a separator

droplet as defined above, and may be cation-specific separator droplet as defined above in connection with power unit (1).

One exemplary embodiment of a power unit according to this aspect of the invention is shown in Fig. 63 and described in Example 3.

5

Method for producing power unit

As discussed above, the present invention provides a method for producing a power unit of the first aspect of the invention, the method comprising the steps of:

- providing one or more amphipathic molecule-coated first droplets, and one or
10 more amphipathic molecule-coated second droplets; and
- contacting said one or more amphipathic molecule-coated first droplets and said one or more amphipathic molecule-coated second droplets in series to provide a power unit of the first aspect.

In the preferred embodiment discussed above, the barrier within the power units of
15 the first aspect of the invention is a separator droplet. Thus, in a preferred embodiment of the method for producing the power unit of the invention, the method comprises the steps of:

- providing one or more amphipathic molecule-coated first droplets, one or more
amphipathic molecule-coated separator droplets, and one or more amphipathic
20 molecule-coated second droplets; and
- contacting said one or more amphipathic molecule-coated first droplets, said one or more amphipathic molecule-coated separator droplets and said one or more amphipathic molecule-coated second droplets in series to provide a power unit of the first aspect.

25 As discussed above, in a preferred embodiment of the invention, the potential energy difference is an ionic gradient, such that the series of droplets of the power unit comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more high salt fluids,
- (b) one or more droplets of one or more cation selective fluids or one or more
30 droplets of one or more anion selective fluids, and
- (c) one or more droplets of one or more salt diffusion target fluids, wherein

each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

In this case, the method for producing the power unit of the invention comprises the steps of:

- 5 • providing:
 - (a) one or more amphipathic molecule-coated droplets of one or more high salt fluids,
 - (b) one or more amphipathic molecule-coated droplets of one or more cation selective fluids or one or more amphipathic molecule-coated droplets of one or more anion selective fluids, and
 - 10 (c) one or more amphipathic molecule-coated droplets of one or more salt diffusion target fluids; and
- contacting said one or more amphipathic molecule-coated droplets of the above (a), one or more amphipathic molecule-coated droplets of the above (b), and one or more amphipathic molecule-coated droplets (c), in series to provide a power unit of the first aspect.
- 15

As discussed above, in a particularly preferred embodiment the present invention provides a power unit comprising a series of droplets, wherein said series of droplets comprises, in this order or the reverse thereof:

- 20 (a) one or more droplets of one or more high salt fluids,
- (b) one or more droplets of one or more cation selective fluids,
- (c) one or more droplets of one or more salt diffusion target fluids,
- (d) one or more droplets of one or more anion selective fluids, and
- (e) one or more droplets of one or more high salt fluids;
- 25 wherein the one or more droplets of the above (a) may be the same one or more droplets as the one or more droplets of the above (e), and wherein
- each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

Thus, as also discussed above, the present invention provides a method for producing the power unit of the above particularly preferred embodiment of the first aspect, the method comprising the steps of:

- providing:

(a) one or more amphipathic molecule-coated droplets of one or more high salt fluids,

(b) one or more amphipathic molecule-coated droplets of one or more cation selective fluids,

5 (c) one or more amphipathic molecule-coated droplets of one or more salt diffusion target fluids, and

(d) one or more amphipathic molecule-coated droplets of one or more anion selective fluids; and

- contacting said one or more amphipathic molecule-coated droplets of the above
- 10 (a), one or more amphipathic molecule-coated droplets of the above (b), one or more amphipathic molecule-coated droplets (c), and one or more amphipathic molecule-coated droplets of the above (d) in series to provide a power unit of the above particularly preferred embodiment of the first aspect.

As discussed above, in a preferred embodiment of the invention, the potential

15 energy difference is the relative stability of ions within different ion donor/acceptor materials, such that the series of droplets of the power unit comprises, in this order or the reverse thereof:

(a) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,

20 (b) one or more droplets of one or more separator fluids, and

(c) one or more droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material, wherein

- the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
- 25 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein

each droplet is separated from its one or more neighbouring droplets by an

30 amphiphilic membrane.

In this case, the method for producing the power unit of the invention comprises the steps of:

- providing:
 - (a) one or more amphipathic molecule-coated droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
 - (b) one or more amphipathic molecule-coated droplets of one or more separator fluids, and
 - (c) one or more amphipathic molecule-coated droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material,
- contacting said one or more amphipathic molecule-coated droplets of the above (a), one or more amphipathic molecule-coated droplets of the above (b), and one or more amphipathic molecule-coated droplets (c) in series to provide a power unit of the first aspect.

In the broader embodiments of the method of the invention, the one or more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids. More preferably, the one or more first droplets, the one or more second droplets, and the optional one or more separator droplets are preferably each droplets of fluids that are each solutions or suspensions in a droplet medium, wherein solutions in a droplet medium are most preferred.

Similarly, the one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids, and one or more anion selective fluids are each solutions or suspensions in a droplet medium, wherein solutions in a droplet medium are most preferred.

Similarly, the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids are each solutions or suspensions in a droplet medium

Typically, each droplet is prepared by depositing a volume of fluid in a suspension medium that is immiscible with the droplet medium, wherein:

- (i) said suspension medium contains amphipathic molecules, and/or
- (ii) said droplet medium contains amphipathic molecules, and/or
- (iii) amphipathic molecules are added to the suspension medium after the volume of solution is deposited into the suspension medium.

Most conveniently, the suspension medium contains amphipathic molecules.

The contacting is carried out by positioning automatically by printer or manually by pipette. Most typically, the contacting is carried out positioning automatically by printer. A printer for use in microfluidic applications is most preferably used, such as those manufactured by Formlabs (e.g. SolidPrint3D).

- 5 The droplets may be prepared by deposition into a mould that is appropriately dimensioned to permit convenient construction of the series of droplets, or that is appropriately dimensioned to permit contacting of multiple droplets (conveniently, seven droplets) of the same type to enable construction of parallel series of droplets.

- For the avoidance of doubt, the compositions of the droplets are as defined above in
10 connection with the power source of the invention. For instance, the fluids are as defined above in connection with the power source of the invention, the gelling agents are as defined above in connection with the power source of the invention, one or more salts (and suitable concentrations thereof) are defined as above in connection with the power source of the invention, the polymers having anionic groups attached to (or forming part of) the
15 polymer backbone are as defined above in connection with the power source of the invention, the polymers having anionic groups attached to (or forming part of) the polymer backbone are as defined above in connection with the power source of the invention, and the polymers having cationic groups attached to (or forming part of) the polymer backbone are as defined above in connection with the power source of the invention.

- 20 Similarly, in the situation where the potential energy difference is the relative stability of ions within different ion donor/acceptor materials, the compositions of the droplets are as defined above in connection with the power source of the invention. For instance, the fluids are as defined above in connection with the power source of the invention, the gelling agents are as defined above in connection with the power source of
25 the invention, the electron-conducting materials are defined as above in connection with the power source of the invention, the mobile ions are as defined above in connection with the power source of the invention, and the first and second ion donor/acceptor materials are as defined above in connection with the power source of the invention.

- Similarly, the suspension medium is as defined above in connection with the power
30 source of the invention. The volumes of the droplets are as defined above in connection with the power source of the invention.

The amphipathic molecules are also as defined above in connection with the power source of the invention. They may be used within the suspension medium or droplet medium, or added to the suspension medium after the volume of solution is deposited into the suspension medium, at any concentration. However, typically, they are present in the suspension medium, preferably at a total concentration of from 0.2 to 10 mM, more preferably 0.5 to 5 mM, preferably 1 to 3 mM, most preferably around 2 mM. Alternatively they are present in the suspension medium at a total concentration of from 0.5 to 20 mM, more preferably 1 to 10 mM, preferably 2 to 6 mM, most preferably around 4 mM.

Where the droplets contain a gelling as defined above, the droplets are preferably deposited in order to retain the gelling agent in a form where it is not gelled or is only partly gelled (for instance to provide not more than 10%, not more than 20%, or not more than 50% of the strength of the fully-gelled form). For example, when the gelling agent is agarose, the droplets are preferably deposited at a temperature of greater than 30 °C, typically around 37 °C. Analogously, when the gelling agent is a gelling agent that is gelled using UV light (such as silk fibroin), the droplets are preferably deposited under UV-excluding conditions (such as in a dark room, under yellow/red light).

The power unit of the present invention is typically a soft power unit.

Method for activating power unit

As discussed above, the present invention provides a method for activating a power unit of the invention, the method comprising the step of transforming the series of droplets into a series of compartments wherein each compartment is diffusively continuous with its one or more neighbouring compartments. Thus, diffusion of the battery components (in the case of the ionic gradient system, ions) between the compartments becomes possible, creating the electromotive force.

The transforming may take place by any means known to the persons skilled in the art. In one embodiment, the transforming comprises permeabilising the amphiphilic membranes separating the droplets of the power source of the invention, for instance by introduction of transmembrane pores or channels, or by activating transmembrane pores or channels located within the amphiphilic membrane that were previously closed (thereby

preventing diffusion. Suitable transmembrane pores or channels will be well known to the skilled person.

In another embodiment, the transforming comprises disassembling the amphiphilic membranes. Preferably, the amphiphilic membranes are disassembled by introducing the power unit into a disassembling medium and/or by washing the power unit with a disassembling medium. This step removes (or substantially removes, for instance by reducing their concentration by more than 10 times, preferably more than 100 times, preferably more than 1000 times) the amphiphilic molecules, such that no amphiphilic membrane is present between the droplets.

The disassembling medium contains no amphipathic molecules. The disassembling medium is a medium that is immiscible with the droplet medium. Accordingly, typically, the disassembling medium may be as defined for the suspension medium above, and is consequently preferably oil, preferably hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), particularly preferably undecane and/or polyphenylmethylsiloxane. However, in another embodiment, the disassembling medium is an gel, preferably an organogel. Organogels are well known to the person skilled in the art, and any organogel may in principle be used as the disassembling medium. However, typically, the organogel is polymer gel within an organogel medium (wherein the organogel medium is typically an oil as defined above, preferably hydrocarbon oil (preferably C₈₋₃₀ hydrocarbon, more preferably C₁₀₋₂₀ hydrocarbon) and/or a silicone oil (preferably a poly di(C₁₋₆ alkyl)siloxane or a polyphenyl(C₁₋₆ alkyl)siloxane), particularly preferably undecane and/or polyphenylmethylsiloxane). The polymer gel may be formed of any appropriate polymer (for instance, based on polystyrene, polyethylene, polypropylene, and polybutylene) but is typically a co-polymer of polystyrene, polybutylene and, optionally, polyethylene. Most preferably, the polymer is SEBS (poly(styrene-b-ethylene-co-butylene-b-styrene) triblock copolymer). This polymer is conveniently forms a gel in a temperature-sensitive fashion (for instance, on cooling to below 37 °C, preferably below 25 °C, more preferably below 10 °C, preferably around 4 °C). The polymer may be present within the organogel medium at any concentration, but is preferably present at a concentration of from 1 to 100 mg/mL, preferably 5 to 50 mg/mL, more preferably 10 to 30 mg/mL, most preferably around 20 mg/mL. Typically, the

cationic polymer has a weight average molecular weight of around 10,000 to 200,000 g/mol, preferably around 20,000 to 150,000 g/mol, most preferably around 120,000 g/mol.

The disassembling medium may contain a detergent. The detergent may be, for example, F68 flake.

5 Where one or more droplets contains a gelling agent, the step of transforming the series of series of droplets into the series of compartments preferably comprises gelling the one or more gelling agents such that the series of droplets becomes a series of gel compartments wherein each gel compartment is diffusively continuous with its one or more neighbouring gel compartments. The gelling may take place before, simultaneously
10 with, or after the permeabilising or disassembling. Most preferably, the gelling takes place simultaneously with the permeabilising or disassembling.

 In one particularly preferred embodiment, it is the gelling of the gelling agent that transforms the series of droplets into a series of gel compartments wherein each gel compartment is diffusively continuous with its one or more neighbouring gel
15 compartments. Thus, in one embodiment, the gelling of the gelling agent ruptures the amphiphilic membranes separating each droplet from its one or more neighbouring droplets such that each droplet becomes a gel compartment wherein each gel compartment is diffusively continuous with its one or more neighbouring gel compartments. As one
20 example, a gelling agent that is capable — on gelling — of rupturing the amphiphilic membranes separating each droplet from its one or more neighbouring droplets is silk fibroin.

 The gelling may take place by any process suitable for gelling the gelling agent, for instance by treatment with UV light or by reducing the temperature. For example, where the gelling agent is agarose, the gelling takes place by cooling (for instance by cooling to
25 below 37 °C, preferably below 25 °C, more preferably below 10 °C, preferably around 4 °C). Similarly, when the gelling agent is a gelling agent susceptible to crosslinking under UV light (such as silk fibroin), the gelling takes place by irradiation with UV light (i.e. light having a wavelength of from 100 to 400 nm, preferably 200 to 400 nm, more
preferably 300 to 400 nm, more preferably still 350 to 400 nm, most preferably around 365
30 nm). The irradiation with UV light may take place, for instance, with a UV light power density of greater than 0.01 mW/cm², preferably greater than 0.1 mW/cm², most preferably greater than 0.5 mW/cm². Typically, the irradiation may take place for a time period of

from 1 s to 1 hour, such as from 10 s to 10 minutes, preferably from 30 s to 5 minutes, preferably around 60 s.

Active power unit (1)

5 As discussed above, the present invention also provides an active power unit obtainable by the method for activating a power unit of the invention.

The present invention also provides an active power unit comprising a series of compartments, wherein said series of compartments comprises:

 one or more first compartments, and
10 one or more second compartments,
 wherein there is a potential energy difference between the one or more first compartments and the one or more second compartments, and wherein
 each compartment is diffusively continuous with its one or more neighbouring compartments.

15 The active power unit of the invention is thus a form of battery in an active state - it contains a potential energy difference across a barrier that is selectively permeable. In one embodiment, the barrier is a selectively permeable amphiphilic membrane between the first compartment and second compartment. However, in a preferred embodiment, the barrier is a separator compartment. Thus, in a preferred embodiment of the invention, the active
20 power unit is a power unit comprising a series of compartments, wherein said series of compartments comprises, in this order or the reverse thereof:

 (a) one or more first compartments,
 (b) one or more separator compartments, and
 (c) one or more second compartments,
25 wherein there is a potential energy difference between the one or more first compartments and the one or more second compartments, and wherein
 each compartment is diffusively continuous with its one or more neighbouring compartments.

 The skilled person would be aware that any battery chemistry can in principle be
30 employed within the active power unit of the invention to provide a potential energy difference between the one or more first compartments and the one or more second compartments. However, in a preferred embodiment of the invention, the potential energy

difference is an ionic gradient (i.e. a difference in salt concentration across the barrier). This potential energy difference is an electromotive force across the barrier when the barrier is selectively permeable to either the cationic portion of the salt or the anionic portion of the salt (for instance, by the introduction of ion-selective channels in the amphiphilic membrane, or by the use of an anionic or cationic polymer within the separator compartments). Thus, in a preferred embodiment, the first compartments are high salt compartments and the second compartments are salt diffusion target compartments (wherein the “high salt compartment” contains one or more salts in a concentration higher than that of the “salt diffusion target compartment” such that there is a driving force for an anion or cation of the salt to diffuse across the anion or cation-selective permeable barrier to the “salt diffusion target compartment”).

Accordingly, it is preferred that the active power unit of the invention is a power unit comprising a series of compartments, wherein said series of compartments comprises, in this order or the reverse thereof:

- (a) one or more high salt compartments,
- (b) one or more cation selective compartments or one or more anion selective compartments, and
- (c) one or more salt diffusion target compartments, and wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

In this case, the above cation selective compartments/anion selective compartments are separator compartments.

Suitably, an increased current may be obtained in the power unit of the invention by arranging a number of series of compartments in parallel. Thus, it is preferred that the power unit comprises a plurality of series of compartments, wherein the plurality of series of compartments are arranged in parallel such that compartments of the same type within each series of compartments are positioned adjacent to one another.

In a particularly preferred embodiment the present invention provides an active power unit comprising a series of compartments, wherein said series of compartments comprises, in this order or the reverse thereof:

- (a) one or more high salt compartments,
- (b) one or more cation selective compartments,

- (c) one or more salt diffusion target compartments,
- (d) one or more anion selective compartments, and
- (e) one or more high salt compartments;

wherein the one or more compartments of the above (a) may be the same one or
5 more compartments as the one or more compartments of the above (e), and wherein
each compartment is diffusively continuous with its one or more neighbouring
compartments.

Where the one or more compartments of the above (a) are the same one or more
compartments as the one or more compartments of the above (e), the active power unit is
10 present in a circular form, wherein the cations and anions from the high salt compartments
move in different directions around the circle.

Thus, this particularly preferred embodiment of the invention contains two
compartments as barriers, wherein one barrier is selectively permeable to the cationic
portion of the salt in the one or more compartments of the above (a) and the other barrier is
15 selectively permeable to the anionic portion of the salt in the one of compartmentss of the
above (e) (such that cations from the one or more compartments of the above (a) and
anions from the one or more compartments of the above (e) will be able to diffuse into the
one or more compartments of the above (c)). Thus, an electromotive force is created
across the one or more compartments of (a) and the one of more compartments of the
20 above (e).

This embodiment of the invention is particularly preferred as it allows for the
voltage of the active power unit of the invention to be conveniently increased by placing
the series of compartments (a) to (e) in a series arrangement in order to increase the overall
voltage of the power unit. Thus, it is preferred that the series of compartments of the
25 particularly preferred embodiment further comprises, between the one or more
compartments of the above (a) and the one or more compartments of the above (b), an
optionally repeating sub-series of compartments comprising, in this order:

- (i) one or more cation selective compartments,
- (ii) one or more salt diffusion target compartments,
- 30 (iii) one or more anion selective compartments, and
- (iv) one or more high salt compartments.

In the broader embodiments of the active power source of the invention, the one of more first compartments, the one or more second compartments, and the optional one or more separator compartments are each compartments containing a compartment medium.

Similarly, the one or more high salt compartments, one or more cation selective
5 compartments, one or more salt diffusion target compartments, and one or more anion selective compartments are each compartments containing a compartment medium.

The compartment medium is preferably defined in the same terms as the droplet medium above.

Similarly, with the exception of the optional gelling agent (gel discussed further
10 below), each compartment preferably contains the same contents as defined above for the corresponding droplet (i.e. the one or more high salt compartments have the same contents as the one or more droplets of one or more high salt fluids, the one or more cation selective compartments have the same contents as the one or more droplets of one or more cation selective fluids, the one or more salt diffusion target compartments have the same contents
15 as the one or more droplets of one or more salt diffusion target fluids, and the one or more anion selective compartments have the same contents as the one or more droplets of one or more anion selective fluids).

Advantageously, each compartment is a gel compartment, such that the one or more high salt compartments are one or more high salt gel compartments, the one or more cation
20 selective compartments are one or more cation selective gel compartments, the one or more salt diffusion target compartments are one or more salt diffusion target gel compartments, and the one or more anion selective compartments are one or more anion selective gel compartments.

In each case, the gel compartments are each compartments of one or more gels
25 within a compartment medium. Preferably, the one or more gels of each gel compartment are the same one or more gels. More preferably still, the gel compartments are each compartments of one gels, most preferably the same one gel.

Preferably, each gel is gel derived from a polymer or a polymerizable monomer or oligomer. As the compartment medium is most preferably water, the gel is preferably a
30 hydrogel.

Typically, the gels derived from a polymer are gels derived from polymer selected from a polysaccharide (such as agar, gellan gum, xanthan gum, guar gum, isubgol,

carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (such as DNA and RNA), a polyamide (such as collagen, gelatin, and silk fibroin, most preferably silk fibroin), a polyphenol (such as ligin), a polyester (such as polycaprolactone and
 5 polylactic acid), a polyether (such as polyethyleneglycol), a vinyl polymer (such as polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (such as polyacrylic acid), an acrylamide polymer (such as polyacrylamide). The polymer may also be a copolymer or a grafted form of one or more of the previously-recited polymers, and may contain functional groups that permitted the polymer to be crosslinked (such as
 10 acryloyl groups). Preferably, the polymer is a polysaccharide, a polynucleic acid, a polyamide, or a polyphenol. More preferably, the polymer is a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably agarose.

Typically, the gels derived from a polymerizable monomer or oligomer are gels derived from a compound having one or more polymerizable groups, wherein said
 15 compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group. More preferably, the polymerizable monomer or oligomer gelling agent is a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an
 20 amide group), particularly preferably methyl acrylate, methyl methacrylate and acrylamide, most preferably acrylamide.

Most preferably, the gel is a gel derived from a polymer.

The gel may be present in the compartments in any concentration. For instance, the gel may be present in an amount of from 0.1 to 50% w/v, preferably from 0.5 to 25% w/v,
 25 more preferably from 1 to 10% w/v, more preferably still from 1.5 to 5% w/v, most preferably around 2% w/v.

In a most preferred embodiment, each gel compartment is a biocompatible gel compartment such that the one or more high salt compartments are one or more high salt biocompatible gel compartments, the one or more cation selective compartments are one or
 30 more cation selective biocompatible gel compartments, the one or more salt diffusion target compartments are one or more salt diffusion target biocompatible gel compartments,

and the one or more anion selective compartments are one or more anion selective biocompatible gel compartments.

Thus, the present invention provides an active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments
5 comprises, in this order or the reverse thereof:

- (a) one or more high salt biocompatible gel compartments,
- (b) one or more cation selective biocompatible gel compartments,
- (c) one or more diffusion target biocompatible gel compartments,
- (d) one or more anion selective biocompatible gel compartments, and
- 10 (e) one or more high salt biocompatible gel compartments;

wherein the one or more high salt biocompatible gel compartments of the above (a) may be the same one or more high salt biocompatible gel compartments as the one or more high salt biocompatible gel compartments of the above (e); and wherein

each gel compartment is diffusively continuous with its one or more neighbouring
15 gel compartments.

Suitable, biocompatible gel compartments are gel compartments in which:

(a) the compartment medium is water,

(b) the one or more gels are each gels derived from a polymer as defined above (wherein, preferably, the polymer is a polysaccharide or polyamide, particularly preferably
20 agarose or silk fibroin, most preferably agarose),

(c) the one or more salts are non-toxic (and are preferably lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride; more preferably, the one or more salts are each independently selected from lithium chloride, sodium chloride, potassium chloride and calcium chloride; most preferably, only
25 one salt is used and the salt used is calcium chloride); and

(d) the cationic and anionic polymers are not polymers having polyacrylamide monomeric units (and, preferably, the cationic polymers are poly-L-lysine hydrochloride, poly-L-histidine hydrochloride, poly-L-arginine hydrochloride, poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), poly-L-lysine
30 hydrobromide, poly-L-histidine hydrobromide, poly-L-arginine hydrobromide, poly(diallyldimethylammonium bromide), and poly(allylamine hydrobromide); and, preferably, the anionic polymer is poly(sodium 4-styrenesulfonate), poly(sodium 3-

styrenesulfonate), poly(sodium 2-styrenesulfonate), poly-L-glutamic acid sodium, poly-L-aspartic acid sodium, poly(sodium acrylate), poly(potassium 4-styrenesulfonate), poly(potassium 3-styrenesulfonate), poly(potassium 2-styrenesulfonate), poly-L-glutamic acid potassium, poly-L-aspartic acid potassium, poly(potassium acrylate), poly(ammonium 4-styrenesulfonate), poly(ammonium 3-styrenesulfonate), poly(ammonium 2-styrenesulfonate), poly-L-glutamic acid ammonium, poly-L-aspartic acid ammonium, and poly(ammonium acrylate).

In all embodiments, the volume of each gel compartment may be from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL. In a particularly preferred embodiment, each compartment has a volume of around 1.84 nL.

Preferably, at least one compartment within the active power unit of the invention comprises magnet particles. More preferably, all compartments within the power unit of the invention comprises magnetic particles. The magnetic particles are, for example, iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3) or nickel (Ni) particles. In one embodiment, the magnetic particles are iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3). In order embodiment, the magnetic particles are nickel (Ni) particles. These magnetic particles advantageously permit the active power unit of the invention to be moved remotely using magnetic fields.

In an embodiment, the active power unit is contained in an active power unit medium. The active power unit medium may be defined as for the disassembling medium, and is consequently preferably oil, preferably hydrocarbon oil (preferably C_{8-30} hydrocarbon, more preferably C_{10-20} hydrocarbon) and/or a silicone oil (preferably a poly di(C_{1-6} alkyl)siloxane or a polyphenyl(C_{1-6} alkyl)siloxane), particularly preferably undecane and/or polyphenylmethylsiloxane. However, in another embodiment, the active power unit medium is a gel, preferably an organogel. The organogel may be defined as provided above in connection with the disassembling medium, including preferred sub-embodiments. Accordingly, particularly preferably, the active power unit is contained with a SEBS (poly(styrene-b-ethylene-co-butylene-b-styrene) triblock copolymer gel.

In another embodiment, the active power unit may be surrounded by amphiphilic molecules. For instance, this may be the case when it is the gelling of the gelling agent that transforms the series of droplets into a series of gel compartments wherein each gel

compartment is diffusively continuous with its one or more neighbouring gel compartments, i.e. when the gelling agent of the power unit of the invention is silk fibroin.

The active power unit of the present invention is typically a soft active power unit.

5 *Active power unit (2)*

As discussed above, the present invention also provides an active power unit obtainable by the method for activating a power unit of the invention.

The present invention also provides an active power unit comprising a series of compartments, wherein said series of compartments comprises:

- 10 one or more first compartments, and
 one or more second compartments,
 wherein there is a potential energy difference between the one or more first compartments and the one or more second compartments, and wherein
 each compartment is diffusively continuous with its one or more neighbouring
15 compartments.

The active power unit of the invention is thus a form of battery in an active state - it contains a potential energy difference across a barrier that is selectively permeable. In one embodiment, the barrier is a selectively permeable amphiphilic membrane between the first compartment and second compartment. However, in a preferred embodiment, the barrier
20 is a separator compartment. Thus, in a preferred embodiment of the invention, the active power unit is a power unit comprising a series of compartments, wherein said series of compartments comprises, in this order or the reverse thereof:

- (a) one or more first compartments,
 (b) one or more separator compartments, and
25 (c) one or more second compartments,
 wherein there is a potential energy difference between the one or more first compartments and the one or more second compartments, and wherein
 each compartment is diffusively continuous with its one or more neighbouring
 compartments.

30 The skilled person would be aware that any battery chemistry can in principle be employed within the active power unit of the invention to provide a potential energy difference between the one or more first compartments and the one or more second

compartments. However, in a preferred embodiment of the invention, the potential energy difference is an relative stability of ions within different ion donor/acceptor materials (i.e. a difference in chemical potential energy when an ion is present in one ion donor/acceptor material relative to its presence in another ion donor/acceptor material). This potential
5 energy difference can be converted into an electromotive force across the barrier when the barrier is made permeable to the ion (for instance, by the introduction of channels in the amphiphilic membrane, or by the use of ion-permeable separator compartments). Thus, in a preferred embodiment, the first compartments are discharge cathodic compartments containing a first ion donor/acceptor material and the second compartments are discharge
10 anodic compartments containing a second ion donor/acceptor material (wherein the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions, one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material, and one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion
15 donator material). Thus, there is a driving force for the ion to diffuse out of the discharge ion donor material (i.e. the material in which in the ion is in a higher chemical potential environment), across the barrier, and into the discharge ion acceptor material (i.e. the material in which in the ion is in a lower chemical potential environment).

It is to be noted that the “discharge cathodic compartments” and “discharge anodic
20 compartments” are termed as such because they are compartments that act as cathodes and anodes respectively during discharge. It will be understood, therefore, that the discharge cathodic compartment will act as an anode (i.e. as an anodic compartment) during re-charge. Similarly, it will be understood that the discharge anodic compartment will act as a cathode (i.e. as a cathodic compartment) during re-charge.

25 The nature of the compartments to alternate as cathodes and anodes during discharge and re-charge is also why the first ion donor/acceptor materials and second ion/donor acceptor materials are termed as such and are assigned as discharge ion acceptor materials and discharge ion donator materials. During discharge, one of the first and second ion/donor acceptor materials acts as ion acceptor material (typically — i.e. when
30 the ions of the ion donor/acceptor materials are cations — this will be the first ion donor/acceptor material, the ion donor/acceptor material within the discharge cathodic compartment) and the other acts as ion donor material (typically — i.e. when the ions of

the ion donor/acceptor materials are cations — this will be the second ion donor/acceptor material, the ion donor/acceptor material within the discharge anodic compartment). However, in re-charge, the first ion/donor materials swap roles (thus, typically — i.e. when the ions of the ion donor/acceptor materials are cations — the first ion donor/acceptor material (in the discharge cathodic compartment) will act as ion donor and the second ion donor/acceptor material (in the discharge anodic compartment) will act as ion acceptor).

Accordingly, it is preferred that the active power unit of the invention is a power unit comprising a series of compartments, wherein said series of compartments comprises, in this order or the reverse thereof:

- (a) one or more discharge cathodic compartments containing a first ion donor/acceptor material,
- (b) one or more droplets of one or more separator compartments, and
- (c) one or more droplets of one or more discharge anodic compartments containing a second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

In one embodiment, the active power unit may be in a circular form. In this embodiment said series of compartments comprises, in this order or the reverse thereof:

- (a) one or more discharge cathodic compartments containing a first ion donor/acceptor material,
- (b) one or more separator compartments,
- (c) one or more discharge anodic compartments containing a second ion donor/acceptor material, and
- (d) one or more droplets of one or more separator compartments, wherein

at least one of the one or more or more compartments of the above (d) is in contact with the one or more compartments of the above (a); and wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

5 Suitably, an increased current may be obtained in the active power unit of the invention by arranging a number of series of compartments in parallel. Thus, it is preferred that the power unit comprises a plurality of series of compartments, wherein the plurality of series of compartments are arranged in parallel such that compartments of the same type within each series of compartments are positioned adjacent to one another.

10 Similarly, to increase the voltage of the active power unit, the series of compartments may be presented in a series arrangement. Specifically, in one embodiment, said series of compartments further comprises, between the one or more compartments of the above (a) and the one or more compartments of the above (b), an optionally repeating sub-series of compartments comprising, in this order:

- 15 (i) one or more separator compartments,
 (ii) one or more discharge anodic compartments containing a second ion donor/acceptor material,
 (iii) one or more separator compartments,
 (iv) one or more discharge cathodic compartments containing a first ion
20 donor/acceptor material.

As discussed above, in the broader embodiments of the active power source of the invention, the one of more first compartments, the one or more second compartments, and the optional one or more separator compartments are each compartments containing a compartment medium.

25 Similarly, the one or more discharge cathodic compartments, one or more separator compartments, and one or more discharge anodic compartments are each compartments containing a compartment medium.

The compartment medium is preferably defined in the same terms as the droplet medium above.

30 Similarly, with the exception of the optional gelling agent (gel discussed further below), each compartment preferably contains the same contents as defined above for the corresponding droplet (i.e. the one or more discharge cathodic compartments have the

same contents as the one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material, the one or more separator compartments have the same contents as the one or more droplets of one or more separator fluids, and the one or more discharge anodic compartments have the same contents as the one or more
 5 discharge anodic fluids containing a second ion donor/acceptor material).

Advantageously, each compartment is a gel compartment, such that the one or more discharge cathodic compartments are one or more discharge cathodic gel compartments, the one or more separator compartments are one or more separator gel compartments, and the one or more discharge anodic compartments are one or more discharge anodic gel
 10 compartments.

In each case, the gel compartments are each compartments of one or more gels within a compartment medium. Preferably, the one or more gels of each gel compartment are the same one or more gels. More preferably still, the gel compartments are each compartments of one gels, most preferably the same one gel.

15 Preferably, each gel is gel derived from a polymer or a polymerizable monomer or oligomer. As the compartment medium is most preferably water, the gel is preferably a hydrogel.

Typically, the gels derived from a polymer are gels derived from polymer selected from a polysaccharide (such as agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (such as DNA and RNA), a polyamide (such as collagen, gelatin, and silk fibroin, most preferably silk fibroin), a polyphenol (such as lignin), a polyester (such as polycaprolactone and polylactic acid), a polyether (such as polyethyleneglycol), a vinyl polymer (such as
 20 polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (such as polyacrylic acid), an acrylamide polymer (such as polyacrylamide). The polymer may also be a copolymer or a grafted form of one or more of the previously-recited polymers, and may contain functional groups that permitted the polymer to be crosslinked (such as acryloyl groups). Preferably, the polymer is a polysaccharide, a polynucleic acid, a
 25 polyamide, or a polyphenol. More preferably, the polymer is a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably silk fibroin.
 30

Typically, the gels derived from a polymerizable monomer or oligomer are gels derived from a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group. More preferably, the polymerizable monomer or oligomer gelling agent is a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group), particularly preferably methyl acrylate, methyl methacrylate and acrylamide, most preferably acrylamide.

Most preferably, the gel is a gel derived from a polymer.

The gel may be present in the compartments in any concentration. For instance, the gel may be present in an amount of from 0.1 to 50% w/v, preferably from 0.5 to 25% w/v, more preferably from 1 to 10% w/v, more preferably still from 1.5 to 7% w/v, most preferably around 5% w/v.

In a most preferred embodiment, each gel compartment is a biocompatible gel compartment such that the one or more discharge cathodic compartments are one or more discharge cathodic biocompatible gel compartments, the one or more separator compartments are one or more separator biocompatible gel compartments, and the one or more discharge anodic compartments are one or more discharge anodic biocompatible gel compartments.

Thus, the present invention provides an active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

(a) one or more discharge cathodic biocompatible gel compartments containing a first ion donor/acceptor material,

(b) one or more separator biocompatible gel compartments, and

(c) one or more discharge anodic biocompatible gel compartments containing a second ion donor/acceptor material, wherein

- the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,

- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,

- one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.
- 5 Suitable, biocompatible gel compartments are gel compartments in which:
- (a) the compartment medium is water,
 - (b) the one or more gels are each gels derived from a polymer as defined above (wherein, preferably, the polymer is a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably silk fibroin),
- 10 (c) the mobile ions and mobile counterions are Li ions (Li^+ ions), Mg ions (Mg^{2+} ions), K ions (K^+ ions), Na ions (Na^+ ions) and Zn ions (Zn^{2+} ions), and the mobile counterions are Cl^- , Br^- , SO_4^{2-} and NO_3^- , and so, preferably, the soluble salt of the mobile ion with a mobile cation may be MgCl_2 , MgBr_2 , MgSO_4 and $\text{Mg}(\text{NO}_3)_2$, KCl , KBr , K_2SO_4 and KNO_3 , NaCl , NaBr , Na_2SO_4 and NaNO_3 , ZnCl_2 , ZnBr_2 , ZnSO_4 and $\text{Zn}(\text{NO}_3)_2$, LiCl ,
- 15 LiBr , Li_2SO_4 and LiNO_3 , more preferably MgCl_2 , KCl , NaCl , ZnCl_2 and LiCl , most preferably LiCl ; and
- (d) the first and second ion discharge donor/acceptor materials are aqueous-stable materials (for example, when the charge carriers (i.e. the ions) are Li cations (i.e. Li^+ ions), then
- 20 - the Li ion acceptor material is selected from lithium manganese oxide (such as LiMn_2O_4), lithium manganese nickel oxide (such as $\text{LiMn}_{(2-x)}\text{Ni}_x\text{O}_4$, for example $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$), lithium iron phosphate (LiFePO_4), and lithium cobalt oxide (LiCoO_2), more preferably lithium manganese oxide, most preferably LiMn_2O_4 ; and
- 25 - the Li ion donor material is selected from molybdenum sulfide (such as Mo_6S_8) and lithium titanate (such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$), more preferably lithium titanate, most preferably $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
- In all embodiments, the volume of each gel compartment may be from 10 pL to 10 μL , preferably from 50 pL to 1 μL , further preferably from 100 pL to 500 nL, more
- 30 preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL. In a particularly preferred embodiment, each compartment has a volume of around 1.84 nL.

Preferably, at least one droplet within the power unit of the invention comprises magnet particles. More preferably, all droplets within the power unit of the invention comprises magnetic particles. The magnetic particles are, for example, iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3) or nickel (Ni) particles. In one embodiment, the magnetic particles are iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3). In order embodiment, the magnetic particles are nickel (Ni) particles. These magnetic particles advantageously permit the power unit of the invention to be moved remotely using magnetic fields.

In an embodiment, the active power unit is contained in an active power unit medium. The active power unit medium may be defined as for the disassembling medium, and is consequently preferably oil, preferably hydrocarbon oil (preferably C_{8-30} hydrocarbon, more preferably C_{10-20} hydrocarbon) and/or a silicone oil (preferably a poly di(C_{1-6} alkyl)siloxane or a polyphenyl(C_{1-6} alkyl)siloxane), particularly preferably undecane and/or polyphenylmethylsiloxane. However, in another embodiment, the active power unit medium is a gel, preferably an organogel. The organogel may be defined as provided above in connection with the disassembling medium, including preferred sub-embodiments. Accordingly, particularly preferably, the active power unit is contained with a SEBS (poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) triblock copolymer gel.

In another embodiment, the active power unit may be surrounded by amphiphilic molecules. For instance, this may be the case when it is the gelling of the gelling agent that transforms the series of droplets into a series of gel compartments wherein each gel compartment is diffusively continuous with its one or more neighbouring gel compartments, i.e. when the gelling agent of the power unit of the invention is silk fibroin.

The active power unit of the present invention is typically a soft active power unit.

Kit

In view of the above, the present invention further provides a kit of parts comprising a power unit of the present invention and a disassembling medium. For the avoidance of doubt, the disassembling medium is a disassembling medium as defined above in connection with the method for activating the power unit of the invention.

30

Device

As discussed above, the present invention provides a device comprising:

(a) the power unit according invention, or an active power unit according to the invention, and

(b) one or more electronic components.

Typically, the device is configured such that the power unit of the invention is able
5 to power the electronic components when it is active (i.e. when current is generated).

The device is unrestricted and may be, for example, a wearable device or a mobile device. Alternative, the device may be a bio-integrated device, such as a biohybrid interface or implant, or the device may be a synthetic tissue or a microrobot. Specifically, the device may be a pacemaker.

10 The electronic components are unrestricted, but may be, for example, an LED or a pulse generator circuit.

The present invention therefore further provides the use of the power unit of the invention, or the active power unit of the invention, in powering a device having one or more electronic components. Suitably, the device is a biohybrid interface, an implant, a
15 synthetic tissue, or a microrobots. In a particularly preferred embodiment, the device is a pacemaker.

For the avoidance of doubt, the device may contain a multiplicity of power units or active power units of the invention, wherein the power units or active power units are appropriate connection (in series or parallel) with electronically conductive means.

20

Method for generating ionic current

The present invention provides a method of generating an ionic current, said method comprising the steps of, either:

(i) providing a power unit according to invention, wherein the power unit of the
25 invention is a power unit having an ionic gradient, and activating the power unit by the method for activating a power unit according the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit having an ionic gradient.

Thus, as a result of the method of the invention, in discharge current flows inside
30 the compartments (formed from the droplets) in the direction of the high salt compartment to the low salt compartment through the cation selective compartment and/or in the

direction of low salt compartment to the high salt compartment through the anion selective compartment.

The present invention also provides a method of generating an ionic current wherein the power unit and active power units of the invention do not themselves contain an ionic gradient (as a battery chemistry). Thus, the present invention also provides a method of generating an ionic current wherein the power unit and active power units are for generating an electric current. In this embodiment, typically, the power unit or active power unit comprises conversion means for converting an electric current into an ionic current. In one embodiment, the converting means may be a redox-active material such as a conductive polymer as defined in connection with the electron-conducting material. Most preferably, the converting means is poly(3,4-ethylenedioxythiophene mixed with poly 2-styrene sulfonate (i.e. PEDOT:PSS). The converting means may be contained in the discharge anodic droplet and/or discharge cathodic droplet (in the power unit of the invention) or in the discharge anodic compartment and/or discharge cathodic droplet (in the active power unit of the invention), or may be contained in a droplet or compartment that is adjacent to or diffusively continuous with the anodic/cathodic droplets/compartments. Preferably, the converting means is contained in a droplet or compartment that is adjacent to or diffusively continuous with the anodic/cathodic droplets/compartments.

Thus, according to this embodiment, the present invention provides a method of generating an ionic current, said method comprising the steps of, either:

(i) providing a power unit according to invention, wherein the power unit of the invention is a power unit for generating an electric current and further comprising converting means, and activating the power unit by the method for activating a power unit according to the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit having an ionic gradient generating an electric current and further comprising converting means. The present invention therefore further provides the use of the power unit of the invention, or the active power unit of the invention, in generating an ionic current.

Use in driving translocation of charged molecules

The present invention provides the use of an active power unit according to the invention in translocating charged molecules, for instance from one cell (synthetic or biological) into another. Typically, the use is in translocating charged molecules from one synthetic cell into another synthetic cell. A synthetic cell may comprise, for example, an aqueous droplet within an oil suspension medium (as defined above), or may comprise, for example, an aqueous droplet surrounded by an amphiphilic membrane (as defined above). Where the cell is an aqueous droplet surrounded by amphiphilic membrane (as defined above), the amphiphilic membrane typically comprises pore proteins (such as alpha hemolysin) to permit the diffusion of the charged molecules.

Typically, the cell which is to receive the charged molecules is referred to as the charged molecule target cell, and the cell which is the source of the charged molecules is referred to as the charged molecule source cell. The charged molecule target cell and the charged molecule source cell are typically diffusively connected, either directly or via one or more other cells.

The use in driving translocation of charged molecules may comprise the steps of, either:

(i) providing a power unit according to invention, wherein the power unit of the invention is a power unit having an ionic gradient, and activating the power unit by the method for activating a power unit according the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit having an ionic gradient;

wherein the power unit or active power unit are in the presence of, or diffusively connected to, the charged molecule target cell.

In another embodiment, the use in driving translocation may comprise the conversion of an electric current generated by an active power unit of the invention into an ionic current. In this embodiment, typically, the power unit or active power unit comprises conversion means for converting an electric current into an ionic current. In one embodiment, the converting means may be a redox-active material such as a conductive polymer as defined in connection with the electron-conducting material. Most preferably, the converting means is poly(3,4-ethylenedioxythiophene mixed with poly 2-styrene sulfonate (i.e. PEDOT:PSS). The converting means may be contained in the discharge anodic droplet and/or discharge cathodic droplet (in the power unit of the invention) or in

the discharge anodic compartment and/or discharge cathodic droplet (in the active power unit of the invention), or may be contained in a droplet or compartment that is adjacent to or diffusively continuous with the anodic/cathodic droplets/compartments. Preferably, the converting means is contained in a droplet or compartment that is adjacent to or diffusively
5 continuous with the anodic/cathodic droplets/compartments.

In this embodiment, the use in driving translocation of charged molecules may comprise the steps of, either:

(i) providing a power unit according to invention, wherein the power unit of the invention is a power unit for generating an electric current and further comprising
10 converting means, and activating the power unit by the method for activating a power unit according the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit having an ionic gradient generating an electric current and further comprising converting means;

15 wherein the power unit or active power unit are in the presence of, or diffusively connected to, the charged molecule target cell.

Method for generating electric current

As discussed above, the present invention provides a method of generating an
20 electric current, said method comprising the steps of either:

(i) providing a power unit according to invention, connecting two droplets within the series of droplets with electronically conductive means, and activating the power unit by the method for activating a power unit according the invention, or

(ii) providing an active power unit according to the invention, and connecting two
25 compartments within the series of compartments with electronically conductive means.

Preferably, the electronically conductive means comprises electrodes, i.e. a cathode and an anode. In the ionic gradient system of the invention, the cathode and the anode are chemically active. The chemically active cathode may be, for example, a silver chloride electrode. The chemically active anode may be, for example a silver electrode.

30 In the ionic gradient system having droplets/compartments (a) to (c) wherein droplet/compartment (b) is cation selective, the anode is preferably present in the droplet (a) and the cathode is preferably present in the droplet (c).

In the ionic gradient system having droplets/compartments (a) to (c) wherein droplet/compartment (b) is anion selective, the anode is preferably present in the droplet (c) and the cathode is preferably present in the droplet (a).

In the ionic gradient system having droplets/compartments (a) to (e), the anode is preferably present in the droplet/compartment (a) and the cathode is preferably present in the droplet/compartment (e).

Thus, as a result of the method of the invention, in discharge current flows inside the compartments (formed from the droplets) from the anode to the cathode in the direction of the high salt compartment to the low salt compartment through the cation selective compartment and/or in the direction of low salt compartment to the high salt compartment through the anion selective compartment.

More simply, in the relative ion stability system, the electronically conductive means may be any means capable of conducting electrons, and the electronically conductive means typically connect a droplet/compartment (a) with a droplet/compartment (c).

The present invention therefore further provides the use of the power unit of the invention, or the active power unit of the invention, in generating an electronic current.

Method for recharging a depleted power unit of the invention

Following discharge of the active power unit of the invention, the power unit of the invention is termed a depleted power unit of the invention. The depleted power unit thus corresponds to the active power unit of the invention except there is no (or substantially no) potential energy difference across the compartments. For a depleted power unit using the ionic gradient, the concentration of the one or more salts in the high salt compartment and the salt diffusion target compartment is the same. For a depleted power unit using the relative ion stability system, the discharge ion acceptor material has accepted all (or substantially all) of the ions donated by the discharge ion donator material.

Accordingly, the invention further provides a method for recharging a depleted active power unit of the invention, the method comprising applying an electric current across the depleted active power unit of the invention. Preferably, the method comprises providing a depleted active power unit according to the invention, connecting two

compartments within the series of compartments with electronically conductive means, and applying an electric current across the series of compartments.

Preferably, the electronically conductive means comprises electrodes, i.e. a cathode and an anode. In the ionic gradient system of the invention, the cathode and the anode are chemically active. The chemically active anode may be, for example, a silver chloride electrode. The chemically active cathode may be, for example a silver electrode.

In the ionic gradient system having droplets/compartments (a) to (c) wherein droplet/compartment (b) is cation selective, the cathode is preferably present in the droplet (a) and the anode is preferably present in the droplet (c).

In the ionic gradient system having droplets/compartments (a) to (c) wherein droplet/compartment (b) is anion selective, the cathode is preferably present in the droplet (c) and the anode is preferably present in the droplet (a).

In the ionic gradient system having droplets/compartments (a) to (e), the cathode is preferably present in the droplet/compartment (a) and the anode is preferably present in the droplet/compartment (e).

More simply, in the relative ion stability system, the electronically conductive means may be any means capable of conducting electrons, and the electronically conductive means typically connect a droplet/compartment (a) with a droplet/compartment (c).

The electric current is applied across the depleted power unit of the invention in the reverse direction to the direction of current flow in discharge. As a result, recharge current flows inside the compartments (formed from the droplets) from the anode to the cathode in the direction of the low salt compartment to the high salt compartment through the cation selective compartment and/or in the direction of high salt compartment to the low salt compartment through the anion selective compartment. As a result, ions (such as Li ions) flows inside the compartments (formed from the droplets) from the in the direction of the discharge ion acceptor material to the discharge ion donator material through the separator.

Thus, the method for recharging a depleted active power unit, where the power unit is a power unit having an ionic gradient, employs the principle of reverse electrodialysis

30

Method for modulating the activities of one or more cells or tissues

As discussed above, the present invention provides a method of modulating the activities of one or more cells or tissues, the method comprising a step of either:

(i) providing a power unit according to the invention, wherein the power unit of the invention is a power unit having an ionic gradient, and activating the power unit by the method for activating a power unit according to the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit having an ionic gradient, wherein one or more cells or tissues are contained within, or are in the presence of, the power unit according to the invention, or the active power unit according to the invention.

Preferably, the one or more cells or tissues are contained within the power unit according to the invention or the active power unit according to the invention. Most preferably, the one or more cells or tissues are contained within the salt diffusion target droplets/compartments.

Preferably, the one or more cells are neurons. Preferably, the one or more tissues are brain tissues.

Correspondingly, the present invention provides a method of modulating the activities of one or more cells or tissues, the method comprising a step of either:

(i) providing a power unit according to the invention, wherein the power unit of the invention is a power unit (preferably with a relative ion stability battery chemistry), and activating the power unit by the method for activating a power unit according to the invention, or

(ii) providing an active power unit according to the invention, wherein the active power unit of the invention is a power unit (preferably with a relative ion stability battery chemistry),

wherein one or more cells or tissues are contained within, or are in the presence of, the power unit according to the invention, or the active power unit according to the invention.

Preferably, the one or more cells or tissues are in the presence of the power unit according to the invention or the active power unit according to the invention. Most preferably, the one or more cells or tissues are adjacent to (and preferably in contact with) the power unit according to the invention or active power unit according to the invention.

Preferably, the one or more cells are cardiomyocytes. Preferably, the one or more tissues are heart tissues. Optionally, the heart tissues may be within a whole heart, such that the modulation of the activities of the tissues may be useful in treating heart conditions such as ventricular arrhythmias(e.g., ventricular tachycardia and fibrillation). Thus, the power units of the inventions may be used in heart defibrillation.

The present invention therefore further provides the use of the power unit of the invention, or the active power unit of the invention, in modulating the activities of one or more cells or tissues.

Thus, the present invention provides the use of the power unit of the invention, or the active power unit of the invention, in modulating the activity of cellular constructs. The cellular constructions may be brain organoids and assembloids.

Further, the present invention further provides the use of the power unit of the invention, or the active power unit of the invention, in *in vivo* energy delivery.

EXAMPLES

Example 1

Bio-integrated devices need power sources to operate^{1,2}. Despite widely used technologies that can provide power to large-scale targets, such as wired energy supplies from batteries or wireless energy transduction³, a need to efficiently stimulate cells and tissues on the microscale is still pressing. The ideal miniaturized power source should be biocompatible, mechanically flexible, and able to generate an ionic current for biological stimulation, instead of using electron flow as in conventional electronic devices⁴⁻⁶. An intriguing approach is to use soft power sources inspired by the electrical eel^{7,8}; however, power sources that combine the required capabilities have not yet been produced, because it is challenging to obtain miniaturized units that both conserve contained energy before usage and are easily triggered to produce an energy output. Here we develop a miniaturized soft power source by depositing lipid-supported networks of nanolitre hydrogel droplets that use internal ion gradients to generate energy. Compared to the original eel-inspired design⁷, our approach can shrink the volume of a power unit by more than 10⁵-fold and

store energy for longer than 24 h, enabling operation on-demand with a 680-fold greater power density of $\sim 1300 \text{ W m}^{-3}$. Our droplet device can serve as a biocompatible and biological ionic current source to modulate neuronal network activity in 3D neural microtissues and in *ex vivo* mouse brain slices. Our soft microscale ionotronic may be
5 integrated into living organisms.

Main

Soft microscale power sources promise increased biocompatibility and flexibility compared to conventional bulky batteries⁹. The electric organ of the electric eel is an
10 intriguing example of a biological energy source, which uses ion fluxes to generate electricity. Although a few studies have investigated the electrogenic behavior of the organ and others have developed large power arrays over hundreds of square centimeters that mimic this behavior^{7,8}, none has created multicompartment microscale ionic power sources that can be turned on on-demand, and interact with living cells.

15 Here we report a miniaturized soft power source made by depositing nanolitre lipid-supported hydrogel droplet networks¹⁰⁻¹² that use internal ion gradients to generate energy output. The droplet power source stores energy at high density and is biocompatible, mechanically flexible, scalable, and portable after encapsulation. We demonstrate that the attachment of neuron-containing droplets with the droplet device enables ionic current
20 modulation of neuronal network activity by stimulating intracellular Ca^{2+} waves.

A bioinspired soft ionic power source

The electricity-generating capability of the electric eel (e.g., *Electrophorus electricus*) relies on stacking thousands of electrocytes in series (Extended Data Fig. 1), where the
25 cations Na^+ and K^+ can pass unidirectionally through ion-selective protein channels in the cell membranes driven by concentration gradients^{13,14}. We mimicked the general layout and mechanism of the eel's electric organ by combining five aqueous nanolitre pre-gel (agarose) droplets in sequence (Fig. 1a). In a single unit, the droplets were in the order: high-salt (e.g., CaCl_2 , KCl , or NaCl), cation-selective, low-salt, anion-selective, and
30 another high-salt droplet. They were deposited in a lipid-containing oil by using an electronic microinjector (Methods). The droplets were initially surrounded by monolayers of lipid, which formed droplet interface bilayers (DIBs) within seconds upon contact with

one another, thereby creating a stabilized, support-free structure^{12,15} (Fig. 1b). To activate the power source, the assembled droplets were moved into lipid-free oil to remove the lipids and disassemble the DIBs. The droplets were then gelled at 4 °C to create a continuous hydrogel structure (Fig. 1c, Supplementary Fig. 1, Extended Data Fig. 2).

5 A major advantage of our strategy is that, before transfer to lipid-free oil and gelation, each droplet is separated from its neighbours by lipid bilayers, which prevent ion flow between the droplets while mechanically stabilizing the structure. After disruption of the insulating lipid bilayers, ions moved through the conductive hydrogel, from high-salt to low-salt droplets, passing through the selectively permeable compartments^{12,16} (Supplementary

10 Note 1). By using chemically active Ag/AgCl electrodes^{10,17}, the energy released from the salt gradients was transformed into electricity, and the hydrogel structure could act as an energy source and power external components (Fig. 1d). The lipid plays a critical role, enabling the formation of a stable droplet network without energy dissipation and the on-demand activation of powering activity; our approach provides a means to build a soft

15 ionic power source on a microscale, which has not been achieved previously^{7,8} (Supplementary Note 2).

In addition to liquid oil, we also used a thermoreversible organogel^{18,19} to disassemble the DIBs and thereby create a freestanding, portable droplet power source. The organogel precursor poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) triblock copolymer (SEBS) was

20 dissolved in a high-melting point alkane mixture to produce a gel-liquid transition temperature of below 37 °C (Supplementary Fig. 2). The molten organogel (37–40 °C) served as a lipid-free medium to replace the lipid-free oil used during DIBs disassembly. The organogel solidified along with the droplet power source during the gelation process at 4 °C. After gelation, the organogel-droplet composite was gently detached from the mould

25 to yield a freestanding, encapsulated droplet power source. The organogel encapsulation could support compression and twisting (Fig. 1d) and prevent ionic leakage in physiological environments (Extended Data Fig. 3), which greatly expands the portability of the droplet power source for potential implantable and wearable applications^{20,21}.

The electrical outputs of a single power unit before and after activation were measured

30 (Fig. 1e). After assembly, the droplets (50 nL each, 200-fold gradient in salt concentration) in a lipid-containing oil adhered to each other through the DIBs. We left the structures at ambient temperature (25 °C) for 5 mins to allow the droplets to partially gel and reach their

equilibrium contact angles. When we inserted electrodes into the two end droplets of high salinity, no current was recorded, indicating that the insulation of the DIBs prevented energy dissipation. Then, we removed the lipid with lipid-free oil and triggered full gelation at 4 °C for 1 min, thereby establishing an ionically conductive pathway. The activated droplet power source generated 127 mV at open circuit (V_{OC}), a value comparable to the potential generated by a single electrocyte (100–150 mV). The short-circuit current (I_{SC}) reached a peak value of 2.2 μ A within seconds and gradually decreased to lower values due to the limited quantities of the contained salts (100 nmol in each of the two high-salt droplets), in agreement with simulations (Supplementary Fig. 3). An output current persisted after 30 min with a value of $\sim$ 30 nA. In addition, the droplet power source could be stored and used on-demand, as ensured by the robust hydrogel compositions (Supplementary Fig. 4) and insulating DIBs. We stored the droplet power sources in a lipid-containing oil to test energy preservation over time (Fig. 1f). After activation, the droplet power sources gave a less than 10% variation in the V_{OC} after 36 h storage. Over the same period, the volume of the droplets slightly decreased, likely due to water loss.

Output optimization

To improve the output performance of the droplet power source, we analyzed several key parameters that affect the electrogenic behavior based on the principle of reverse electrodialysis^{17,22}: An ionic gradient across a selectively permeable membrane gives rise to an electromotive force across that membrane. First, the type of salt, concentration gradient, and external resistance were optimized. Calcium chloride produced the highest output voltage compared to sodium chloride and potassium chloride at the same salt concentration (Supplementary Fig. 5a). Charged organic compounds can also create concentration gradient under certain conditions and be used to build power sources (Supplementary Fig. 5b). Increasing the concentration ratio (gradient) between the high- and low-salt droplets increased the output voltage (Extended Data Fig. 4), but decreasing the low-salt concentration to produce a larger ratio resulted in a decrease in output current due to the increased internal resistance of the droplet power source (Supplementary Note 3). Then, using the optimal 200-fold CaCl_2 gradient, the dependences of the output voltage, current, and power on external resistance were measured, showing the resistance of a

power unit made of 50 nL droplets to be $\sim 78 \text{ k}\Omega$ and the maximum output power to be $\sim 75 \text{ nW}$.

One of the advantages of using lipid-supported hydrogel droplets to build soft power sources is the ease of miniaturization. Decreasing the volume of the droplets from 1000 to 1.84 nL (99.8% shrinkage) resulted in a concomitant decrease in output voltage (36%, from 136 to 87 mV) and current (70%, from 2.7 to 0.83 μA) (Fig. 2a). These decreases may be attributed to an increase in the internal resistance of the droplets (Supplementary Note 3) and the increased concentration polarization²³ across the selective droplets. However, the decreases were small compared to the shrinkage in volume; in fact, the average energy density at the matching resistance greatly increased after shrinkage to 1.84 nL per droplet by around 100 times to $\sim 1300 \text{ W m}^{-3}$, representing a ~ 680 -fold increase over the previous eel-inspired design⁷ and a ~ 5 -fold increase over the subsequent paper-gel design⁸ (Fig. 2b, Extended Data Table 1). Although the total released charge was lower for the miniaturized power sources (Fig. 2b, Supplementary Fig. 6), we could combine multiple power units in series and/or in parallel to increase the output voltage and/or current. V_{OC} increases with the number of units in series; I_{SC} and the total released charge increase with the number of units in parallel (Fig. 2c).

Scalable power source networks

For larger-scale droplet networks, it is important to increase the contact area between different functional droplet layers without increasing the thickness of droplets. This is because the internal resistance of droplets is negatively correlated to the contact area and positively correlated to the thickness (Supplementary Note 3). Hence, keeping a low internal resistance—small size—while increasing the number of units in series or in parallel increases the output voltage or current, respectively. To scale up the assembly of small droplets for larger-scale applications, we adopted a template method, depositing multiple droplets into 3D-printed resin moulds to produce power units of pre-designed patterns (Fig. 3a and b). Template-assisted self-assembly of spherical units, ranging from the nanoscale to the microscale, has been widely used for fabricating patterned structures^{24,25}; an attractive force between the units and confinement within the template are two conditions necessary for self-assembly²⁶. Here, the formation of lipid-based DIBs

provides an attractive force between droplets (spring constant of $\sim 4 \text{ mN m}^{-1}$, tensile strength of $\sim 25 \text{ Pa}$)¹¹, while the boundary of the mould limits their separation.

We fabricated cylindrical moulds with inner diameters of $600 \text{ }\mu\text{m}$, ~ 3 -times larger than the diameter of a 4 nL droplet. In each mould, we deposited 7 droplets (4 nL), which

5 spontaneously assembled into a hexagonal ‘flower-like’ pattern within seconds (Fig. 3c and d, Methods). Next, we stacked five self-assembled droplet hexagons, with contents corresponding to the five droplets of a power unit, in a deeper cylindrical mould to form a larger power source network in three dimensions (Fig. 3e). An even larger network of 20 hexagons (28 units, 140 droplets) took less than 10 min to form (Fig. 3e). Automation of
10 the construction process might be achieved with a 3D droplet printer^{11,27,28} to produce droplet networks composed of thousands of power units.

To demonstrate the increased output of a multi-droplet assembly, we assembled 20 5-droplet units in series in a spiral mould (Fig. 3f). The high-salt droplets were deposited first, the cation-selective droplets second, the low-salt droplets third, and the anion-selective droplets last (Fig. 3g). The template confined the droplets during deposition and
15 the DIBs kept the droplets closely attached to each other in a chain. The structure was maintained after washing with lipid-free oil. The spiral power source could light up a light-emitting diode (LED), which required an applied potential of $\sim 2 \text{ V}$ (Fig. 3h). The output power was sufficient for additional applications, such as charging a capacitor and powering
20 a pulse generator (Supplementary Fig. 7). Importantly, the droplet power sources could be recharged via electrodialysis by applying a reverse potential (200 mV) to the droplet network^{29,30}, recovering over 60% of the original I_{sc} after ten discharges (Supplementary Fig. 8).

25 **Neuronal modulation by the generated ionic current**

We examined the influence of our droplet device on the activity of neurons. The high-salt and ion-selective droplets together can act as an open droplet device that can be attached to external components through its termini (Fig. 4a). When this open device is attached to droplets with lower ion concentrations, a conductive pathway is completed that allows the
30 ionic current ($\sim 2.6 \text{ }\mu\text{A}$) to flow through the attached droplets (Fig. 4b and c, Supplementary Fig. 9). If neurons are embedded in the low-salt droplets, the generated extracellular ionic current will modulate individual neuronal activity^{4,31} and, in turn, reflect

neuronal network activities³². To test this, we used a microfluidic printer to generate neural microtissues consisting of Matrigel spheres (~570 μm diameter) laden with human neural progenitor cells (NPCs). The neural microtissues were coated with low-salt agarose hydrogel containing neuron culture medium to form the neuron-containing droplets (Fig. 4a: red droplets, Methods, Supplementary Fig. 10). The droplet device was then attached to the neuron-containing droplets in a circular container (Supplementary Fig. 11). With 0.5 M CaCl_2 in the high-salt droplets, the neurons remained at high viability after 10 min modulation as verified by cell viability assays with PrestoBlue, live/dead staining with Calcein-AM and propidium iodide (PI), and immunofluorescence staining with the neuronal marker TUJ1 and the apoptosis marker caspase 3 (Extended Data Fig. 5). Neuronal activities were measured by confocal imaging using Fluo-4 Direct™ as an intracellular calcium dye^{28,33}, which does not respond to extracellular calcium (Methods, Supplementary Note 4, Supplementary Fig. 12). Time-lapse recordings revealed the spatiotemporal course of neuronal modulation when the droplet device was attached to the neuron-containing droplets (Fig. 4d). The correlation of the neuronal activity with the ionic current indicated that the activity was caused by the droplet device and was not spontaneous^{34,35}.

The modulation of neuronal activities was demonstrated by applying Ca^{2+} -based ionic current to the neural microtissues with different amount of culture time (3, 10 and 17 days) and *ex vivo* mouse brain slices (Supplementary Fig. 13). The droplet device contained 0.5 M CaCl_2 in the high-salt droplets. Direct contact with 0.5 M CaCl_2 droplets did not produce ionic current and there was no significant intracellular calcium fluctuation in neurons within 10 min modulation (Extended Data Fig. 6). In comparison, when ionic current generated by the droplet device flowed through the neuronal network in the #1 droplet from left to right, a stronger fluorescence was observed. Moreover, the intensified fluorescence spread directionally from left to right along the day 3 neural microtissue to form a wave-like fluorescence pattern³², indicating that the day 3 neural microtissues were locally modulated by the ionic current (Supplementary Video 1). To further verify the modulation was induced by ionic current instead of changing the extracellular concentration of specific ions, e.g., Ca^{2+} and Cl^- , we used Ag/AgCl electrodes to apply an electrical input on neural microtissues embedded in Ca^{2+} -free droplets (Extended Data Fig. 6). Because of the redox chemistry of the Ag/AgCl electrodes, the electrical input can

induce an ionic current without creating a significant change in ion concentrations or Cl^- gradient. We observed a similar intracellular Ca^{2+} wave generated in the neuronal network by applying an input current intensity equivalent to our droplet device (Supplementary Note 5). Further, we applied a membrane potential-sensitive dye, FluoVolt™, to the neural microtissues during modulation with our droplet devices. The results showed the influence of droplet devices on changing neuronal membrane potential and inducing depolarization (Methods, Extended Data Fig. 7).

By contrast, in experiments using the day 17 neural microtissues, the neurons in #1 droplet were simultaneously modulated within 15 s in connection with the droplet device without showing the wave-like fluorescence pattern previously observed with the day 3 neural microtissues (Fig. 4d, Supplementary Video 2). We calculated the center of fluorescence (weighted-mean distance) of each network to quantify the displacement of the ionic current modulation indicated by the fluorescence intensity (Fig. 4e, Methods). Day 17 neural microtissues showed similar fluorescence displacements as *ex vivo* mouse brain tissue, which were significantly lower than displacements in day 3 and day 10 neural microtissues (Fig. 4f, Extended Data Fig. 8 and 9). Day 17 neural microtissues also showed a faster propagating speed of the induced Ca^{2+} waves compared to day 3 counterparts, in agreement with a previous study³⁶ (Supplementary Fig. 14). These results suggest that the neurons gradually formed connected neuronal networks during prolonged culture and consequently showed simultaneous response under modulation^{37,38}. The Ca^{2+} -based ionic current from the droplet device presumably induced the release of excitatory messengers^{32,39}, through which the modulation passed to connected neurons, resulted in the simultaneously modulation in the neuronal network (Supplementary Note 5). To test our hypothesis that the presumed network activity was related to synaptic activity, we treated the day 17 neural microtissues with 30 μM γ -aminobutyric acid (GABA), which is an inhibitory neurotransmitter that lowers the intracellular potential and correspondingly the effectiveness of excitatory inputs⁴⁰. The expression of GABA receptors in the experimented NPCs was previously substantiated by immunofluorescence staining⁴¹. In the presence of GABA (Fig. 4f, Extended Data Fig. 8), neurons from the day 17 neural microtissues failed to exhibit simultaneous modulation; the wave-like fluorescence pattern was partially restored with increased fluorescence displacement under modulation from the

ionic current. These results suggest that the biocompatible droplet device can modulate neuronal network activities in neural microtissues.

Summary

- 5 We have designed a microscale soft ionic power source based on the electric organ of the electric eel. Our power source differs from previous efforts⁷; the unit volume is reduced by more than 10⁵-fold, it can be turned on on-demand, and the power density is increased by 680-fold to ~1300 W m⁻³. We show that our droplet device can produce extracellular ionic current that modulates neuronal network activity by stimulating intracellular Ca²⁺ waves.
- 10 The SEBS and other encapsulating methods enable the ionic power source to power wearables and other mobile devices. The power source of the invention works in a physiological environment so it can be employed *in vivo* for biological regulation. The present droplet power source uses temperature change to irreversibly trigger its activity and needs SEBS encapsulation to work in aqueous environments. A combination of aqueous
- 15 transfer with the dewetting method⁴² and the use of light-controllable lipids⁴³ or membrane proteins⁴⁴ may be used achieve *in vivo* application by producing 3D-printed droplet power sources in an aqueous environment with remote, reversible on-off switches. On this basis, incorporating other stimulus-responsive materials¹², such as magnetic particles, into the hydrogel endow remote-controlled mobility to perform *in vivo* energy delivery through
- 20 narrow biological environments. The power source of the invention can be used to power next-generation bio-hybrid interfaces, implants, synthetic tissues, and microrobots. The droplet device also permits the modulation of various miniaturized cellular constructs, such as the brain organoids^{45,46} and assembloids⁴⁷.

References

- 1. Choi, S., Lee, H., Ghaffari, R., Hyeon, T. & Kim, D.-H. Recent Advances in Flexible and Stretchable Bio-Electronic Devices Integrated with Nanomaterials. *Adv. Mater.* **28**, 4203-4218 (2016).
- 2. Kim, J., Campbell, A. S., de Ávila, B. E.-F. & Wang, J. Wearable biosensors for healthcare monitoring. *Nat. Biotechnol.* **37**, 389-406 (2019).
- 3. Chung, H. U. *et al.* Binodal, wireless epidermal electronic systems with in-sensor analytics for neonatal intensive care. *Science* **363**, eaau0780 (2019).
- 4. Wang, C. *et al.* Inverted battery design as ion generator for interfacing with biosystems. *Nat. Commun.* **8**, 1-7 (2017).
- 5. Yang, C. & Suo, Z. Hydrogel ionotronics. *Nat. Rev. Mater.* **3**, 125-142 (2018).
- 6. Xiao, K., Wan, C., Jiang, L., Chen, X. & Antonietti, M. Bioinspired ionic sensory systems: the successor of electronics. *Adv. Mater.* **32**, 2000218 (2020).
- 7. Schroeder, T. B. H. *et al.* An electric-eel-inspired soft power source from stacked hydrogels. *Nature* **552**, 214-218 (2017).
- 8. Guha, A. *et al.* Powering Electronic Devices from Salt Gradients in AA-Battery-Sized Stacks of Hydrogel-Infused Paper. *Adv. Mater.* **33**, 2101757 (2021).
- 9. Whittingham, M. S. History, evolution, and future status of energy storage. *Proc. IEEE* **100**, 1518-1534 (2012).
- 10. Holden, M. A., Needham, D. & Bayley, H. Functional bionetworks from nanoliter water droplets. *J. Am. Chem. Soc.* **129**, 8650-8655 (2007).
- 11. Villar, G., Graham, A. D. & Bayley, H. A tissue-like printed material. *Science* **340**, 48-52 (2013).
- 12. Downs, F. G. *et al.* Multi-responsive hydrogel structures from patterned droplet networks. *Nat. Chem.* **12**, 363-371 (2020).
- 13. Xu, J. & Lavan, D. A. Designing artificial cells to harness the biological ion concentration gradient. *Nat. Nanotechnol.* **3**, 666-670 (2008).
- 14. Catania, K. C. Leaping eels electrify threats, supporting Humboldt's account of a battle with horses. *Proc. Natl. Acad. Sci.* **113**, 6979-6984 (2016).
- 15. Booth, M. J., Restrepo Schild, V., Downs, F. G. & Bayley, H. Functional aqueous droplet networks. *Mol. Biosyst.* **13**, 1658-1691 (2017).

- 16. Krishna Kumar, R. *et al.* Droplet printing reveals the importance of micron-scale structure for bacterial ecology. *Nat. Commun.* **12**, 857 (2021).
- 17. Xu, J., Sigworth, F. J. & LaVan, D. A. Synthetic protocells to mimic and test cell function. *Adv. Mater.* **22**, 120-127 (2010).
- 5 ➤ 18. Venkatesan, G. A. & Sarles, S. A. Droplet immobilization within a polymeric organogel improves lipid bilayer durability and portability. *Lab Chip* **16**, 2116-2125 (2016).
- 19. Challita, E. J., Najem, J. S., Monroe, R., Leo, D. J. & Freeman, E. C. Encapsulating networks of droplet interface bilayers in a thermoreversible organogel. *Sci. Rep.* **8**, 1-11 (2018).
- 10 ➤ 20. Zhang, Y. *et al.* Self-Powered Multifunctional Transient Bioelectronics. *Small* **14**, 1802050 (2018).
- 21. Zhang, Y. & Tao, T. H. A Bioinspired Wireless Epidermal Photoreceptor for Artificial Skin Vision. *Adv. Funct. Mater.* **30**, 2000381 (2020).
- 15 ➤ 22. Pattle, R. Production of electric power by mixing fresh and salt water in the hydroelectric pile. *Nature* **174**, 660-660 (1954).
- 23. Wang, L., Wang, Z., Patel, S. K., Lin, S. & Elimelech, M. Nanopore-Based Power Generation from Salinity Gradient: Why It Is Not Viable. *ACS Nano* **15**, 4093-4107 (2021).
- 20 ➤ 24. Kim, S. *et al.* Silk inverse opals. *Nat. Photonics* **6**, 818-823 (2012).
- 25. Wang, Y. *et al.* Modulation of multiscale 3D lattices through conformational control: painting silk inverse opals with water and light. *Adv. Mater.* **29**, 1702769 (2017).
- 26. Matsui, S., Takenaka, M. & Yoshida, H. in *Nanolithography* Vol. 8 (ed Martin Feldman) 287-314 (Elsevier, 2014).
- 25 ➤ 27. Alcinesio, A. *et al.* Controlled packing and single-droplet resolution of 3D-printed functional synthetic tissues. *Nat. Commun.* **11**, 1-13 (2020).
- 28. Zhou, L. *et al.* Lipid-bilayer-supported 3D printing of human cerebral cortex cells reveals developmental interactions. *Adv. Mater.* **32**, 2002183 (2020).
- 30 ➤ 29. Gumuscu, B. *et al.* Desalination by Electrodialysis Using a Stack of Patterned Ion-Selective Hydrogels on a Microfluidic Device. *Adv. Funct. Mater.* **26**, 8685-8693 (2016).

- 30. Zuo, K. *et al.* Selective membranes in water and wastewater treatment: Role of advanced materials. *Mater. Today* **50**, 516-532 (2021).
- 31. Zhang, L. I. & Poo, M.-m. Electrical activity and development of neural circuits. *Nat. Neurosci.* **4**, 1207-1214 (2001).
- 5 ➤ 32. Ross, W. N. Understanding calcium waves and sparks in central neurons. *Nat. Rev. Neurosci.* **13**, 157-168 (2012).
- 33. Grienberger, C. & Konnerth, A. Imaging calcium in neurons. *Neuron* **73**, 862-885 (2012).
- 34. Rienecker, K. D., Poston, R. G. & Saha, R. N. Merits and limitations of studying neuronal depolarization-dependent processes using elevated external potassium. *ASN Neuro.* **12**, 1759091420974807 (2020).
- 10 ➤ 35. Song, Y.-A. *et al.* Electrochemical activation and inhibition of neuromuscular systems through modulation of ion concentrations with ion-selective membranes. *Nat. Mater.* **10**, 980-986 (2011).
- 15 ➤ 36. Fujii, Y., Maekawa, S. & Morita, M. Astrocyte calcium waves propagate proximally by gap junction and distally by extracellular diffusion of ATP released from volume-regulated anion channels. *Sci. Rep.* **7**, 13115 (2017).
- 37. Moutaux, E. *et al.* Neuronal network maturation differently affects secretory vesicles and mitochondria transport in axons. *Sci. Rep.* **8**, 1-14 (2018).
- 20 ➤ 38. Domínguez-Bajo, A. *et al.* Nanostructured gold electrodes promote neural maturation and network connectivity. *Biomaterials* **279**, 121186 (2021).
- 39. Dolphin, A. C. & Lee, A. Presynaptic calcium channels: specialized control of synaptic neurotransmitter release. *Nat. Rev. Neurosci.* **21**, 213-229 (2020).
- 40. Proctor, C. M. *et al.* Electrophoretic drug delivery for seizure control. *Sci. Adv.* **4**, eaau1291 (2018).
- 25 ➤ 41. Burman, R. J. *et al.* Molecular and electrophysiological features of spinocerebellar ataxia type seven in induced pluripotent stem cells. *PLoS One* **16**, e0247434 (2021).
- 42. Alcinesio, A., Krishna Kumar, R. & Bayley, H. Functional Multivesicular Structures with Controlled Architecture from 3D-Printed Droplet Networks. *ChemSystemsChem*, e2100036 (2021).
- 30 ➤ 43. Urban, P. *et al.* Light-Controlled Lipid Interaction and Membrane Organization in Photolipid Bilayer Vesicles. *Langmuir* **34**, 13368-13374 (2018).

- 44. Booth, M. J., Schild, V. R., Graham, A. D., Olof, S. N. & Bayley, H. Light-activated communication in synthetic tissues. *Sci. Adv.* **2**, e1600056 (2016).
- 45. Paşca, S. P. The rise of three-dimensional human brain cultures. *Nature* **553**, 437-445 (2018).
- 5 ➤ 46. Revah, O. *et al.* Maturation and circuit integration of transplanted human cortical organoids. *Nature* **610**, 319-326 (2022).
- 47. Paşca, S. P. *et al.* A nomenclature consensus for nervous system organoids and assembloids. *Nature* **609**, 907-910 (2022).

Methods

Hydrogel materials

All materials were purchased from Sigma-Aldrich (Merck KGaA). For all droplet power sources, low gelling temperature (LGT) agarose was used to build the hydrogel scaffold.

5 This material has enough gel strength for fabrication at around room temperature. Other materials were dissolved in Milli-Q water with 30 min ultrasonication (Branson 2800) and then mixed with the LGT agarose powder to form various precursor solutions (pre-gels). Final pre-gels had 2% w/v LGT agarose and the following compositions. High-salt hydrogel: 2 M CaCl_2 . Low-salt hydrogel: 0.01 M CaCl_2 , 10% v/v poly(ethylene glycol)

10 (number average molecular weight 400). NaCl and KCl can replace CaCl_2 if necessary (Supplementary Fig. 5). However, to obtain optimum output voltage, CaCl_2 was used during electrical measurements except where noted. The cation-selective hydrogel contained 20% w/v poly(sodium 4-styrenesulfonate) (average molecular weight 70,000) and the anion-selective hydrogel contained 20% w/v poly(allylamine hydrochloride)

15 (average molecular weight 50,000). Pre-gel solutions were first heated to 90 °C to dissolve agarose and then kept molten at 37 °C before and during droplet deposition. Food dyes were only used for photography and were absent during electrical recording and biological experiments.

20 Preparing lipid/oil solutions

Agarose pre-gel droplets were deposited in a lipid-containing oil and acquired lipid coatings, which subsequently formed lipid bilayers at the interface when droplets were brought into contact. Lipids were purchased from Avanti Polar Lipids in powder form and stored at -80 °C. Undecane and silicone oil AR20 (Sigma-Aldrich) were filtered through

25 0.22 μm filters (Corning) under vacuum before use. Lipid films were prepared by bringing ampoules to room temperature and dissolving the lipids in anhydrous chloroform (Sigma-Aldrich) at 25 mg mL^{-1} to give the lipid stock solution. Using glass syringes (Hamilton), lipid stock solutions of 1,2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC, 90 μL) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC, 40 μL) were transferred into a

30 Teflon-capped glass vial (Supelco, 7 mL) that had been cleaned with isopropanol. The chloroform was evaporated under a slow stream of nitrogen while the vial was rotated by hand to produce an even lipid film. The film was dried under vacuum for 24 h, and stored

under nitrogen at -80 °C until use. When required for droplet fabrication, films were left at room temperature for 30 min, then 2 mL of a pre-mixed solution of undecane and silicone oil (35:65 by volume) was added to the film, followed by sonication (Branson 2800) for 1 h. The total concentration of lipids was 2 mM with a molar ratio of DPhPC:POPC of 2:1.

- 5 Lipid films were kept for a maximum of 2 months.

Depositing droplet power sources

- Droplets were formed in custom-made transparent resin mould, produced using a 3D printer (Formlabs, Solid Print3D). Depending on the shape of the mould, various self-
- 10 assembled patterns were formed. Typically, moulds were filled with 200 µL of lipid-containing oil. In each mould, droplets of pre-gel solution were printed with a programmable microinjector (FemtoJet, Eppendorf), which ejected droplets from a loaded glass nozzle (Femtotips, Eppendorf) with volumes that ranged from femtoliters to microliters. Single droplet power units were obtained by depositing droplets into contact
- 15 with one another and allowing bilayers to form at the interfaces, which happened within seconds. Larger droplet networks self-assembled into pre-designed shapes in templates, such as the hexagonal 'flower-like' pattern (Fig. 3). After formation, droplet networks, along with surrounding oil, were drawn into a truncated pipette tip by capillary action, and could then be rearranged, stacked in deeper templates, or placed in three dimensions. An
- 20 infrared radiation (IR) heater (Beurer, 150 W) was used to keep the temperature of the nozzles and the resin mould at approximately 37 °C. After fabrication, the droplet power sources could be stored for more than 2 days within a lipid/oil solution in a humid incubator at 37 °C to prevent water evaporation (Fig. 1f) without energy dissipation due to the insulating DIBs.

25

Triggering droplet power sources

- To use a power source, the lipid insulation was removed by transferring the power source into oil without lipid and triggering full gelation at low temperature. To do so, the deposited droplet power sources were left for 5 min at ambient temperature (around 22 °C)
- 30 to partially gel the agarose and allow the droplets to reach their equilibrium contact angles. Next, droplet power sources were washed with silicone oil by removing the lipid/oil solution from the mould and then adding 500 µL fresh silicone oil, containing no lipid.

After the transfer to lipid-free oil, the droplet power sources were moved to a fridge (4 °C) for 1 min to allow complete disruption of the insulating DIBs and consequent formation of a continuous hydrogel structure. For *in situ* measurements of the electric output during the rupture of DIBs and low-temperature gelation, a Peltier cooler (14 W, 62 × 62 mm, RS PRO) and a heat sink (85 × 85 × 6mm, RS PRO) were integrated to the bottom of the droplet measurement system (Extended Data Fig. 2). Such integration enabled the droplet deposition, power source activation, and electrical measurement in an all-in-one set up.

Encapsulating droplet power sources

A polymer-based organogel was prepared by mixing SEBS (molecular weight ~118,000, Sigma-Aldrich) with 1% by wt F68 flake (Pluronic, Sigma-Aldrich) and undecane/hexadecane oil (50:50 by volume) at a concentration of 20 mg mL⁻¹. The mixture was then stirred at 95 °C in a closed vial. Once a clear liquid had been formed, it was cooled to 37–40 °C before use. Organogel encapsulation was conducted by replacing the silicone oil with the molten polymer-oil mixture at the last oil transfer step. Lipid-free organogel (1 mL) was used to wash and cover the droplet power sources. After the transfer to organogel, the encapsulated droplet power sources were moved to a fridge (4 °C) in which the organogel solidified. The final construct was gently extracted from the mould, forming a freestanding droplet power source. Electrodes can pierce through the solidified organogel for measurement of the power output.

Characterization of droplet power sources

We used Ag/AgCl wire electrodes (100 µm diameter, Sigma-Aldrich) to contact the first and last compartments of the droplet power source, which were both high-salt droplets. The ion flux in the droplets was converted to electron flow in an external circuit (Supplementary Note 1). We recorded V_{OC} and I_{SC} using a Keithley 617 programmable multimeter set to voltage measurement mode with high input impedance (~2 TΩ) and current measurement mode as a feedback-type picoammeter. The effective output power of the droplet power source was evaluated by monitoring the voltage and current with resistances ranging from 0.01 to 0.5 MΩ.

Simulations

To validate the output voltage and current of the droplet power source under various settings, we made simulations based on the experimental setup shown in Supplementary Fig. 3. We used COMSOL Multiphysics 5.6 and coupled Nernst Planck Poisson equations. The two ion-selective droplets were assumed to act as ion-exchange membranes with
 5 opposite fixed charges of 1000 C m^{-3} . The modeled ions were K^+ and Cl^- , with defined initial concentrations of 2 M and 0.01 M in the high-salt and low-salt droplets, respectively. Modeling conditions for interfaces were the combination of tertiary current distribution and the Nernst Planck interface, with Poisson-type charge conservation. Results were calculated using time-varied (transient) analysis with a time range from 0 to
 10 1800 s.

Powering electronic components with droplet power sources

To light up an LED (Fig. 3h), four types of droplet component were deposited in a spiral mould (Fig. 3f) to form 20 power units in series connected to a red LED (Broadcom
 15 HLMP-K150). A capacitor ($0.47 \mu\text{F}$, RS PRO) could be connected in series to store the released energy from droplet power source and subsequently light up the red LED (Supplementary Fig. 7a). A pulse generator circuit based on a 555-timer chip (TLC555IP, RS PRO) was also powered by the droplet power source (Supplementary Fig. 7c).

Neuron culture and brain tissue harvest

NPCs were derived from human induced pluripotent stem cells (iPSCs), kindly provided by Dr. S. Cowley (James Martin Stem Cell Facility, Oxford). Neural differentiation of iPSCs and NPC culture were performed according to published procedures^{28,48}. NPCs were maintained as two-dimension adherent cultures on Geltrex-coated (Life Technologies,
 25 A141133-02) culture plates in neural maintenance medium, which consists of N-2 medium and B-27 medium (1:1 v/v). The N-2 medium contains DMEM/F12 medium (Life Technologies; 21331020), $1 \times$ N-2 (Gibco, 17502048), and 1 mM GlutaMax (Gibco, 35050-038). The B-27 medium contains neurobasal medium (Gibco, 21103-049S), $1 \times$ B-27 (Gibco, 17504044), and 1 mM GlutaMax (Gibco, 35050-038). Day 26 (since neural
 30 induction) NPCs were harvested by incubating with Accutase (Life Technologies, A11105-01) for 5 min at 37°C and dissociated into a cell suspension with gentle pipetting. The cells were then centrifuged (5 min at $200 \times g$) and the supernatant was removed. Pre-

thawed Matrigel (Corning) was added to the cell pellet and mixed to make a bio-ink with a cell density of 2×10^7 cells mL⁻¹.

NPCs labelled with red-fluorescent-protein (RFP) were derived from RFP-iPSCs^{28,48}. The cells were cultured and passaged the same as the non-labelled NPCs except for the addition of 2.5 µg mL⁻¹ puromycin (Thermo Fisher Scientific) in neural maintenance medium for RFP selection.

Mouse brain tissues were acquired from Prof. M. Lei, Department of Pharmacology, University of Oxford. Adult C57BL/6 mice were sacrificed following a Schedule 1 procedure. The brain was surgically removed, and 300 µm brain slices were prepared by using Compresstome vibrating microtome (Precisionary, VF-300-0Z) equipped with an HP35-coated microtome blade (Thermo Fisher Scientific, 3150743). Brain slices were collected in chilled Earl's balanced salt solution bubbled with carbogen (95% O₂ and 5% CO₂) and transferred onto 30 mm cell-culture inserts (Millicell, PICM0RG50) in six-well plates. The brain slices were incubated at 37°C, with 5% CO₂, for no more than three days in 75% BrainPhys medium with SM1 supplements (Stemcell Technologies, 05792), 25% horse serum (GIBCO, 16050130), and 100 U Penicillin-Streptomycin (GIBCO, 15140122).

Fabrication of droplets containing cells or tissues

The procedure contained two major steps: firstly, we used a home-built microfluidic printing system to generate 3D cellular microtissues⁴⁹. Then, we cultured the microtissues and coated them with low-salt agarose hydrogel made from neuron culture medium, immediately before use to form a continuous hydrogel structure with an attached droplet power source (Fig. 4a).

In the first step for the construction of neural microtissues, the harvested neural cells (NPCs) were pelleted and re-suspended in Matrigel (Corning) and loaded into a syringe at 8 °C at 2×10^7 cells mL⁻¹. The cell-laden Matrigel and oil (tetradecane, Sigma-Aldrich) were then pumped into a 3-way polydimethylsiloxane (Sigma-Aldrich) connector by a programmable neMESYS syringe-pump (Cetoni, Korbussen). At an optimized flow rate, spherical Matrigel droplets containing cells, separated by the carrier oil, were formed in a polytetrafluoroethylene tube (Cole-Parmer). The droplet diameter was determined by the inner diameter of the tube (e.g., 570 µm). Then, the tube containing the cell-laden

microtissues and oil was placed in a culture chamber at 37°C for 2 h to allow gelation of the Matrigel, thereby forming 3D cell-laden microtissues. Finally, the microtissues were ejected from the exit tube, transferred to medium, and cultured before use. The day of forming neural microtissues was marked as day 0. The 3D neural microtissues were

5 cultured in a neural maintenance medium supplemented with 50 U mL⁻¹ penicillin and streptomycin (Gibco, 15140-122). Cell medium was changed every 3 days²⁸.

In the second step for embedding the neural tissues in agarose droplets, the cultured neural microtissues were transferred into a mould filled with silicone oil using truncated pipette tips (200 µL). An IR heater was used to keep the surrounding temperature at approximately

10 37 °C. Residual medium was carefully removed before adding low-salt hydrogel solution (0.5 µL) with a 7000 series Hamilton syringe to coat each neural microtissue. The low-salt hydrogel contained 2% agarose, and ~1 mM Ca²⁺, ~4 mM K⁺, and ~140 mM Na⁺ from the neuron culture medium. Due to the surrounding oil, the hydrogel solution rapidly covered the neural microtissues. Then, the mould was kept at 20 °C for 10 min to gel the hydrogel

15 coating. This final gel coating unified the size variation of different neural constructs, made them easy to handle, confined the ionic current channel, and dissipated possible compressive forces on the embedded microtissues. The coated droplets were then returned to culture medium for dyeing and used for neuronal modulation. *Ex vivo* mouse brain slices could also be processed according to the same second step to obtain droplets containing

20 tissues.

Neuron live/dead staining, viability determination, and immunostaining

To image the live/dead distribution of neurons after power source modulation, neuron-containing droplets were incubated with 2.5 µM Calcein-AM (C1430, Thermo Fisher

25 Scientific) and 5.0 µM PI (Sigma Aldrich) for 60 min at 37 °C before imaging with an epifluorescence microscope (Leica DMI8). PrestoBlue assays (Thermo Fisher Scientific) were used to determine live cell number and viability according to the manufacturer's instructions. A microplate reader (CLARIOstar Plus) was used to quantify the fluorescence and hence the number of living cells.

30 For immunostaining, neural microtissues were firstly fixed in 4% v/v paraformaldehyde (Sigma Aldrich) for 30 min at room temperature and then quenched in 50 mM glycine (Sigma Aldrich). The samples were incubated with blocking solution, 5% donkey serum in

triton phosphate buffered saline (TPBS) containing 0.1% v/v Triton X-100 (Thermo Fisher Scientific) for 1 h at room temperature. Primary antibodies TUJ1 (Synaptic Systems) and Caspase 3 (Thermo Fisher Scientific) were added in blocking solution and samples were incubated overnight at 4°C. The next day, samples were washed 3 times (10 mins each) in phosphate buffered saline (PBS) and then incubated with secondary antibodies for 2 h at room temperature. Samples were then washed in PBS for another 3 times (10 mins each), followed by the incubation with 4',6-diamidino-2-phenylindole ($5 \mu\text{g mL}^{-1}$) in TPBS for 15 min and washed again. Z-stack images of all immunostained neural microtissues were acquired using a fluorescence confocal microscope (Leica SP5).

10

Neuronal modulation by droplet devices

A droplet device consisting of 3 high-salt and 2 ion-selective droplets was deposited in a circular container that was integrated upon an imaging dish (μ -Dish, Ibidi). Droplets formed a continuous hydrogel structure after oil transfer with lipid-free oil. The droplet device was then attached to 3 low-salt hydrogel droplets that contains neural microtissues or brain tissues, completing a ring structure (Supplementary Fig. 11). The droplet device could then produce ionic current to modulate neurons or tissues in the closed loop. Droplets containing neurons or brain tissues were combined with droplet devices for 10 min and then put back in culture medium for 20 min, as one modulation-relaxation cycle. Neurons recovered to the initial active state after each cycle (Extended Data Fig. 5). To validate the network modulation by the droplet device, neuron-containing droplets were treated with GABA (Sigma-Aldrich) at a concentration of $30 \mu\text{M}$, which has previously been determined to be an inhibitory but nontoxic concentration⁴⁰.

Neuronal imaging

For calcium imaging, a Fluo-4 Direct™ calcium assay kit (Invitrogen, F10471) was used according to the manufacturer's instructions to measure calcium activity. Briefly, droplets containing neurons or brain tissues were transferred to 48-well plates and incubated with neural maintenance medium and Fluo-4 calcium imaging reagents (1:1 v/v) for 1 h at 37 °C. Time-lapse (XYZTime) fluorescence images were acquired at 1.28 s per frame under the optical settings suggested by Invitrogen by using a fluorescence confocal microscope (Leica SP5) at Ex/Em 488/525 nm. Z-stack images were acquired between the bottom of

neural microtissues to ~50 μm above with a step of 5 μm per image. Maximum Z projection was then conducted to generate the final time-lapse images. Bright-field images were recorded with a stereomicroscope (Leica EZ4 W) and a wide-field light microscope (Leica DMi8). Images were processed using the Leica Application Suite X and Fiji (ImageJ).

For membrane potential imaging, a FluoVolt™ membrane potential kit (Thermo Fisher Scientific) was used according to the manufacturer's instructions to measure neuronal membrane potential. Time-lapse fluorescence images were acquired at 0.37 s per frame under the optical settings suggested by the manufacturer by using a fluorescence confocal microscope (Leica SP5). Images were processed using the Leica Application Suite X and Fiji (ImageJ).

Calculating imaging results

The fluorescence intensities of neurons were obtained using the Fiji freehand tool and profile plots function. To obtain the relative ion concentration distributions of Ca^{2+} and Cl^- on a selected line plot (Fig. 4c), the relative concentration (C) is defined as

$$C = \frac{Fluo(t) - F_0}{F_{final} - F_0} \quad (1)$$

$Fluo(t)$ is the fluorescence intensity at time t (Supplementary Fig. 9). F_0 is the initial fluorescence intensity before forming a continuous hydrogel network. Due to different fluorescence responses, F_{final} are the maximum fluorescence intensities across three droplets after 20 min for Ca^{2+} (fluorogenic response) and the minimum for Cl^- (quenching response).

To calculate the moving speed of Ca^{2+} waves across a neuronal network (Fig. 4d and e), we needed to first calculate the center of fluorescence of the neuronal network. We chose the method of weighted mean to represent the position of the center of fluorescence, which is defined as

$$\text{Weighted} - \text{mean Distance} = \frac{\sum(\text{Intensity} \times \text{Distance})}{\sum \text{Intensity}} \quad (2)$$

$\sum \text{Intensity}$ is the summation of each fluorescence value on a selected line plot.

$\sum(\text{Intensity} \times \text{Distance})$ is the summation of each fluorescence value multiplied by the distance from the origin (boundary of cells or brain tissues) of the selected line plot.

Knowing the position of the center of fluorescence, we can calculate the relative displacement of fluorescence (Fig. 4f), which is defined as

$$\text{Relative Displacement} = \frac{\Delta(\text{Weighted-mean Distance})}{\text{Total Length}} \quad (3)$$

$\Delta(\text{Weighted-mean Distance})$ is the variation of weighted-mean distance before and after modulation. *Total Length* is the length of the selected line plot.

Statistics

Statistical analyses were performed using Origin and the p-value was determined by unpaired one-way analysis of variance (ANOVA). Each experiment used a minimum of three independent droplet power sources.

Additional References

- 48. Haenseler, W. *et al.* A highly efficient human pluripotent stem cell microglia model displays a neuronal-co-culture-specific expression profile and inflammatory response. *Stem Cell Rep.* **8**, 1727-1742 (2017).
- 49. Ma, S., Mukherjee, N., Mikhailova, E. & Bayley, H. Gel microrods for 3D tissue printing. *Adv. Biosyst.* **1**, 1700075 (2017).

Supplementary Note 1. Theoretical background for the droplet power source

In brief, the mechanisms of the ionic droplet power source can be described in four parts (Schematic S1).

1.1 Part 1

The direct current droplet power source is based on droplets containing different salt concentrations connected by charge-selective droplets that act as ion filters. Ions flow from high to low concentration through the charge-selective droplets, a process combining diffusion and Donnan exclusion, releasing the chemical energy stored in the ion concentration gradient (Schematic S1a) and giving rise to an electromotive force across the charge-selective droplets, as embodied in the Nernst-Planck equation and the Goldman-Hodgkin-Katz current equation^{1,2}. Briefly, the flux of ions *s* in an electric field is given by J_s (mol m⁻² s⁻¹), where:

$$J_s = -D_s \left(\nabla C_s + \frac{FZ_s}{RT} C_s \nabla \varphi \right) \quad (S1)$$

where D_s ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of s in its medium, C_s (mol m^{-3}) is the molar concentration of s , F (C mol^{-1}) is Faraday's constant, Z_s is the charge of s , R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) is the temperature, and φ (V) is the electrical potential. The ion flux in current form, using assumptions based on the Goldman-Hodgkin-Katz current equation^{1,2}, is given by:

$$I_s = P_s V F^2 Z_s^2 \frac{C_{s_{in}} - C_{s_{out}} e^{-VF \frac{Z_s}{RT}}}{RT \left(1 - e^{-VF \frac{Z_s}{RT}} \right)} \quad (S2)$$

I_s (A m^{-2}) is the current density carried by ions s across a charge-selective droplet, P_s (m s^{-1}) is the permeability of s through the droplet, V (V) is the generated voltage across the droplet, and $C_{s_{in}}$ and $C_{s_{out}}$ (mol m^{-3}) are the concentrations of s inside and outside the droplet. For example, when formulated to consider only KCl in the high- and low-salt droplets, the total ionic current density I (A m^{-2}) is the sum of I_K and I_{Cl} .

$$I = \frac{VF^2}{RT \left(1 - e^{-\frac{VF}{RT}} \right)} \left[\left(P_{K^+} C_{K_{in}^+} + P_{Cl^-} C_{Cl_{out}^-} \right) - \left(P_{K^+} C_{K_{out}^+} + P_{Cl^-} C_{Cl_{in}^-} \right) e^{-\frac{VF}{RT}} \right] \quad (S3)$$

1.2 Part 2

Equations S1 to S3 formulate the relationship between the intrinsic electromotive force (V_{source} , overall V across cation-selective and anion-selective droplets of the power source) and the ideal ion flux of the droplet power source in electrochemical theory; in actual use and measurement, we also need to consider the ion flux in the low-salt droplet (Schematic S1a). In the low-salt droplet, ions of the salt initially present and inflowing oppositely-charged ions would move to neutralise the inflowing ions to keep electroneutrality, thus completing an ionic pathway. For example, inflowing Cl^- from right high-salt droplet and initial Cl^- in the low-salt droplet would move to neutralise the inflowing K^+ ions from the left high-salt droplet. As a result, the ion fluxes from left and right of a power source unit will be equal to maintain electroneutrality. The voltage division can be modeled in terms of the internal resistance (R_{source}) of the droplet power source (Schematic S1b). The resistance of each droplet is strongly dependent on the ionic strength within it^{3,4}, so that the low-salt droplet contributes the main resistance in the

system ($R_{Source} \approx R_{Low-salinity}$)^{2,5}. At open circuit, the power source connects to a very large external resistance within the connected meter ($R_{Meter} \rightarrow \infty \gg R_{Source}$), forcing the droplet power source into a regime with high output voltage but very low current ($I = 0$). Equation S3 then reduces to

$$5 \quad V_{Meter} = V_{Source} = V_{OC} = \frac{RT}{F} \ln \left(\frac{P_{K^+} + C_{K^+}_{out} + P_{Cl^-} - C_{Cl^-}_{in}}{P_{K^+} + C_{K^+}_{in} + P_{Cl^-} - C_{Cl^-}_{out}} \right) \quad (S4)$$

At short circuit ($R_{Meter} \rightarrow 0 \ll R_{Source}$, $V_{Meter} = 0$), Equation S3 then reduces to

$$I_{Meter} = I_{SC} = \frac{V_{Source}}{R_{Source}} \approx \frac{V_{OC}}{R_{Low-salinity}} \quad (S5)$$

Therefore, the low-salt droplet affects V_{OC} by its concentration gradient with the high-salt droplet (Extended Data Fig. 4a), and limits I_{SC} by its resistance (Extended Data Fig. 4b and
10 c). Decreasing salt concentration in the low-salt droplet will increase the V_{OC} but decrease the I_{SC} due to the increased resistance. As a trade-off, we used 0.01 M salt in the low-salt droplet except where noted.

1.3 Part 3

15 The ion flux of the droplet power source can be converted into electron flow in the external circuit by using chemically active electrodes (Schematic S1a). We used Ag/AgCl wire electrodes to contact with the first and the last high-salt droplets: on the anode side (droplet of high-salt connected to cation-selective droplet), anions are converted into electrons by $Ag(solid) + Cl^- \rightarrow AgCl(solid) + e^-$; on the cathode side (droplet of high-salt connected to
20 anion-selective droplet), electrons are converted into anions by $AgCl(solid) + e^- \rightarrow Ag(solid) + Cl^-$. Therefore, as a whole, the droplet power source follows the law of electroneutrality.

1.4 Part 4

25 If neurons are embedded in the low-salt droplets, the inflowing ions will move in the extracellular space of the neurons and modulate neuronal activity. The modulation is the result of the ionic current⁶⁻⁹ generated by the droplet device. Hence, this modulation is dynamic and stops when the droplet device reaches the final balance of salt concentration.

Supplementary Note 2. Research background

Inspired by the electric eel, a soft hydrogel power source has been developed by Prof. Michael Mayer's group as an alternative to conventional solid batteries^{2,5}. Their system used ionic gradients between polyacrylamide hydrogels bounded by cation- and anion-selective hydrogel membranes to generate output electricity. However, their soft power source focused on large-area gel fabrication in order to increase the output voltage and power, while the potential material toxicity and assembly methods were not designed for microscale-to-mesoscale biological applications.

Firstly, they used acrylamide to build the gel scaffold of their power source by photoinitiated radical crosslinking to form polyacrylamide. However, acrylamide monomer has neurotoxic effects^{10,11} if it has not been fully reacted or washed out. Further, their cation- and anion-selective materials (3-sulfopropyl acrylate (potassium salt), 2-acrylamido-2-methylpropane sulfonic acid, and (3-acrylamidopropyl) trimethylammonium chloride) also have potential biocompatibility issues if they have not been fully crosslinked with the gel scaffold. Moreover, Mayer and colleagues used a scalable stacking or folding geometry, e.g., *Miura-ori* folding, to achieve mechanical contact of multiple power units in series while circumventing power dissipation before contact. However, this method is only suitable for large-area assembly and presents challenges in terms of methods for microscale assembly that avoid self-discharge before usage.

Notably, three- and six-droplet power sources have previously been constructed, based on the concentration cell¹². These networks function by incorporating an engineered anion-selective *Staphylococcal* α -hemolysin nanopore into a lipid bilayer separating two droplets containing different concentrations of NaCl, thus converting the ionic gradient energy into output electricity. However, at this point, such a droplet power source is still in its infancy and faces a multitude of fundamental challenges that limit its applicability for powering useful activities. First, the use of a protein nanopore as the ion-selective material greatly limited the output current to ~60 pA, which is insufficient to drive most devices. Moreover, because the power source relied on a restricted salt concentration gradient (10-fold at a maximum) to prevent droplet coalescence, it ran for only less than an hour with a low open-circuit voltage, before ion and water transport across the bilayer, the latter by osmosis, balanced the salt concentrations and severely reduced the output. In addition, issues such as recharging capability, large-scale fabrication, remote triggering (stimulus-

responsiveness), and energy generation in a biological environment remain unexplored in this context.

In brief, although previous work has presented inspiring examples of soft power sources, our research addresses previous limitations and demonstrates unique biological

5 applications by the modulation of neuronal activity.

Supplementary Note 3. Additional output optimization

Based on the aforementioned discussion and previous work^{1,2}, the electrogenic performance of the droplet power source depends on the following factors: the concentration gradient between the high-salt and low-salt droplets, the volume of each
10 droplet, the ion permeabilities of the two charge-selective droplets, and the external resistance. Some of these factors are analyzed in the main text, while others are discussed here.

15 3.1 Volume and internal resistance of droplets

The volume of a droplet can range from femtoliters to microliters, which affects the output performance (Fig. 2a and b). For example, the internal resistance of the droplet power source depends on droplet volume. The low-salt compartment contains only 0.01 M salt and thus contributes most of the system's electrical resistance (R , also see 1.2 Part 2),
20 which is directly proportional to the length of the ionically conductive pathway (l) and inversely proportional to the average cross-sectional area ($S_{average}$) of the droplet (Equation S6). ρ is the resistivity of the droplet. Relating l and $S_{average}$ to the diameter (D) of the spherical droplet, we obtain:.

$$R \approx \frac{\rho l}{S_{average}} = \frac{\rho D}{\frac{1}{6}\pi D^3} = \frac{6\rho}{\pi D} \quad (S6)$$

25 Therefore, as the volume and hence the diameter decrease, the internal resistance of droplet power source will increase and the output performance will decrease.

3.2 Ion permeabilities of the two charge-selective droplets

According to the Donnan effect and the Goldman-Hodgkin-Katz equation^{1,2,13}, an
30 increased ratio of the permeability of the selected ion relative to the permeability of the disfavored ion across a charge-selective membrane results in an increased voltage across

that membrane. Hence, it is important to choose charge-selective materials that have high permselectivities for counter ions. In our work, we used poly(sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) as the cation-selective and anion-selective materials, respectively. Notably, PSS and PAH have been commonly used as ion exchange polymers for water treatment due to their biocompatibility and high permselectivity ($> 10^3$)^{14,15}. In addition, both PSS and PAH are water-soluble and can be mixed with agarose hydrogel on account of their good hydrophilicity and long-chain entanglement¹⁵. Therefore, we used these charge-selective materials to produce the high output performance of our droplet power source.

10

3.3 External resistance

The last influencing factor is the external resistance. The importance of impedance matching is well known for traditional galvanic cells, which have maximum output power (P_{max}) when the internal resistance ($R_{internal}$) equals the external resistance (R_{load})¹ (Equation S7). In previously reported work, the low-salt gel contributed most of the total internal resistance of a power unit^{2,5}. Here, we constructed the resistance–voltage–power curves (Extended Data Fig. 4c) and obtained the maximum output power by connecting a series of known-load resistances to the power sources while monitoring the voltage across the load. By repeating this measurement with various sizes of droplets, we obtained the power densities ($\rho_{density}$) of power units with various droplet volumes (Fig. 2b). The total volume of a droplet power unit is five times of the volume of a single droplet. Shrinking down the size of droplets can slightly increase the internal resistance and thus decrease the output voltage/current (Equation S6); however, the increase of energy density is more significant (Equation S8). For example, by reducing the size to below 100 nanolitres (1.87 nL), the energy density of our droplet power source increased by approximately 100 times to 1.3 kW m⁻³.

25

$$P_{max} = \frac{V_{load}^2}{R_{load}} = \frac{V_{OC}^2}{4R_{internal}} \quad (S7)$$

$$\rho_{density} = \frac{P_{max}}{5 \times Volume} = \frac{6P_{max}}{5\pi D^3} \quad (S8)$$

D is the diameter of the droplet.

30

Supplementary Note 4. Mechanisms of neuronal imaging

Ca²⁺ serves as an intracellular second messenger that controls key functions that are necessary for many neuronal processes, including firing, synaptic plasticity, and gene transcription^{16,17}. Hence, imaging Ca²⁺ in neurons is particularly important and has been commonly achieved by using fluorogenic dyes^{18,19}. Fluorogenic Ca²⁺ indicators are widely
 5 used for in-cell measurement of agonist-stimulated and antagonist-inhibited Ca²⁺ signaling through G protein-coupled receptors, a large and active target class involved in neuronal activity. To test the activity of the neurons in our printed droplets, we performed Ca²⁺ imaging with Fluo-4 Direct™.

A Fluo-4 Direct™ calcium assay kit (Invitrogen, F10471) was used according to the
 10 manufacturer's instructions. The assay kit can be used in the presence of complete culture media and will efficiently suppress background fluorescence without sacrificing the specific intracellular fluorescence generated in the assay. The visible excitation wavelength, high sensitivity, and large fluorescence increase upon binding Ca²⁺ have made Fluo-4 Direct™ the choice of indicator for our work. Importantly, contributions to baseline
 15 fluorescence by ions (e.g., K⁺, Cl⁻, or Ca²⁺) from the droplet devices are eliminated by the addition of a suppression dye (contained in the Fluo-4 Direct™). Therefore, the imaging reflects intracellular neuronal Ca²⁺ levels.

Supplementary Note 5. Intracellular Ca²⁺ waves induced by ionic current

20 We observed two differences between modulation induced by electrodes (Extended Data Fig. 6) and by the droplet devices. The response time and the relative fluorescence change of the induced Ca²⁺ wave were slightly longer (over 1 min) and lower respectively for the ionic current produced by using Ag/AgCl electrodes in Ca²⁺-free droplets, in agreement with previous studies on neuronal networks²⁰. These results might be explained by a
 25 neuronal model of regenerative Ca²⁺ release and wave propagation^{7,9,21,22}. In brief, Ca²⁺ in neurons is contributed from two main sources: external Ca²⁺ entry through voltage-gated calcium channels and internal Ca²⁺ release through channels in the endoplasmic reticulum (e.g., inositol trisphosphate receptors). Ca²⁺ waves can propagate and be amplified like the 'toppling dominos' when there is Ca²⁺ available by extracellular entry and/or by
 30 intracellular release (Schematic S2). Therefore, when we used the droplet devices with Ca²⁺ ions, the device might have induced both intracellular Ca²⁺ release and extracellular Ca²⁺ entry which caused the Ca²⁺ waves to be slightly faster (less than 15 s) and stronger

compared to Ca^{2+} -free electrical modulation. These results uncouple the electrical and ionic effects induced by the droplet devices on neurons. They also demonstrate the combination of electrical and ionic effects in one device, which cannot be achieved with conventional electrode-based stimulation.

5

Reference

- 1 Xu, J., Sigworth, F. J. & LaVan, D. A. Synthetic protocells to mimic and test cell function. *Adv. Mater.* **22**, 120-127 (2010).
- 2 Schroeder, T. B. H. *et al.* An electric-eel-inspired soft power source from stacked hydrogels. *Nature* **552**, 214-218 (2017).
- 3 Długolecki, P. *et al.* On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport. *J. Membr. Sci.* **349**, 369-379 (2010).
- 4 Galama, A. *et al.* Membrane resistance: The effect of salinity gradients over a cation exchange membrane. *J. Membr. Sci.* **467**, 279-291 (2014).
- 5 Guha, A. *et al.* Powering Electronic Devices from Salt Gradients in AA-Battery-Sized Stacks of Hydrogel-Infused Paper. *Adv. Mater.* **33**, 2101757 (2021).
- 6 Wang, C. *et al.* Inverted battery design as ion generator for interfacing with biosystems. *Nat. Commun.* **8**, 1-7 (2017).
- 7 Ryglewski, S., Pflueger, H. J. & Duch, C. Expanding the Neuron's Calcium Signaling Repertoire: Intracellular Calcium Release via Voltage-Induced PLC and IP3R Activation. *PLoS Biol.* **5**, e66 (2007).
- 8 Zhang, L. I. & Poo, M.-m. Electrical activity and development of neural circuits. *Nat. Neurosci.* **4**, 1207-1214 (2001).
- 9 Scemes, E. & Giaume, C. Astrocyte calcium waves: what they are and what they do. *Glia* **54**, 716-725 (2006).
- 10 Spencer, P. S. & Schaumburg, H. H. Nervous system degeneration produced by acrylamide monomer. *Environ. Health Perspect.* **11**, 129-133 (1975).
- 11 Hamilton, P. D., Aliyar, H. & Ravi, N. Biocompatibility of novel polyacrylamide copolymer suitable for intra-ocular lenses. *Invest. Ophthalmol. Visual Sci.* **45**, 1728-1728 (2004).
- 12 Holden, M. A., Needham, D. & Bayley, H. Functional bionetworks from nanoliter water droplets. *J. Am. Chem. Soc.* **129**, 8650-8655 (2007).
- 13 Crow, D. R. *Principles and applications of electrochemistry*. Vol. 6. Electrode potentials and electrochemistry cells (Routledge, 2017).
- 14 Zuo, K. *et al.* Selective membranes in water and wastewater treatment: Role of advanced materials. *Mater. Today* **50**, 516-532 (2021).

- 15 White, N., Misovich, M., Yaroshchuk, A. & Bruening, M. L. Coating of Nafion
Membranes with Polyelectrolyte Multilayers to Achieve High Monovalent/Divalent
Cation Electrodialysis Selectivities. *ACS Appl. Mater. Interfaces* **7**, 6620-6628 (2015).
- 16 Zhou, L. *et al.* Lipid-bilayer-supported 3D printing of human cerebral cortex cells
5 reveals developmental interactions. *Adv. Mater.* **32**, 2002183 (2020).
- 17 Citri, A. & Malenka, R. C. Synaptic plasticity: multiple forms, functions, and
mechanisms. *Neuropsychopharmacol.* **33**, 18-41 (2008).
- 18 Grienberger, C. & Konnerth, A. Imaging calcium in neurons. *Neuron* **73**, 862-885
(2012).
- 10 19 Ricardo Augusto de Melo Reis, F., Hércules Rezende, Fernando Garcia de Mello. Cell
Calcium Imaging as a Reliable Method to Study Neuron–Glial Circuits. *Front.*
Neurosci. **14** (2020).
- 20 Fujii, Y., Maekawa, S. & Morita, M. Astrocyte calcium waves propagate proximally by
gap junction and distally by extracellular diffusion of ATP released from volume-
15 regulated anion channels. *Sci. Rep.* **7**, 13115 (2017).
- 21 Ross, W. N. Understanding calcium waves and sparks in central neurons. *Nat. Rev.*
Neurosci. **13**, 157-168 (2012).
- 22 Warren, N. J., Tawhai, M. H. & Crampin, E. J. Mathematical modelling of calcium
wave propagation in mammalian airway epithelium: evidence for regenerative ATP
20 release. *Exp. Physiol.* **95**, 232-249 (2010).
- 23 Nakamura, T. *et al.* Risks and Benefits of Sodium Polystyrene Sulfonate for
Hyperkalemia in Patients on Maintenance Hemodialysis. *Drugs R&D* **18**, 231-235
(2018).

25 **Example 2**

Advances in the development of tiny smart devices with sizes below a few cubic millimeters require a corresponding decrease in the volume of the driving power sources. In the case of minimally invasive biomedical devices to interface biological tissues,

30 prospective power sources must be fabricated from soft materials. Our previous endeavours on microscale droplet-based devices have produced promising soft miniature power sources; however, a droplet-based secondary battery has remained out of reach.

Additional capabilities such as high capacity, biocompatibility and biodegradability, triggerable activation, and remote-control of function and mobility would be advantageous. Here we report a microscale soft flexible lithium-ion (Li-ion) droplet battery (LiDB) based on the lipid-supported assembly of droplets constructed from a biocompatible silk
5 hydrogel. Our LiDB is light-activated, rechargeable and biodegradable after use. With a volume of 30 nL (0.03 mm^3), the LiDB is more than 10^3 -fold smaller than previous soft Li-ion batteries and sustains a superior volumetric capacity of $\sim 570 \text{ nAh } \mu\text{L}^{-1}$. We have used the LiDB to power the electrophoretic translocation of charged molecules between synthetic cells and to mediate the defibrillation and pacing of *ex vivo* mouse hearts. By the
10 inclusion of magnetic particles to mediate propulsion, the LiDB can function as a mobile energy courier. Our work sets a benchmark for biomedical applications through the fabrication of a tiny soft Li-ion battery with an exceptional volumetric capacity.

Main

15 The miniaturization of smart devices is a burgeoning area of research¹⁻³. Therefore, the development of tiny batteries to power these devices is of critical importance and techniques such as three-dimensional (3D) printing⁴⁻⁶ and micro-origami assembly⁷ are beginning to have an impact. For minimally invasive applications in biomedicine, batteries are also preferred to be soft, biocompatible and biodegradable, with additional
20 functionality and responsiveness, such as triggerable activation and remote-controlled mobility⁸. However, at present, such a multifunctional microscale soft battery is not available. Although hydrogel-based lithium-ion (Li-ion) batteries demonstrate some of these features⁹⁻¹², none of them exhibit microscale fabrication of the battery architecture, in terms of self-assembled integration of hydrogel-based cathode, separator, and anode at the
25 sub-millimetre level. Manual assembly of pre-crosslinked compartments¹¹ or multistep deposition and crosslinking⁴ are necessary to avoid the mixing of materials from different compartments at the pre-gel (liquid) state or during the gelation process. This limitation not only makes it difficult to shrink hydrogel-based functional architectures but also hinders the implementation of high-density energy storage.
30 Towards that end, we have reported a miniaturized ionic power source by depositing lipid-supported networks of nanolitre hydrogel droplets¹³. The power source mimics the electrical eel by using internal ion gradients to generate ionic current¹⁴, and can induce

neuronal modulation. However, the stored salt gradient produces less power than conventional Li-ion batteries and the device cannot be fully recharged. In addition, activation of the power source relies on temperature-triggered gelation and oil for buffer exchange. Third, an ion gradient functionality of the power source generates ionic output, leaving the full versatility of synthetic tissues unexploited¹⁵⁻¹⁷. Finally, while the power source can modulate the activity of neural microtissues, organ-level stimulation necessitates a higher and more stable output performance in physiological environments¹⁸. Here we present a miniature, soft, rechargeable Li-ion droplet battery (LiDB) made by depositing self-assembling, nanolitre, lipid-supported, silk hydrogel droplets. The tiny hydrogel compartmentalization produces a superior energy density and mediates many other valuable capabilities. The battery is switched on by ultraviolet (UV) light, which crosslinks the hydrogel and breaks the lipid barrier between droplets. The droplets are soft, biocompatible and biodegradable. The LiDBs can power charged molecule translocation between synthetic cells, defibrillate mouse hearts with ventricular arrhythmias and pace heart rhythms. Further, the LiDB can be translocated from one site to another magnetically.

Design and performance of LiDBs

A single LiDB unit comprised three silk-hydrogel droplets that contained lithium manganese oxide (LiMn_2O_4 , LMO) particles and carbon nanotubes (CNT) in the cathode droplet, lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) particles and CNT in the anode droplet, and a central droplet containing lithium chloride (LiCl) as a separator (Fig. 30a/Example 2 Fig. 1a; detailed material compositions are included in the Methods). The cathode, separator, and anode droplets were deposited in a lipid-containing oil by using a microinjector. The droplets were initially surrounded by monolayers of lipid, which formed droplet interface bilayers (DIBs) within seconds upon contact with one another, thereby creating a stabilized, support-free structure (Fig. 30b/Example 2 Fig. 1b)^{19,20}. The lipid-supported droplet assembly and silk fibroin together played critical roles in a LiDB: First, the silk solution readily mixes with various active components in the pre-gel state. After droplet deposition, the DIBs prevent material diffusion between different droplets, acting as an insulative physical barrier²¹. This approach differs critically from previous fabrication methods of hydrogel batteries, in which components were first separately cast and crosslinked, and then manually assembled to form the final battery⁹⁻¹². Premature assembly

would result in the mixing of active materials that would produce short-circuits and hence battery deactivation. The consequently cumbersome and time-consuming fabrication process limits the minimum size of a soft battery. In contrast, in our approach, the cathode, separator, and anode droplets self-assemble into a tiny LiDB within seconds. The DIBs

5 allow the construct of soft and free-standing hydrogel units with distinct compartments at microscale. Our fabrication device can print droplets as small as 0.5 nL, which are ~ 100 μm in diameter—a ~ 10 -fold decrease than previous works¹¹. Second, photochemical dityrosine crosslinking of the silk hydrogel by UV irradiation for 1 min ruptured the DIBs (Fig. 35/Example 2 Extended Data Fig. 1 and Fig. 43/Example 2 Supplementary Fig. 1),

10 and established a pathway that conducts Li ions (Fig. 30c/Example 2 Fig. 1c), thereby activating the LiDB (Fig. 30d,e/Example 2 Fig. 1d, e). Third, after the formation of hydrogel structure, silk as a static component had a plethora of favourable properties that provided mechanical stability and hosted the energy-generating machinery (Fig. 30d, Example 2 Fig. 1d). The elastic behaviour of the silk hydrogel ensured the robust

15 performance of LiDBs²², including flexibility and compressibility with a modulus of ~ 10 kPa at 80% compression (Fig 44/ Example 2 Supplementary Fig. 2), and stable support of embedded Li-particles and CNT, creating a high electrical conductivity in the two electrodes ($\sim 41.3 \text{ mS cm}^{-1}$, Fig. 36/Example 2 Extended Data Fig. 2). The crosslinked silk fibroin enhanced the cation selectivity by its negatively-charged amino acids, which

20 showed an average zeta potential of -20.2 mV (Fig. 36/ Example 2 Extended Data Fig. 2) that facilitated Li-ion conduction²³. Furthermore, the silk hydrogel is biocompatible²⁴⁻²⁶, biodegradable^{27,28}, and strongly adhesive towards tissues²⁹, properties which are essential for biological use. Given the benefits of using the lipid-supported assembly of silk fibroin-containing droplets (Fig 30f/ Example 2 Fig. 1f), we developed a new fabrication

25 methodology to construct microscale soft batteries composed of biocompatible materials, by contrast with conventional bulky and rigid Li-ion batteries. Device production can be automated readily by using microfluidics and 3D droplet printers¹⁹.

Cyclic voltammograms of cathode and anode hydrogel electrodes were explored with a three-electrode system, which revealed that the silk hydrogel was electrochemically stable

30 within the working potential range and the redox reactions of both electrodes could be reversibly operated (Fig. 45/ Example 2 Supplementary Fig. 3). A mass loading of 10% w/v Li-particles in both hydrogel electrodes prevented particle aggregation (scanning

electron microscope images in Fig. 46/Example 2 Supplementary Fig. 4 and volumetric capacities with various mass loadings in Fig 47/ Example 2 Supplementary Fig. 5). Galvanostatic charge-discharge curves exhibited an average discharge voltage plateau of 0.65 V (Fig. 31a/Example 2 Fig. 2a). A promising output performance of LiDB was realized, with volumetric capacities of 17, 27, and 46 nAh μL^{-1} at 1, 0.5, and 0.2 μA for 1 μL droplets (Fig. 31b/Example 2 Fig. 2b). Moreover, the LiDB performed with high stability with an over 72% retention of output capacity after 50 cycles at 1 μA (Fig. 31c/Example 2 Fig. 2c) and restored its output capacity after applying a lower charge-discharge current of 0.5 μA (Fig. 48/Example 2 Supplementary Fig. 6). The robust hydrogel compositions ensured a stable storage time of more than 48 h (Fig. 49/Example 2 Supplementary Fig. 7). Further, temperature changes during charging and discharging were negligible (Fig. 50/Example 2 Supplementary Fig. 8).

Miniaturization of LiDBs was facilitated by the lipid-supported droplet self-assembly. Decreasing the volume of the droplets increased the surface-to-volume ratio and thus provided more reaction sites per unit of volume during battery charging and discharging (Supplementary Note 1). Therefore, the miniaturization facilitated the electrode reactions and enhanced the coulombic efficiency and volumetric capacity^{3,30}. By shrinking the droplet volume from 3 μL to 10 nL, which resulted in a unit length of $\sim 600 \mu\text{m}$, the released charge of LiDBs was first observed to increase as the volume decreased from 3 to 0.5 μL , due to the enhanced coulombic efficiency, but then decreased with further volume reductions as a result of the reduction in the number of contained Li-particles (Fig. 31d/Example 2 Fig. 2d). During the 99.7% volume shrinkage, we observed a concomitant increase in the volumetric capacity, leading to an unprecedented level of $\sim 570 \text{ nAh } \mu\text{L}^{-1}$ for all-hydrogel Li-ion batteries with a size more than 10^3 -fold smaller than those in previous work (Fig. 31e/Example 2 Fig. 2e and Supplementary Table 1)⁹⁻¹². We also increased the output voltage of LiDBs by connecting multiple units in series in a custom-made well (Fig. 32f/Example 2 Fig. 2f). Open-circuit voltage increased with the number of LiDBs in series, reaching $\sim 3.3 \text{ V}$ for 6 units in connection (Fig. 51/Example 2 Supplementary Fig. 9), which powered three light-emitting diodes and other electronic devices, e.g., a liquid-crystal display timer (Fig. 52/Example 2 Supplementary Fig. 10).

Tetherless activation of charged molecule translocation

Synthetic tissues are networks of patterned communicating aqueous compartments, with significant potential for biomedical applications, including the release of therapeutic agents and the repair of damaged organs³¹. To electrically drive the communication between synthetic cells, previous work employing droplet networks demonstrated tetherless
5 powering by light-driven proton pumps³². Nevertheless, such light-powered charged molecule translocation was slow, taking over 15 h to transmit over ~10 mm distance due to the low generated current (~20 pA). The high-output, aqueous, microscale and soft features make the droplet-based LiDB a prospective approach to interface with synthetic cells, providing a direct and tetherless input electric field as well as offering improved stability
10 and pliability. A pair of electron-to-ion converting droplets were devised to convert the electron current into ion flux (Fig. 32a/Example 2 Fig. 3a). We used poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS) as an effective redox-active material for the conversion (Fig. 53/Example 2 Supplementary Fig. 11; see Methods for detailed compositions)^{33,34}. The LiDB with converting droplets connected to its cathode
15 and anode can be attached to other droplets through its termini, generating ion flux that would drive electrophoresis in the connected droplets³², drawing cations to the anode and anions to the cathode.

To demonstrate charged molecule translocation, the fluorescent cationic pyronin Y and anionic 3'-O-(N-methylanthraniloyl) adenosine 5'-triphosphate (MANT-dATP) were
20 chosen. Both hydrogel droplets without DIBs and aqueous droplets with DIBs, but connected by the pore-forming protein α -hemolysin (α HL), thereby acting as synthetic cells^{19,32}, were tested to demonstrate signal transmission in the absence of electrical tethers (i.e., without metal electrodes). A droplet incorporating a fluorescent dye was put at the central position place sandwiched between two droplets missing the dye, and together
25 attached to the LiDB with the converting droplets. Subsequent dye movement was dictated by the interplay between spontaneous diffusion and electrophoresis, and was monitored by the observation of fluorescence changes. After subjection to 10 min of LiDB power, the cationic pyronin Y moved to the anode side (Fig. 32b, c/Example 2 Fig. 3b, c), whereas the anionic MANT-dATP moved to the cathode side (Fig. 32d, e/Example 2 Fig. 3d, e). In the
30 presence of DIBs, charged molecules were still successfully propelled into the target cell through the α HL pores embedded within the DIBs (Fig. 32f, g/Example 2 Fig. 3f, g). We quantified the signal transmission by calculating the fluorescence ratio of the target droplet

over the non-target droplet, e.g., cathode droplet over anode droplet for MANT-dATP (Fig. 37/Example 2 Extended Data Fig. 3). The aqueous synthetic cells showed a higher fluorescence ratio than their hydrogel counterparts, which was likely produced by the inhibition of spontaneous molecule diffusion by the DIBs and therefore less molecular accumulation in the non-target cell.

***Ex vivo* murine heart defibrillation by LiDBs**

Electrical defibrillation is achieved by applying a strong electric field to the fibrillating heart, which restores sinus rhythm. Examples include automated external defibrillators in public places for patients with out-of-hospital cardiac arrest and implantable cardiac defibrillators for long-term treatments. However, the high-energy electric shock far exceeds the pain threshold and has a well-documented negative impact on quality of life, including post-traumatic stress disorder and depression³⁵. The need for more efficient, low-energy, biocompatible defibrillation has promoted the development of miniature pacemakers³⁶, implantable energy transducers³⁷⁻³⁹ and wireless power sources¹⁸. In this regard, LiDBs can produce a direct current electrical discharge (shock) with miniaturized energy outputs and high modulation efficacy when in direct contact with Langendorff-perfused murine hearts as reflected in epicardial electrocardiograms (ECGs) (Fig. 33a, b/Example 2 Fig. 4a, b). A LiDB was gently placed onto the surface of a heart and the hydrogel adhered directly to the epicardium (Fig. 33b/Example 2 Fig. 4b). Maximum effects occurred at the times of attachment and detachment, and were capable of mediating defibrillation. The electrical stimulation and the continuous contact of LiDBs showed no adverse influence on the heart tissue. Biocompatibility of LiDBs was confirmed by co-culturing them with human fibroblasts or cardiomyocytes derived from human induced pluripotent stem cells (iPSCs, Fig. 33c/Example 2 Fig. 4c and Fig. 38/Example 2 Extended Data Fig. 4). Live/dead staining was performed after 48 h to examine the cell viability and proliferation (Fig. 38a, b/Example 2 Extended Data Fig. 4a, b). After the LiDBs' electrical discharge during co-culture, the cells reached a high density similar to the value of the control group and exhibited a typical spreading and intact filamentous morphology. Further results of cell viability, cytotoxicity and apoptosis assays conducted after 7 days of co-culture demonstrated the cytocompatibility of LiDBs (Fig. 38c-e/Example 2 Extended Data Fig. 4c-e).

In parallel with the LiDB stimulation, we conducted optogenetic light pacing to generate a regular heart rhythm (Fig. 54/ Example 2 Supplementary Fig. 12), which eliminated ectopic heartbeats and thereby permitted an accurate manifestation of the heartbeats triggered by the LiDB stimulation (see Methods and Fig. 39/Example 2 Extended Data Fig. 5 for details of the optogenetic regulation)⁴⁰. In contrast with a fully discharged LiDB, a charged LiDB imposed its electrical output on the heart and disrupted the intrinsic electrical activity of the heart muscle (Fig. 4d). The temporary change of electrical activity produced by the LiDB was able to restore normal heart rhythm in unsynchronized cardioversion (defibrillation) as demonstrated in the corresponding ECG traces. Increasing the volume of the droplets in the LiDB enlarged the contact area for stimulation, which increased the amplitude of the shock and temporarily suppressed the intrinsic heartbeats (Fig. 33e/Example 2 Fig. 4e and Fig. 55/Example 2 Supplementary Fig. 13). We verified the involvement of an electrical shock by attaching a pair of electrodes onto the epicardium of hearts and applying direct current ranging from 15 to 45 μA (Fig. 40/Example 2 Extended Data Fig. 6). The stimulation by a LiDB comprising 1 μL droplets was equivalent to a ~ 30 μA direct current stimulation, showing a similar shock signal and subsequent heartbeat restoration in the ECG trace (Figs. 56 and 57/Example 2 Supplementary Fig. 14 and 15).

The electrical shock provided the opportunity to treat ventricular arrhythmias, e.g., ventricular tachycardia and fibrillation, which are injurious in minutes if not treated promptly. The injection of ouabain solution (300 μL , 0.3 mg mL^{-1}) led to ventricular tachycardia due to cytosolic calcium overload in heart cells, which gradually transformed into ventricular fibrillation (Fig. 58/Example 2 Supplementary Fig. 16). The attachment and detachment of a LiDB were set as the start and end of a defibrillation process. Applying the LiDB by direct contact enabled the defibrillation process within 5 seconds and converted ventricular arrhythmias to normal heart rhythms (Fig. 33f, g/Example 2 Fig. 4f, g). Afterwards, the heart recovered to sinus rhythm within 5 seconds without deterioration in heart function. The LiDBs can be applied to hearts repeatedly when multiple arrhythmias occur, which indicates the reliability of the defibrillation process (Fig. 33h/Example 2 Fig. 4h).

More sophisticated control of cardiac activity, such as heart pacing, can be achieved through wired contact with a LiDB-powered pacemaker circuit (Fig. 41/Example 2

Extended Data Fig. 7 and Fig. 54/Example 2 Supplementary Fig. 12), which can produce region-specific pacing of heart rhythms (Fig. 42/Example 2 Extended Data Fig. 8, Supplementary Note 2). These proof-of-concept demonstrations show the potential clinical utility of LiDBs, e.g., to perform low-energy defibrillation for the treatment of heart
5 arrhythmias during cardiac surgery.

Magnetically manoeuvrable LiDBs

The hydrogel compartmentalization endowed LiDBs with the ability to incorporate functions in parallel to energy storage. For example, the inclusion of magnetic nickel (Ni)
10 particles in the central separator droplet imparted magnetic manoeuvrability to LiDBs (Fig. 34a/ Example 2 Fig. 5a). Ni-particles did not affect hydrogel formation (Fig. 34b/ Example 2 Fig. 5b) or significantly change the battery output (Fig. 34c/Example 2 Fig. 5c and Fig. 59/Example 2 Supplementary Fig. 17), yet they allowed manipulation of the entire structure under a magnetic field. By this means, the LiDB can translocate through narrow
15 channels in oil or from oil to an aqueous phase thereby acting as a mobile energy courier. Fig. 34d/Example 2 Fig. 5d depicts a LiDB traversing a maze (Fig. 60/ Example 2 Supplementary Fig. 18) in oil repeatedly from a pair of recharging electrodes to a pair of target electrodes, where it released the contained energy. The LiDB maintained an over 77% output capacity after 10 cycles at 0.5 μ A (Fig. 34e/ Example 2 Fig. 5e). As a proof-of-
20 concept, a 2 mF capacitor was connected to the target electrodes to collect the delivered charge. The capacitor voltage reached 0.51 V after 10 cycles, indicating that 1.02 mC charge (0.26 mJ energy) was delivered by the LiDB (Fig. 34f/Example 2 Fig. 5f and Fig. 61/Example 2 Supplementary Fig. 19).

The robust hydrogel composition also allowed the LiDB to release its energy in aqueous
25 media, which is important for biological use but previously challenging for aqueous vesicles/droplets to yield a stable output performance⁴¹. We magnetically guided a LiDB from oil into aqueous medium containing a pair of target electrodes (Fig. 34g/Example 2 Fig. 5g). Upon entering the aqueous phase, the surrounding oil was repelled from the LiDB and replaced by water that contacted the hydrophilic silk hydrogel. The aqueous phase
30 contained 1 M LiCl to prevent Li leakage from the LiDB. For long-term operation, organogel encapsulation¹³ can also be used to prevent electrolyte leakage in a physiological environment (Fig. 62/Example 2 Supplementary Fig. 20). The LiDB functioned in LiCl

solution, because the output voltage was lower than that required for the electrolysis of water (~ 1.23 V) (Fig. 34h/Example 2 Fig. 5h). The capacity of the battery in LiCl solution was reduced to 67% of that in oil, which was likely due to the hydrogel swelling and thus the decreased surface-to-volume ratio over time (Fig. 34i/Example 2 Fig. 5i). We noted
5 that a LiDB cannot be easily propelled back into the oil for recharging, because of the strong surface tension of water over the hydrogel. Other mechanisms might be used to assist the transport of LiDBs in aqueous media^{42,43}. The silk of the LiDB can be enzymatically biodegraded in the aqueous phase (Fig. 34j/Example 2 Fig. 5j), leaving only nanograms of residual materials.

10

Discussion and outlook

In this work, a miniature soft Li-ion battery was self-assembled from nanolitre hydrogel droplets. The resulting LiDB afforded on-demand activation by UV-crosslinking, had a unit volume more than 10^3 -fold lower than previous devices and stored energy at higher
15 density⁹⁻¹². The output energy density of the LiDB made from 10 nL droplets was ~ 46 $\mu\text{Wh cm}^{-2}$ and the instant output power density was ~ 10 $\mu\text{W cm}^{-2}$, which is sufficient for devices on nW power budgets³. These outcomes were facilitated by using a silk hydrogel, with desirable properties including elasticity, Li-ion conductivity, biocompatibility and biodegradability. The LiDB could be interfaced with synthetic tissues to drive charged
20 molecule translocation and with heart tissues to modulate heart activity. The hydrogel droplet construction also permitted the addition of modules, such as one that allows magnetic manoeuvrability, which may for example allow LiDBs to power microrobots for *in vivo* applications.

The electrochemical stability window of water (~ 1.23 V) limits the output voltage of
25 hydrogel-based batteries in general⁴⁴ to a lower value than that of solid-state batteries⁴⁵⁻⁴⁷. Nonetheless, the cascade connection of multiple LiDBs can generate higher output voltage to suit application needs. Mass loading of Li-particles is preferably limited to less than 20% w/v to prevent nozzle clogging during droplet deposition. However, the use of smaller Li-particles or chemically-treated nozzles may prevent clogging and increase the mass
30 loading. Alternative droplet assembly approaches, such as acoustic printing⁴⁸⁻⁵⁰, microfluidic deposition⁵¹⁻⁵³, and droplet self-assembly assisted by functional interlinkers⁵⁴⁻⁵⁷ may facilitate scaled-up production of LiDBs and increase the energy density by further

decreasing the droplet size. Moreover, our design strategy might be implemented with other hydrogels and aqueous dopants, e.g., zinc particles for zinc-ion batteries and iron oxide particles for magnetic control, to build additional members of a class of tiny energy devices that comprise hydrogel, functional particles, and conducting elements in soft, miniaturized architectures. The microscale soft LiDB might be used in many fields including microrobots, synthetic tissues, abiotic–biotic interfaces, and implantable medical devices.

References

1. Zhu, M. & Schmidt, O. G. Tiny robots and sensors need tiny batteries—Here’s how to do it. *Nature* **589**, 195-197 (2021).
2. Liu, M., Zhang, Y. & Tao, T. H. Recent Progress in Bio-Integrated Intelligent Sensing System. *Adv. Intell. Syst.* **4**, 2100280 (2022).
3. Li, Y. *et al.* On-Chip Batteries for Dust-Sized Computers. *Adv. Energy Mater.* **12**, 2103641 (2022).
4. Wei, T. S., Ahn, B. Y., Grotto, J. & Lewis, J. A. 3D printing of customized Li-ion batteries with thick electrodes. *Adv. Mater.* **30**, 1703027 (2018).
5. Costa, C., Gonçalves, R. & Lanceros-Méndez, S. Recent advances and future challenges in printed batteries. *Energy Storage Mater.* **28**, 216-234 (2020).
6. Lyu, Z. *et al.* Design and manufacture of 3D-printed batteries. *Joule* **5**, 89-114 (2021).
7. Zhang, W. *et al.* Unlocking Micro-Origami Energy Storage. *ACS Appl. Energy Mater.* (2024).
8. Sridhar, V. *et al.* Light-driven carbon nitride microswimmers with propulsion in biological and ionic media and responsive on-demand drug delivery. *Sci. Robot.* **7**, eabm1421 (2022).
9. Zhao, Y. *et al.* A self-healing aqueous lithium-ion battery. *Angew. Chem. Int. Ed.* **55**, 14384-14388 (2016).
10. Liu, Z. *et al.* Towards wearable electronic devices: A quasi-solid-state aqueous lithium-ion battery with outstanding stability, flexibility, safety and breathability. *Nano Energy* **44**, 164-173 (2018).
11. Ye, T. *et al.* A Tissue-Like Soft All-Hydrogel Battery. *Adv. Mater.* **34**, 2105120 (2022).

12. Wang, J. *et al.* Ultrasoft all-hydrogel aqueous lithium-ion battery with a coaxial fiber structure. *Polym. J.*, 1-7 (2022).
13. Zhang, Y. *et al.* A microscale soft ionic power source modulates neuronal network activity. *Nature* **620**, 1001-1006 (2023).
- 5 14. Schroeder, T. B. *et al.* An electric-eel-inspired soft power source from stacked hydrogels. *Nature* **552**, 214-218 (2017).
15. van Stevendaal, M. H., van Hest, J. C. & Mason, A. F. Functional interactions between bottom-up synthetic cells and living matter for biomedical applications. *ChemSystemsChem* **3**, e2100009 (2021).
- 10 16. Elani, Y. Interfacing living and synthetic cells as an emerging frontier in synthetic biology. *Angewandte Chemie* **133**, 5662-5671 (2021).
17. Liu, J. *et al.* Enzyme-Enabled Droplet Biobattery for Powering Synthetic Tissues. *Angew. Chem. Int. Ed.* **In press**, e202408665 (2024).
18. Nair, V. *et al.* Miniature battery-free bioelectronics. *Science* **382**, eabn4732 (2023).
- 15 19. Villar, G., Graham, A. D. & Bayley, H. A tissue-like printed material. *Science* **340**, 48-52 (2013).
20. Allen, M. E., Hindley, J. W., Baxani, D. K., Ces, O. & Elani, Y. Hydrogels as functional components in artificial cell systems. *Nat. Rev. Chem.* **6**, 562-578 (2022).
21. Downs, F. G. *et al.* Multi-responsive hydrogel structures from patterned droplet networks. *Nat. Chem.* **12**, 363-371 (2020).
- 20 22. Whittaker, J. L., Choudhury, N. R., Dutta, N. K. & Zannettino, A. Facile and rapid ruthenium mediated photo-crosslinking of Bombyx mori silk fibroin. *J. Mater. Chem. B* **2**, 6259-6270 (2014).
23. Chen, J. *et al.* Ultrathin and Robust Silk Fibroin Membrane for High-Performance Osmotic Energy Conversion. *ACS Energy Lett.* **5**, 742-748 (2020).
- 25 24. Zhang, Y. & Tao, T. H. Skin-friendly electronics for acquiring human physiological signatures. *Adv. Mater.* **31**, 1905767 (2019).
25. Liu, M., Tao, T. H. & Zhang, Y. Silk Materials Light Up the Green Society. *Adv. Energy Sustainability Res.* **2**, 2100035 (2021).
- 30 26. Liu, M. *et al.* Robotic Manipulation under Harsh Conditions Using Self-Healing Silk-Based Iontronics. *Adv. Sci.* **9**, 2102596 (2022).

27. Zhang, Y. *et al.* Self-Powered Multifunctional Transient Bioelectronics. *Small* **14**, 1802050 (2018).
28. Liu, M. *et al.* Biomimicking Antibacterial Opto-Electro Sensing Sutures Made of Regenerated Silk Proteins. *Adv. Mater.* **33**, 2004733 (2021).
- 5 29. Zhang, Y. & Tao, T. H. A Bioinspired Wireless Epidermal Photoreceptor for Artificial Skin Vision. *Adv. Funct. Mater.* **30**, 2000381 (2020).
30. Liu, Y., Zhu, Y. & Cui, Y. Challenges and opportunities towards fast-charging battery materials. *Nature Energy* **4**, 540-550 (2019).
31. Jin, Y. *et al.* Integration of 3D-printed cerebral cortical tissue into an ex vivo lesioned
10 brain slice. *Nat. Commun.* **14**, 5986 (2023).
32. Hoskin, C. E. G., Schild, V. R., Vinals, J. & Bayley, H. Parallel transmission in a synthetic nerve. *Nat. Chem.* **14**, 650-657 (2022).
33. Simon, D. T. *et al.* Organic electronics for precise delivery of neurotransmitters to modulate mammalian sensory function. *Nat. Mater.* **8**, 742-746 (2009).
- 15 34. Proctor, C. M. *et al.* Electrophoretic drug delivery for seizure control. *Sci. Adv.* **4**, eaau1291 (2018).
35. Versteeg, H., Theuns, D. A., Erdman, R. A., Jordaens, L. & Pedersen, S. S. Posttraumatic stress in implantable cardioverter defibrillator patients: the role of pre-implantation distress and shocks. *Int. J. Cardiol.* **146**, 438-439 (2011).
- 20 36. Bhatia, N. & El-Chami, M. Leadless pacemakers: a contemporary review. *J. Geriatr. Cardiol.* **15**, 249 (2018).
37. Ouyang, H. *et al.* Symbiotic cardiac pacemaker. *Nat. Commun.* **10**, 1821 (2019).
38. Huang, T. *et al.* "Self-matched" tribo/piezoelectric nanogenerators using vapor-induced phase-separated poly (vinylidene fluoride) and recombinant spider silk. *Adv. Mater.* **32**,
25 1907336 (2020).
39. Liu, Z. *et al.* A self-powered intracardiac pacemaker in swine model. *Nat. Commun.* **15**, 507 (2024).
40. Wang, Y. *et al.* Optogenetic control of heart rhythm by selective stimulation of cardiomyocytes derived from Pnmt⁺ cells in murine heart. *Sci. Rep.* **7**, 1-10 (2017).
- 30 41. Villar, G., Heron, A. J. & Bayley, H. Formation of droplet networks that function in aqueous environments. *Nat. Nanotechnol.* **6**, 803-808 (2011).

42. Haller, B. *et al.* Autonomous Directional Motion of Actin-Containing Cell-Sized Droplets. *Adv. Intell. Syst.* **3**, 2000190 (2021).
43. Zhan, P., Jahnke, K., Liu, N. & Göpfrich, K. Functional DNA-based cytoskeletons for synthetic cells. *Nat. Chem.* **14**, 958-963 (2022).
- 5 44. Liang, Y. & Yao, Y. Designing modern aqueous batteries. *Nat. Rev. Mater.* **8**, 109-122 (2023).
45. Zhu, M. & Schmidt, O. G. Batteries for small-scale robotics. *MRS Bull.* **49**, 115-124 (2024).
46. Refino, A. D. *et al.* Advances in 3D silicon-based lithium-ion microbatteries. *Commun.*
10 *Mater.* **5**, 22 (2024).
47. Xu, M. *et al.* Minimally invasive power sources for implantable electronics. *Exploration* **4**, 20220106 (2024).
48. Tian, L. *et al.* Spontaneous assembly of chemically encoded two-dimensional
coacervate droplet arrays by acoustic wave patterning. *Nat. Commun.* **7**, 13068 (2016).
- 15 49. Li, J. *et al.* Building programmable multicompartment artificial cells incorporating
remotely activated protein channels using microfluidics and acoustic levitation. *Nat.*
Commun. **13**, 4125 (2022).
50. Yin, C., Jiang, X., Mann, S., Tian, L. & Drinkwater, B. W. Acoustic trapping: An
emerging tool for microfabrication technology. *Small* **19**, 2207917 (2023).
- 20 51. Baxani, D. K. *et al.* Bilayer networks within a hydrogel shell: a robust chassis for
artificial cells and a platform for membrane studies. *Angew. Chem. Int. Ed.* **55**, 14240-
14245 (2016).
52. Bachler, S., Haidas, D., Ort, M., Duncombe, T. A. & Dittrich, P. S. Microfluidic
platform enables tailored translocation and reaction cascades in nanoliter droplet networks.
25 *Commun. Biol.* **3**, 769 (2020).
53. Hakami, N. *et al.* Functional Integration of Synthetic Cells into 3D Microfluidic
Devices for Artificial Organ-on-Chip Technologies. *Adv. Healthcare Mater.*, 2303334
(2024).
54. Gobbo, P. *et al.* Programmed assembly of synthetic protocells into thermoresponsive
prototissues. *Nat. Mater.* **17**, 1145-1153 (2018).
- 30 55. Luo, R., Göpfrich, K., Platzman, I. & Spatz, J. P. DNA-Based Assembly of Multi-
Compartment Polymersome Networks. *Adv. Funct. Mater.* **30**, 2003480 (2020).

56. McMullen, A., Muñoz Basagoiti, M., Zeravcic, Z. & Brujic, J. Self-assembly of emulsion droplets through programmable folding. *Nature* **610**, 502-506 (2022).
57. Stevens, A. J. *et al.* Programming multicellular assembly with synthetic cell adhesion molecules. *Nature* **614**, 144-152 (2023).
- 5 58. Kleinsorge, M. & Cyganek, L. Subtype-directed differentiation of human iPSCs into atrial and ventricular cardiomyocytes. *STAR Protoc.* **1**, 100026 (2020).

Methods

Materials for LiDBs

All materials except CNT were purchased from Sigma-Aldrich (Merck KGaA). Single-wall CNT dispersion in water purchased from TUBALL (0.8% wt., BATT H₂O). Silk fibroin (50 mg mL⁻¹) was used to build the hydrogel scaffold. Portions of silk solution were stored at -80°C before use. For droplet fabrication, silk solution was first left at room temperature for 30 min. Other materials were then added into the thawed silk solution under stirring to form various precursor solutions with the following compositions. Separator solution contained 1 M lithium chloride, 10% v/v poly(ethylene glycol) 400, and 0.5% w/v Pluronic F-68. In addition to the components of the separator solution, the cathode solution contained 30% v/v CNT/water dispersion and 10% w/v lithium manganese(III,IV) oxide (LMO, catalog number 482277); additional components of the anode solution were 30% v/v CNT/water dispersion and 10% w/v carbon-coated lithium titanate (LTO, catalog number 916196). To form various pre-gels, tris(bipyridine)ruthenium(II) chloride (1 mM final) and sodium persulfate (5 mM final) were added to the precursor solutions and then fully mixed with stirring, whilst preventing exposure to light. Cathode, separator and anode pre-gels were kept in black microcentrifuge tubes before droplet deposition and used within 2 h after preparation.

Lipid/oil solutions

Silk pre-gel droplets were deposited in a lipid-containing oil and thereby acquired lipid coatings, which subsequently formed lipid bilayers at the interface when droplets were brought into contact. Lipids were purchased from Avanti Polar Lipids in powder form and stored at -80°C. Before use, hexadecane (Sigma-Aldrich) was passed through a 0.22 µm filter (Corning) under vacuum. Lipid films were prepared by bringing ampoules to room temperature and dissolving the lipids in anhydrous chloroform (Sigma-Aldrich) at 25 mg mL⁻¹. Using glass syringes (Hamilton), lipid stock solutions 1,2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC, 90 µL) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC, 40 µL) were transferred into a Teflon-capped glass vial (Supelco, 7 mL) that had been cleaned with isopropanol. The chloroform was evaporated under a slow stream of nitrogen while the vial was rotated by hand to produce an even lipid film. The film was dried under vacuum for 24 h, and stored under nitrogen at -80°C before use. When

required for droplet fabrication, films were left at room temperature for 30 min, then 1 mL of hexadecane was added to the film, followed by sonication (Branson 2800) for 1 h. The total concentration of lipids was 4 mM with a molar ratio of DPhPC:POPC of 2:1. Lipid films were kept for a maximum of 2 months.

5

The LiDB fabrication and activation

Droplet deposition was carried out in a dark room under a non-crosslinking yellow/red light. Droplets were formed in custom-made hydrophobic glass wells that contained 200 μ L of lipid-containing oil. Droplets of pre-gel solution were placed in each well with a
10 programmable microinjector (FemtoJet, Eppendorf), which ejected droplets from a loaded glass nozzle (Femtotips, Eppendorf) with volumes that ranged from femtoliters to microliters. Single LiDBs were obtained by depositing droplets so that they contacted one another, allowing lipid bilayers to form at the interfaces, which happened within seconds. After formation, LiDBs could be drawn by capillary action into a truncated pipette tip
15 along with surrounding oil, and then placed in other wells for further characterization and applications. After fabrication, LiDBs could be stored for more than 2 days in the dark within a lipid/oil solution in a humid incubator without energy dissipation due to the insulating DIBs. To activate LiDBs, the droplets were exposed to UV light (365 nm, power density $>0.5 \text{ mW cm}^{-2}$, Thorlab) for 60 s to photo-chemically crosslink the silk fibroins,
20 which disrupted the DIBs and led to the formation of a continuous silk hydrogel structure.

Characterization

A custom-made measurement system containing two 3D manual micromanipulators (NMN-21, Narishige) and an integrated microscope (Stereo Zoom 5, Leica) was used to
25 examine the microscale LiDBs. We used carbon fibre electrodes (Goodfellow) to contact the cathode and anode compartments of the LiDB. Gold electrodes (50 μ m, Sigma-Aldrich) could also be used for smaller droplets. The electrochemical performances of LiDBs were tested by an electrochemical workstation (μ Stat-i 400, Metrohm DropSens), which included cyclic voltammetry, galvanostatic charge-discharge measurement,
30 amperometric detection, electrochemical impedance analysis, and alternating current impedance spectra. To make a three-electrode system, Ag/AgCl electrodes and excessive activated carbon were used as reference and counter electrodes (DRP-11L-U75, Metrohm).

Fourier-transform infrared spectra were measured in attenuated total reflection mode (Bruker Tensor 27 spectrometer). Blank background measurements were subtracted from each spectrum. The zeta potential was measured by a Malvern Zetasizer (Nano-ZS). The compression response was measured by an electromechanical test system (Criterion, MTS Systems).

Powering electronics with LiDBs

Several LiDBs were moved into a custom-made transparent resin well, which was fabricated by a 3D printer (Formlabs, Solid Print3D) and had embedded screen-printed carbon electrodes (CNT paste, Nanoshel) on the well bottom. 6 LiDBs were connected in series over the carbon electrodes to increase the output voltage. Red light-emitting diodes (HLMP-K150, Broadcom), a liquid-crystal display timer (Sigma-Aldrich), and a pulse generator circuit based on a 555-timer chip (TLC555IP, RS PRO) could all be powered by the 6 LiDBs. Capacitor (RS PRO) charging curves were measured by a Keithley 617 programmable multimeter set to voltage measurement mode with high input impedance ($\sim 2 \text{ T}\Omega$). An oscilloscope (PicoScope 2000) was used to measure the generated pulses.

Powering the translocation of molecules

Hydrogel droplets were prepared by dissolving low-gelling-temperature agarose powder (2% w/v, Sigma-Aldrich) in 0.1 M potassium chloride (Sigma-Aldrich) and heating the solution to 90°C. The solution was then cooled down to 37°C before adding other materials. Cationic pyronin Y (10 μM , Sigma-Aldrich) and anionic 3'-O-(N-Methylanthraniloyl) adenosine 5'-triphosphate (MANT-dATP, 100 μM , Thermo Fisher Scientific) were used as fluorescent markers. Aqueous synthetic cells contained 0.1 M potassium chloride, 0.5% w/v Pluronic F-68 (Sigma-Aldrich), and 50 $\mu\text{g mL}^{-1}$ of the pore-forming protein α -hemolysin (αHL , with the mutation T129C, provided by X. Wang (Bayley Group)). The protein was expressed in *E. coli* cells, purified as monomers (confirmed by SDS-PAGE electrophoresis) and stored at -80°C. Aqueous synthetic cells were deposited in lipid-containing hexadecane (4 mM lipids at a molar ratio of DPhPC:POPC of 2:1); DIBs formed between each synthetic cell. The converting hydrogel droplets contained 2% w/v low-gelling-temperature agarose, 0.1 M potassium chloride, and 1.1% w/v PEDOT:PSS (neutral pH, Sigma-Aldrich). Two converting droplets were

attached to the cathode and anode of a LiDB in lipid-free oil, creating a continuous hydrogel LiDB device. The hydrogel droplets were submerged in lipid-free oil and the aqueous synthetic cells were submerged in lipid-containing oil. To enable the charged molecule translocation, the LiDB device was transferred into a well containing the
5 synthetic cells, where the LiDB device was attached to the synthetic cells through its termini to form a closed circle.

Optical recordings

Bright-field images were recorded with a stereomicroscope (EZ4 W, Leica) or a wide-field
10 stereomicroscope (SMZ660, Nikon). A Leica DMI8 inverted epi-fluorescence microscope was used for fluorescence imaging. Images were processed using the Leica Application Suite X and Fiji (ImageJ). Fluorescence intensities were obtained by using the Fiji freehand tool, intensity measurements, and profile plots tool. The hydrogel morphologies were characterized by scanning electron microscopy (HITACHI S4800). All hydrogel
15 droplets were first frozen with liquid nitrogen and then freeze-dried by a vacuum freeze dryer to completely drain the water.

Biocompatibility tests with LiDBs

All cells were seeded into 96-well plates and cultured for 3 days to form uniform layers
20 before testing. Single fully-charged LiDBs formed from 1 μ L droplets were placed above the cells in each well and formed close contact with them through the adhesive silk hydrogel. 3T3 fibroblasts (NIH-3T3, CRL-1658) expressing green-fluorescence protein were used for live/dead imaging. The LiDB was left in the well with the cells during 48 h of culture before imaging. 6 wells were randomly picked and examined in detail. The cells
25 were incubated with 5.0 μ M propidium iodide (Sigma Aldrich) for 60 min at 37°C before imaging with a fluorescence confocal microscope (SP5, Leica). Z-stack images were acquired between the bottom of the cells to 100 μ m above them with a step of 2 μ m per image. Maximum Z projection was then conducted to generate final images, which were processed using the Leica Application Suite X. PrestoBlue assays (Thermo Fisher
30 Scientific) were used to determine live cell numbers and viability. The cells were incubated with 10% v/v PrestoBlue reagents for 60 min at 37°C before fluorescence measurement. A microplate reader (CLARIOstar Plus) was used to quantify the fluorescence and hence the

number of living cells. Further, human dermal fibroblasts (Lonza) and atrial and ventricular cardiomyocytes differentiated from Kolf 2.1J human iPSCs⁵⁸ (The Jackson Laboratory) were used to quantify the effects of LiDBs on cell metabolic activity, cytotoxicity and apoptosis. Cell metabolic activity was measured by using an MTT cell proliferation assay kit (Vybrant, Thermo Fisher Scientific). Cytotoxicity was measured by using a cell cytotoxicity assay kit (Colorimetric, ab112118, Abcam). Apoptosis was measured by using a caspase assay kit (Caspase-Glo 3/7 Assay, Promega). Standard assay protocols were followed after cells had been co-cultured with LiDBs for 7 days.

10 ***Ex vivo* heart preparation and ECG monitoring**

Animal experiments were performed on mice in accordance with the UK Animals Scientific Procedures Act (1986) and were approved by the University of Oxford Pharmacology ethical committee under project licence (PP8557407). All procedures were performed in conformity with the national and institutional guidelines and regulations. All mice including *Pnmt*^{Cre/ChR2} mutant mice⁴⁰ and wild-type (WT) littermates used in this study were maintained in pathogen-free facilities at the University of Oxford. Mice were given *ad libitum* access to food and water. WT mice and genetically modified *Pnmt*^{Cre/ChR2} mice were sacrificed by cervical dislocation (Schedule 1 killing). The heart was immediately removed and cannulated onto the Langendorff system at the aorta to allow retrograde perfusion of Krebs's solution, which contained 128 mM sodium chloride, 4.8 mM potassium chloride, 22 mM sodium bicarbonate, 11 mM glucose, 1 mM magnesium chloride and 1.8 mM calcium chloride. The solution was bubbled with 95% oxygen and 5% carbon dioxide for at least 15 min before use. The perfusion medium was held at 37°C with a flow rate of 3.5 to 4 mL min⁻¹. To monitor cardiac rhythms, we carried out *ex vivo* ECG analysis on the Langendorff-perfused hearts. In addition to the metal cannula, two electrodes were placed adjacent to the right atrium and the bottom left ventricle. The ECG was filtered with low and high cut-off frequencies of 5 and 500 Hz, digitized at a sampling frequency of 1 kHz (1401, Cambridge Electronic Design), and recorded by the Spike 2 software (Cambridge Electronic Design). ECG parameters including RR interval, PR interval, QRS and QT durations were monitored.

Optogenetic stimulation on *ex vivo* heart

Langendorff-perfused *ex vivo* hearts from *Pnnmt^{Cre/ChR2}* mutant mice were subjected to programmed light stimulation through the activation of ChR2 light-sensitive channels. This was achieved by the delivery of 470 nm, 5 ms blue-light pulses generated by OptoFlash (Cairn Research). The pulses were triggered by a 1401 digitizer and Spike 2 software
 5 (Cambridge Electronic Design). The blue light intensity was tuned with an 818-ST2 Wand Detector connected to an 843 R Power meter (both Newport Corporation). ECGs indicative of left atrial pacing in a 1:1 manner were recorded from *Pnnmt^{Cre/ChR2}* hearts when light pulses were delivered to the left atrium.

10 **Heart stimulation by LiDBs**

LiDBs were fully charged for 10 min at a current of 0.5 μ A and immediately used for stimulation to ensure battery output consistency. To quantify direct contact stimulation, *Pnnmt^{Cre/ChR2}* hearts were used under light-regulated pacing to prevent ectopic heartbeat. A single LiDB was drawn into a truncated pipette tip by capillary action and gently placed on
 15 the right side of the heart for each stimulation. Because of the adhesive silk hydrogel, LiDBs attached to the heart surface without falling off. To remove the LiDB, we gently pipetted it away or rinsed it off by using perfusion medium. To create heart fibrillation, we perfused 300 μ L of 0.3 mg mL⁻¹ ouabain solution (Sigma Aldrich) into the hearts and used high-frequency wired burst pacing to trigger the ventricular arrhythmias. Once ECG
 20 signals denoted the beginning of heart fibrillation, we stopped the high-frequency pacing. Heart fibrillation could last for minutes and eventually lead to permanent heart death. We used LiDBs to produce electrical defibrillation in the same manner as the direct contact stimulation.

For the wired stimulation, we used a LiDB power pack of typically 6 LiDBs in series to
 25 drive a home-built pulse generator. The pulse width was $\sim$ 5 ms, and the pacing frequency could be tuned between 1 and 15 Hz. A pair of Ag/AgCl stimulating electrodes was placed on the right atrium (near the sinoatrial node) or on any region of the ventricles of WT mouse hearts to produce pacing pulses.

30 **Magnetically controlled energy delivery and recharging**

To form a magnetically responsive silk hydrogel, the separator solution contained additional 10% v/v nickel particles (MagneHis, Promega). LiDBs were then fabricated as

before. A neodymium magnet (N42, first4magnets) placed at ~2 cm above a LiDB was used to guide movement. The magnet was mounted on a 3D manual micromanipulator (NMN-21, Narishige) for precise navigation. The maze and the double-deck well were fabricated by a 3D printer (Formlabs, Solid Print3D) and featured embedded screen-printed carbon electrodes (CNT paste, Nanoshel) on the well bottom. Copper tape (RS PRO) was used to facilitate connection between the screen-printed carbon electrodes and measurement wires/clips.

Biodegradation of LiDBs

LiDBs were transferred into wells containing 200 μL phosphate-buffered saline (pH 7.4, Gibco) with 30 U mL^{-1} (1 mg mL^{-1}) Proteinase K (Thermo Fisher Scientific) at 37°C. LiDBs were enzymatically degraded after 20 min (6 repeats), precipitating CNT and LMO/LTO particles, which sank to the bottoms of the wells.

Statistics

Statistical analyses were performed using Origin and p-values were determined by unpaired two-way analysis of variance (ANOVA). Six, five, and five independent mouse hearts were used for the shock, defibrillation, and pacing experiments. Each experiment used a minimum of three independent LiDBs.

Supplementary Note 1.

Volume and internal resistance of droplets

The contact area is important in determining the droplet's internal resistance and the volumetric capacity. After stabilization, the contact area (A) between two droplets can be expressed in terms of the contact angle θ and the radius of curvature r of the adhered droplets:

$$A = \pi r^2 \sin^2 \theta \quad (\text{Eq. 1})$$

where θ is determined by the compositions of the lipids, oil and pre-gel solutions¹. The internal resistance (R) of lithium-ion droplet batteries (LiDBs) depends on the droplet volume, which is directly proportional to the length of the ion conductive pathway (l) and

inversely proportional to the average cross-sectional area ($S_{average}$) of the droplet.

Relating l and $S_{average}$ to r and A of the droplets, we obtain:

$$R = \frac{\rho l}{S_{average}} \approx \frac{6\rho r}{A} = \frac{6\rho}{\pi r \sin^2 \theta} \quad (\text{Eq. 2})$$

where ρ is the resistivity of the silk hydrogel. Therefore, as the volume and hence the contact area decrease, the internal resistance of LiDBs will increase and the output current (i.e., the short-circuit current) will decrease. However, decreasing the droplet volume will increase the droplet surface-to-volume ratio, which facilitates the electrode reactions and enhanced the coulombic efficiency and volumetric capacity^{2,3}.

Supplementary Note 2.

10 *Ex vivo* murine heart pacing powered by LiDBs

LiDBs can generate cardiac pacing by powering a pacemaker circuit through wired contact (Fig. 41/Example 2 Extended Data Fig. 7 and Fig. 42/Example 2 Extended Data Fig. 8). Wired contact through an electrical pulse generator promises sophisticated output features that yield regional specific control of cardiac electrical activity. As an example, heart
15 pacing with different pulsing frequencies was mediated by a LiDB power pack and a pacemaker circuit (Fig. 42a/Example 2 Extended Data Fig. 8a). The electrical energy generated from 6 LiDBs was stored in the pacemaker circuit, whose output was connected to the heart by a pair of pacing electrodes (Fig. 42b/Example 2 Extended Data Fig. 8b). Multiple LiDBs had sufficient output intensity to overdrive the intrinsic sinus rhythm (Fig.
20 42c/Example 2 Extended Data Fig. 8c) and generate both atrial and ventricular pacing: The pacing region was located at the right atrium (near the sinoatrial node) to achieve atrial pacing (Fig. 42d/Example 2 Extended Data Fig. 8d) or at any region of ventricles to conduct ventricular pacing (Fig. 42e/Example 2 Extended Data Fig. 8e), showing two different epicardial electrocardiogram (ECG) patterns. The frequency of the stimulation
25 pulse was tuned between 10 and 2.5 Hz with a fixed pulse width of ~5 ms (Fig. 42f/Example 2 Extended Data Fig. 8f). When the pacing stimuli were faster than (e.g., 10 Hz) or near (e.g., 3.5 Hz) the intrinsic heart rhythm (~4 to 5 Hz), the electrical pulses induced contraction and regulated the heart rate. Pulses with a lower frequency (e.g., 2.5 Hz) were not able to override the intrinsic heart rhythm, resulting in a mixed ECG signal
30 reflecting both paced and intrinsic heartbeats. One LiDB power pack could power 3

stimulation cycles with each cycle lasting for ~15 s. In each cycle, with the consumption of the energy by pacing, the pulse frequency declined in the last ~4 s, leaving an invalid pacing ECG at the end. We quantified the proportion of valid pacing during 3 independent cycles (Fig. 42g/ Example 2 Extended Data Fig. 8g). By setting the selection range of $\pm 20\%$ of the pacing frequency, 64% of paced beatings were valid with frequencies larger than 8 Hz for the 10 Hz pacing (425 pulses in total), and 43% beatings were valid with frequencies lower than 3 Hz for the 2.5 Hz pacing (288 pulses in total). This level of working duration was comparable to other reported implantable power sources as to perform first-aid and short-term biomedical functions^{4,5}, and might be further prolonged by using more LiDBs in the power pack. Further electronic engineering of the pulse generator circuit based on the outputs of LiDBs could also prolong the stimulation time.

Supplementary Table 1. Comparison of sizes and volumetric capacities of various hydrogel-based Li-ion batteries and LiDBs of three different volumes. Volumetric capacities of previous works⁵⁻⁸ were calculated from the maximum area capacity (mAh cm⁻²) or specific capacity (mAh g⁻¹) and the size of a battery unit.

Hydrogel	Area (cm ²)	Thickness (cm)	Volumetric capacity (mAh cm ⁻³)
Poly(vinyl alcohol) ⁸	8	0.95	0.067
Carboxymethyl-cellulose ⁹	1	0.9	0.008
Polyacrylamide ¹⁰	0.63	0.25	0.109
Polyacrylamide ¹¹	0.5	0.19	0.432
1 μ L Droplets (This work)	1.21×10^{-2}	0.08	0.020
100 nL Droplets (This work)	2.60×10^{-3}	0.17	0.138
10 nL Droplets (This work)	5.61×10^{-4}	0.37	0.568

References

1. Villar, G., Graham, A. D. & Bayley, H. A tissue-like printed material. *Science* **340**, 48-52 (2013).
2. Liu, Y., Zhu, Y. & Cui, Y. Challenges and opportunities towards fast-charging battery materials. *Nat. Energy* **4**, 540-550 (2019).
3. Li, Y. *et al.* On-Chip Batteries for Dust-Sized Computers. *Adv. Energy Mater.* **12**, 2103641 (2022).
4. Zheng, Q. *et al.* In vivo powering of pacemaker by breathing-driven implanted triboelectric nanogenerator. *Adv. Mater.* **26**, 5851-5856 (2014).
5. Ouyang, H. *et al.* Symbiotic cardiac pacemaker. *Nat. Commun.* **10**, 1-10 (2019).
6. Zhang, Y. & Tao, T. H. Skin-Friendly Electronics for Acquiring Human Physiological Signatures. *Adv. Mater.* **31**, 1905767 (2019).
7. Liu, M. *et al.* Robotic Manipulation under Harsh Conditions Using Self-Healing Silk-Based Iontronics. *Adv. Sci.* **9**, 2102596 (2022).
8. Liu, Z. *et al.* Towards wearable electronic devices: A quasi-solid-state aqueous lithium-ion battery with outstanding stability, flexibility, safety and breathability. *Nano Energy* **44**, 164-173 (2018).
9. Zhao, Y. *et al.* A self-healing aqueous lithium-ion battery. *Angew. Chem. Int. Ed.* **55**, 14384-14388 (2016).
10. Wang, J. *et al.* Ultrasoft all-hydrogel aqueous lithium-ion battery with a coaxial fiber structure. *Polym. J.* **54**, 1383-1389 (2022).
11. Ye, T. *et al.* A Tissue-Like Soft All-Hydrogel Battery. *Adv. Mater.* **34**, 2105120 (2022).

Example 3

Here, we produce a miniature soft biobattery with high energy output and stability by the introduction of enzyme-enabled components within a droplet-based system. The droplets are separated by droplet-interface bilayers DIBs, Fig. 63a/Example 3 Figure 1a, which allow the construction on a microscale of soft and freestanding droplet networks with distinct compartments.[M. J. Booth, V. RestrepoSchild, F.G. Downs, H. Bayley, Mol. BioSyst. 2017, 13, 1658–1691; Y. Jin, et al., Nat. Commun. 2023, 14, 5986.]

In our biobattery, the oxidation and reduction reactions are separated by forming an anode in one droplet and a cathode in another. The cathode and anode droplets self-assemble into a tiny droplet biobattery, in which the DIB prevents material diffusion between the droplet pair. The insertion of monocation-selective gramicidin A gA, channels
5 turns the DIB into a proton exchange membrane akin to that in a conventional battery. [Z. Hemmatian, et al., Nat. Commun. 2016, 7, 12981; M. S. Whittingham, Proc. IEEE 2012, 100, 1518–1534; Y. Liang, Y. Yao, Nat. Rev. Mater. 2023, 8, 109–122]

In the cathode droplet, laccase Lac, catalyzes the oxidation of the electron mediator ABTS with molecular oxygen to the ABTS radical cation ABTS*⁺, which has a greenish
10 colour Fig 63b/ Example 3 Figure 1b. This molecule is reduced back to ABTS on the electrode by gaining an electron, coupled with the oxidation of the reduced form of AQDS on the electrode in the anode droplet. The reduced form of NADH acts as a fuel by converting AQDS back to the reduced state, thereby forming the complete biobattery Fig. 63c/Example 3 Figure 1c. The electrochemical potential thus generated induces electron
15 flow in the external circuit from the anode to the cathode, and compensating monocations flux through the DIB by gA channels accordingly. The biobattery we have developed has the potential to provide energy to natural or artificial tissues, thereby unlocking new possibilities in bioelectronics and bioiontronics.

To construct the droplet-based biobattery, we deposited aqueous droplets of 200nL
20 in a lipid-containing oil, comprising 1,2-diphytanoyl-sn-glycero-3-phosphocholine dissolved in a mixture of hexadecane and silicone oil 50:50 by volume. The droplets formed DIBs within seconds following contact with one another. Following DIB formation, gA was added into the oil phase to 0.1μM. The gA inserted spontaneously into the DIBs to form transmembrane channels.

25 To incorporate the reaction chemistry into the droplets, the anode droplet contained 10mM NADH and 5mM AQDS, whereas the cathode droplet contained 5mM ABTS and 12μM Lac, comparable to reactant concentrations of 0.1 to 100mM for reported biobatteries (K. Stolarczyk, J. Rogalski, R. Bilewicz, Bioelectrochemistry 2020, 135, 107574). Both droplets contained 100mM HEPES and 100mM NaCl, pH 7.4. Under the
30 above concentrations and conditions, the potential of the O₂/H₂O couple catalyzed by Lac 0.1V, measured by cyclic voltammetry is more positive than that of a NADH/NAD⁺ couple — 0.50V. This enables O₂ reduction catalyzed by Lac in the cathode droplet to be

coupled to the oxidation of NADH to NAD⁺ in the anode droplet, facilitated by electron mediators AQDS and ABTS that allow the transport of electrons to and from the electrodes. This final configuration resulted in an output short-circuit current of ~1,800pA over 60min, with an open-circuit potential of ~732mV Fig 63d/Example 3 Figure 1d. The

5 battery consumed the contained NADH during powering and remained stable for over 24h.

ASPECTS

1. A power unit comprising a series of droplets, wherein said series of droplets comprises:
 - 5 one or more first droplets, and
one or more second droplets,
wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
each droplet is separated from its one or more neighbouring droplets by an
10 amphiphilic membrane.
2. A power unit according to aspect 1, wherein said series of droplets comprises, in this order or the reverse thereof:
 - 15 (a) one or more first droplets,
(b) one or more separator droplets, and
(c) one or more second droplets,
wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
each droplet is separated from its one or more neighbouring droplets by an
20 amphiphilic membrane.
3. A power unit according to aspect 2, wherein said series of droplets comprises, in this order or the reverse thereof:
 - 25 (a) one or more droplets of one or more high salt fluids,
(b) one or more droplets of one or more cation selective fluids or one or more droplets of one or more anion selective fluids, and
(c) one or more droplets of one or more salt diffusion target fluids, and wherein
each droplet is separated from its one or more neighbouring droplets by an
amphiphilic membrane.
30
4. A power unit according to aspect 3, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more high salt fluids,
 (b) one or more droplets of one or more cation selective fluids,
 (c) one or more droplets of one or more salt diffusion target fluids,
 (d) one or more droplets of more or more anion selective fluids, and
 5 (e) one or more droplets of one or more high salt fluids;
 wherein the one or more droplets of the above (a) may be the same one or more droplets as the one or more droplets of the above (e), and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

10

5. The power unit according to aspect 4, wherein:

- said series of droplets further comprises, between the one or more droplets of the above (a) and the one or more droplets of the above (b), an optionally repeating sub-series of droplets comprising, in this order:

15

- (i) one or more droplets of one or more cation selective fluids,
 (ii) one or more droplets of one or more salt diffusion target fluids,
 (iii) one or more droplets of more or more anion selective fluids, and
 (iv) one or more droplets of one or more high salt fluids; and/or

- the power unit comprises a plurality of said series of droplets, wherein the plurality
 20 of series of droplets are arranged in parallel such that droplets of the same type within each series of droplets are positioned adjacent to one another.

6. The power unit according to any one of aspects 3 to 5, wherein said one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids,
 25 and one or more anion selective fluids are each solutions or suspensions (preferably solutions) in a droplet medium, wherein, preferably, the droplet medium is water.

7. The power unit according to aspect 6, wherein the power unit is suspended in a suspension medium that is immiscible with the droplet medium, wherein, preferably, the
 30 suspension medium is oil.

8. The power unit according to any one of aspects 3 to 7, wherein the one or more high salt fluids, one or more cation selective fluids, one or more low salt fluids, and one or more anion selective fluids each contain one or more gelling agents (preferably one gelling agent, further preferably the same one gelling agent), wherein, preferably, each gelling agent is a polymer or a polymerizable monomer or oligomer, wherein, further preferably:
- the polymer is selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium aginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably lignin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide, particularly preferably agarose or silk fibroin; and
 - the polymerizable monomer or oligomer is a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group, more preferably a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group), most preferably acrylamide.
9. The power unit according to any one of aspects 3 to 8, wherein:
- said one or more high salt fluids each contain one or more salts, and the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 10 M to 0.2 M, preferably from 5 M to 0.5 M, more preferably from 4 M to 1 M, even more preferably from 2.5 to 1.5 M; and/or
 - said one or more salt diffusion target fluids each contain no salt or contain one or more salts, wherein, preferably, said one or more salt diffusion target fluids each contain one or more salts, and further preferably:

- the total concentration of the one or more salts in each of the one or more salt diffusion target fluids is independently from 0.05 M to 0.001 M, preferably from 0.03 M to 0.002 M, more preferably from 0.02 M to 0.005 M, even more preferably from 0.015 to 0.005 M; and/or
- 5 - the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 2000 to 1.1 times, preferably 1000 to 10 times, preferably from 800 to 50 times, more preferably from 500 to 100 times, even more preferably from 300 to 150 times, higher than the total concentration of the one or more salts in each of the salt diffusion target
- 10 fluids.

10. The power unit according to aspect 9, wherein the one or more salts are each independently salts of the formula $A^{p+}_n X^{q-}_m$, wherein:
 A is selected from metal cations and organic cations;

15 X is selected from halogen anions, inorganic anions, and organic anions; and
 p, q, n and m are each integers from 1 to 4, wherein $p \times n = q \times m$; and wherein, further preferably, the one or more salts are each independently selected from lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride, most preferably calcium chloride.

20

11. The power unit according to any one of aspects 3 to 10, wherein:

- said cation-selective fluids contain one or more polymers having anionic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having anionic groups attached to, or forming part of, the polymer backbone is
- 25 poly(sodium 4-styrenesulfonate); and/or
- said anion-selective fluids contain one or more polymers having cationic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having cationic groups attached to, or forming part of, the polymer backbone is
- poly(allylamine hydrochloride).

30

12. The power unit according to any one of aspects 1 to 11, wherein the amphiphilic membrane comprises one or more types of amphipathic molecules, wherein said

amphipathic molecules are selected from one or more of lipids, surfactants, and block copolymer amphiphiles, and are preferably lipids, most preferably phospholipids.

13. The power unit according to any one of aspects 1 to 12, wherein the volume of each
5 droplet is from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL.

14. A method for producing a power unit according to any one of aspects 1 to 13, the
10 method comprising the steps of:

- providing one or more amphipathic molecule-coated first droplets, and one or more amphipathic molecule-coated second droplets; and
- contacting said one or more amphipathic molecule-coated first droplets and said one or more amphipathic molecule-coated second droplets in series to provide a
15 power unit according to any one of aspects 1 to 13.

15. The method according to aspect 14, wherein the method is for producing a power unit according to any one of aspects 4 to 13, the method comprising the steps of:

- providing:
20 (a) one or more amphipathic molecule-coated droplets of one or more high salt fluids,
(b) one or more amphipathic molecule-coated droplets of one or more cation selective fluids,
(c) one or more amphipathic molecule-coated droplets of one or more salt
25 diffusion target fluids, and
(d) one or more amphipathic molecule-coated droplets of one or more anion selective fluids; and
- contacting said one or more amphipathic molecule-coated droplets of the above
(a), one or more amphipathic molecule-coated droplets of the above (b), one or
30 more amphipathic molecule-coated droplets (c), and one or more amphipathic molecule-coated droplets of the above (d) in series to provide a power unit according to any one of aspects 4 to 13.

16. The method according to aspect 15, wherein said one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids, and one or more anion selective fluids are each solutions or suspensions (preferably solutions) in a droplet medium, and

each droplet is prepared by depositing a volume of fluid in a suspension medium that is immiscible with the droplet medium, wherein:

- (i) said suspension medium contains amphipathic molecules, and/or
- (ii) said droplet medium contains amphipathic molecules, and/or
- (iii) amphipathic molecules are added to the suspension medium after the volume of solution is deposited into the suspension medium.

17. The method according to aspects 15 or aspect 16, wherein:

- the one or more high salt fluids, the one or more cation selective fluids, the one or more salt diffusion target fluids, and the one or more anion selective fluids are as defined in any one of aspects 6 and 8 to 11; and/or
- the suspension medium is as defined in aspect 7; and/or
- the amphipathic molecules are as defined in aspect 12; and/or
- the volume of each droplet is as defined in aspect 13.

20

18. A method for activating a power unit according to any one of aspects 1 to 13, the method comprising the step of transforming the series of droplets into a series of compartments wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

25

19. The method according to aspect 18, wherein the step of transforming the series of series of droplets into the series of compartments comprises disassembling or permeabilising the amphiphilic membranes, preferably disassembling the amphiphilic membranes, wherein, further preferably

the amphiphilic membranes are disassembled by introducing the power unit into a disassembling medium and/or by washing the power unit with a disassembling medium,

30

wherein the disassembling medium is a medium that is that is immiscible with the droplet medium, and is preferably oil or an organogel.

20. The method according to aspect 18 or aspect 19, wherein the power unit is a power unit according to aspect 8, wherein the step of transforming the series of droplets into the series of compartments comprises gelling the one or more gelling agents such that the series of droplets becomes a series of gel compartments wherein each gel compartment is diffusively continuous with its one or more neighbouring gel compartments.

21. An active power unit obtainable by the method of any one of aspects 18 to 20.

22. An active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

- (a) one or more high salt biocompatible gel compartments,
- (b) one or more cation selective biocompatible gel compartments,
- (c) one or more salt diffusion target biocompatible gel compartments,
- (d) one or more anion selective biocompatible gel compartments, and
- (e) one or more high salt biocompatible gel compartments;

wherein the one or more high salt biocompatible gel compartments of the above (a) may be the same one or more high salt biocompatible gel compartments as the one or more high salt biocompatible gel compartments of the above (e); and wherein

each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.

25

23. The active power unit according to aspect 22, wherein:

- said series of biocompatible gel compartments further comprises, between the one or more biocompatible gel compartments of the above (a) and the one or more biocompatible gel compartments of the above (b), an optionally repeating sub-series of biocompatible gel compartments comprising, in this order:

30

- (i) one or more cation selective biocompatible gel compartments,
- (ii) one or more salt diffusion target biocompatible gel compartments,

- (iii) one or more anion selective biocompatible gel compartments, and
 - (iv) one or more high salt biocompatible gel compartments; and/or
 - the active power unit comprises a plurality of said series of biocompatible gel compartments, wherein the plurality of series of biocompatible gel compartments are arranged in parallel such that biocompatible gel compartments of the same type within each series of biocompatible gel compartments are positioned adjacent to one another.
24. The active power unit according to aspect 22 or aspect 23, wherein:
- the one or more high salt biocompatible gel compartments, one or more cation selective biocompatible gel compartments, one or more salt diffusion target biocompatible gel compartments, and one or more anion selective biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the compartment medium is water; and/or
 - the one or more high salt biocompatible gel compartments, one or more cation selective biocompatible gel compartments, one or more salt diffusion target biocompatible gel compartments, and one or more anion selective biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the one or more biocompatible gels are selected from gels derived from a polymer selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium aginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably ligin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide, particularly preferably agarose or silk fibroin; and/or

- 5 • said one or more high salt biocompatible gel compartments each contain one or more salts, and the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 10 M to 0.2 M, preferably from 5 M to 0.5 M, more preferably from 4 M to 1 M, even more preferably from 2.5 to 1.5 M; and/or
- 10 • said one or more salt diffusion target biocompatible gel compartments each contain no salt or contain one or more salts, wherein, preferably, said one or more salt diffusion target biocompatible gel compartments each contain one or more salts, and further preferably:

 - 10 - the total concentration of the one or more salts in each of the one or more salt diffusion target biocompatible gel compartments is independently from 0.05 M to 0.001 M, preferably from 0.03 M to 0.002 M, more preferably from 0.02 M to 0.005 M, even more preferably from 0.015 to 0.005 M; and/or
 - 15 - the total concentration of the one or more salts in each of the one or more high salt biocompatible gel compartments is independently from 2000 to 1.1 times, preferably 1000 to 10 times, preferably from 800 to 50 times, more preferably from 500 to 100 times, even more preferably from 300 to 150 times, higher than the total concentration of the one or more salts in each of

20 the salt diffusion target fluids; and/or
- 25 • said one or more high salt biocompatible gel compartments, and optionally said one or more salt diffusion target biocompatible gel compartments, each contain one or more salts, wherein the one or more salts are each independently salts of the formula $A^{p+}_n X^{q-}_m$, wherein:

 - 25 A is selected from metal cations and organic cations;

 X is selected from halogen anions, inorganic anions, and organic anions;

 and

 p, q, n and m are each integers from 1 to 4, wherein $p \times n = q \times m$; and wherein, preferably the one or more salts are each independently selected from

30 lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride, most preferably calcium chloride; and/or

- said cation selective biocompatible gel compartments contain a polymer having anionic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having anionic groups attached to, or forming part of, the polymer backbone is poly(sodium 4-styrenesulfonate); and/or
 - 5 • said cation selective biocompatible gel compartments contain a polymer having cationic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having cationic groups attached to, or forming part of, the polymer backbone is poly(allylamine hydrochloride); and/or
 - 10 • the volume of each biocompatible gel compartment is from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL.
25. The active power unit according to any one of aspects 21 to 24, wherein the active
- 15 power unit is contained in a gel, preferably an organogel.
26. A device comprising:
- (a) the power unit according to any one of aspects 1 to 13, or an active power unit according to any one of aspects 21 to 25, and
- 20 (b) one or more electronic components.
27. A method of generating an electric current, said method comprising the steps of either:
- (i) providing a power unit according to any one of aspects 1 to 13,
- 25 connecting two droplets within the series of droplets with electronically conductive means, and activating the power unit by the method for activating a power unit according to any one of aspects 18 to 20, or
- (ii) providing an active power unit according to any one of aspects 21 to 25, and connecting two compartments within the series of compartments with
- 30 electronically conductive means.

28. A method of modulating the activities of one or more cells or tissues, the method comprising a step of either:
- (i) providing a power unit according to any one of aspects 3 to 13 and activating the power unit by the method for activating a power unit according to any one of aspects 18 to 5 20, or
 - (ii) providing an active power unit according to any one of aspects 21 to 25, wherein one or more cells or tissues are contained within, or are in the presence of, the power unit according to according to any one of aspects 3 to 13, or the active power unit according to any one of aspects 21 to 25; and wherein, preferably, the one or more cells are 10 neurons and/or the one or more tissues are brain tissues.

CLAIMS

1. A power unit comprising a series of droplets, wherein said series of droplets comprises:
- 5 one or more first droplets, and
 one or more second droplets,
 wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
 each droplet is separated from its one or more neighbouring droplets by an
10 amphiphilic membrane.
2. A power unit according to claim 1, wherein said series of droplets comprises, in this order or the reverse thereof:
- (a) one or more first droplets,
15 (b) one or more separator droplets, and
 (c) one or more second droplets,
 wherein there is a potential energy difference between the one or more first droplets and the one or more second droplets, and wherein
 each droplet is separated from its one or more neighbouring droplets by an
20 amphiphilic membrane.
3. A power unit according to claim 2, wherein said series of droplets comprises, in this order or the reverse thereof:
- (a) one or more droplets of one or more high salt fluids,
25 (b) one or more droplets of one or more cation selective fluids or one or more droplets of one or more anion selective fluids, and
 (c) one or more droplets of one or more salt diffusion target fluids, and wherein
 each droplet is separated from its one or more neighbouring droplets by an
30 amphiphilic membrane.
4. A power unit according to claim 3, wherein said series of droplets comprises, in this order or the reverse thereof:

- (a) one or more droplets of one or more high salt fluids,
 (b) one or more droplets of one or more cation selective fluids,
 (c) one or more droplets of one or more salt diffusion target fluids,
 (d) one or more droplets of more or more anion selective fluids, and
 5 (e) one or more droplets of one or more high salt fluids;
 wherein the one or more droplets of the above (a) may be the same one or more droplets as the one or more droplets of the above (e), and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

10

5. The power unit according to claim 4, wherein:

- said series of droplets further comprises, between the one or more droplets of the above (a) and the one or more droplets of the above (b), an optionally repeating sub-series of droplets comprising, in this order:

15

- (i) one or more droplets of one or more cation selective fluids,
 (ii) one or more droplets of one or more salt diffusion target fluids,
 (iii) one or more droplets of more or more anion selective fluids, and
 (iv) one or more droplets of one or more high salt fluids; and/or

- the power unit comprises a plurality of said series of droplets, wherein the plurality
 20 of series of droplets are arranged in parallel such that droplets of the same type within each series of droplets are positioned adjacent to one another.

6. The power unit according to any one of claims 3 to 5, wherein said one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids,
 25 and one or more anion selective fluids are each solutions or suspensions (preferably solutions) in a droplet medium, wherein, preferably, the droplet medium is water.

7. The power unit according to claim 6, wherein the power unit is suspended in a suspension medium that is immiscible with the droplet medium, wherein, preferably, the
 30 suspension medium is oil.

8. The power unit according to any one of claims 3 to 7, wherein the one or more high salt fluids, one or more cation selective fluids, one or more low salt fluids, and one or more anion selective fluids each contain one or more gelling agents (preferably one gelling agent, further preferably the same one gelling agent), wherein, preferably, each gelling agent is a polymer or a polymerizable monomer or oligomer, wherein, further preferably:
- 5 - the polymer is selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium aginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably lignin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide,
- 10 particularly preferably agarose or silk fibroin; and
- the polymerizable monomer or oligomer is a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group, more preferably
- 15 a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group), most preferably acrylamide.
- 20
9. The power unit according to any one of claims 3 to 8, wherein:
- 25 - said one or more high salt fluids each contain one or more salts, and the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 10 M to 0.2 M, preferably from 5 M to 0.5 M, more preferably from 4 M to 1 M, even more preferably from 2.5 to 1.5 M; and/or
- said one or more salt diffusion target fluids each contain no salt or contain one or
- 30 more salts, wherein, preferably, said one or more salt diffusion target fluids each contain one or more salts, and further preferably:

- the total concentration of the one or more salts in each of the one or more salt diffusion target fluids is independently from 0.05 M to 0.001 M, preferably from 0.03 M to 0.002 M, more preferably from 0.02 M to 0.005 M, even more preferably from 0.015 to 0.005 M; and/or
- 5 - the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 2000 to 1.1 times, preferably 1000 to 10 times, preferably from 800 to 50 times, more preferably from 500 to 100 times, even more preferably from 300 to 150 times, higher than the total concentration of the one or more salts in each of the salt diffusion target
- 10 fluids.

10. The power unit according to claim 9, wherein the one or more salts are each independently salts of the formula $A^{p+}_n X^{q-}_m$, wherein:
 A is selected from metal cations and organic cations;

15 X is selected from halogen anions, inorganic anions, and organic anions; and
 p, q, n and m are each integers from 1 to 4, wherein $p \times n = q \times m$; and wherein, further preferably, the one or more salts are each independently selected from lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride, most preferably calcium chloride.

20 11. The power unit according to any one of claims 3 to 10, wherein:

- said cation-selective fluids contain one or more polymers having anionic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having anionic groups attached to, or forming part of, the polymer backbone is
- 25 poly(sodium 4-styrenesulfonate); and/or
- said anion-selective fluids contain one or more polymers having cationic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having cationic groups attached to, or forming part of, the polymer backbone is
- 30 poly(allylamine hydrochloride).

12. The power unit according to any one of claims 1 to 11, wherein the amphiphilic membrane comprises one or more types of amphipathic molecules, wherein said

amphipathic molecules are selected from one or more of lipids, surfactants, and block copolymer amphiphiles, and are preferably lipids, most preferably phospholipids.

13. The power unit according to any one of claims 1 to 12, wherein the volume of each
5 droplet is from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL.

14. A power unit according to claim 2, wherein said series of droplets comprises, in
10 this order or the reverse thereof:

- (a) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
- (b) one or more droplets of one or more separator fluids, and
- (c) one or more droplets of one or more discharge anodic fluids containing a
15 second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
 - 20 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein each droplet is separated from its one or more neighbouring droplets by an amphiphilic membrane.

25 15. The power unit according to claim 14, wherein:

- said series of droplets further comprises, between the one or more droplets of the above (a) and the one or more droplets of the above (b), an optionally repeating sub-series of droplets comprising, in this order:
 - (i) one or more droplets of one or more separator fluids,
 - 30 (ii) one or more droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material,
 - (iii) one or more droplets of one or more separator fluids,

(iv) one or more droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material; and/or

- the power unit comprises a plurality of said series of droplets, wherein the plurality of series of droplets are arranged in parallel such that droplets of the same type within each series of droplets are positioned adjacent to one another.

16. The power unit according to any one of claims 14 or 15, wherein said one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids are each solutions or suspensions in a droplet medium, wherein, preferably, the droplet medium is water.

17. The power unit according to claim 16, wherein the power unit is suspended in a suspension medium that is immiscible with the droplet medium, wherein, preferably, the suspension medium is oil.

18. The power unit according to any one of claims 14 to 17, wherein the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain one or more gelling agents (preferably one gelling agent, further preferably the same one gelling agent), wherein, preferably, each gelling agent is a polymer or a polymerizable monomer or oligomer, wherein, further preferably:

- the polymer is selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably lignin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide, particularly preferably agarose or silk fibroin, most preferably silk fibroin; and
- the polymerizable monomer or oligomer is a compound having one or more polymerizable groups, wherein said compound is preferably a compound having one or

more groups selected from a carboxylic acid group, an aldehyde group, a hydroxy group, an amino group, an epoxide group, an alkenyl group and an alkynyl group, more preferably a compound having an alkenyl group that is conjugated to one or more electron-withdrawing groups (preferably a carboxylic acid group, an ester group, an amide group),
 5 most preferably acrylamide.

19. The power unit according to any one of claims 14 to 18, wherein said one or more discharge cathodic fluids and said one or more discharge anodic fluids each contain one or more electron-conducting materials (preferably one electron-conducting material, further
 10 preferably the same one electron-conducting material), wherein, further preferably, each electron-conducting material is selected from a carbon nanomaterial (such as carbon nanotubes, graphene, carbon nanodiamonds, carbon nanohorns, carbon nanofibers, preferably carbon nanotubes), nanowires (such as nickel, platinum, gold and silver
 nanowires, preferably silver nanowires) and a conductive polymer (such as
 15 poly(acetylene), poly(p-phenylenevinylene), poly(pyrrole), poly(aniline), poly(thiophene), poly(3,4-ethylenedioxythiophene), and poly(p-phenylene sulfide), preferably poly(3,4-ethylenedioxythiophene)), preferably a carbon nanomaterial.

20. The power unit according to any one of claims 14 to 19, wherein the one or more
 20 discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain mobile ions, wherein the mobile ions are the same ions as are donated/accepted by the first ion donor/acceptor material and the second ion donor/acceptor material, and wherein, preferably, the mobile ions are present in the form a
 soluble salt of the mobile ion with a mobile counterion.

25

21. The power unit according to any one of claims 14 to 20, wherein:
 - said first ion donor/acceptor material is a discharge ion acceptor material, and
 - said second ion donor/acceptor material is a discharge ion donor material.

30 22. The power unit according to claim 21, wherein:
 (a) said first ion donor/acceptor material is a first Li ion donor/acceptor material and said discharge ion acceptor material is a discharge Li ion acceptor material, and

(b) said second ion donor/acceptor material is a second Li ion donor/acceptor material and said discharge ion donor material is a discharge Li ion donor material.

- 5 23. The power unit according to claim 22, wherein;
- said one or more discharge Li ion acceptor materials are each independently selected from lithium nickel cobalt aluminium oxide, lithium nickel manganese cobalt oxide, lithium nickel cobalt manganese aluminium oxide, lithium manganese oxide, lithium manganese nickel oxide, lithium vanadium oxide, lithium iron phosphate, lithium nickel oxide and lithium cobalt oxide, preferably lithium manganese oxide, lithium manganese nickel oxide, lithium iron phosphate, and lithium cobalt oxide, more preferably lithium manganese oxide, most preferably LiMn_2O_4 ; and/or
 - said one or more discharge Li ion donor materials are each independently selected from graphite, hard carbon, silicon, silicon/carbon, tin/cobalt alloy, copper/tin alloy, copper/antimony alloy, manganese/tin alloy, molybdenum sulfide, lithium titanate, niobates, preferably molybdenum sulfide, lithium titanate, and niobates, more preferably molybdenum sulfide, and lithium titanate, more preferably still lithium titanate, most preferably $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

- 20
24. The power unit according to claim 22 or claim 23, wherein the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain mobile Li ions, wherein, preferably, the mobile Li ions are present in the form a soluble salt of the Li ion with a mobile counterion such as LiCl, LiBr, LiPF_6 , LiBF_4 , LiClO_4 , Li_2SO_4 and LiNO_3 , preferably LiCl, LiBr, Li_2SO_4 and LiNO_3 , most preferably LiCl.

25. The power unit according to any one of claims 14 to 24, wherein the amphiphilic membrane comprises one or more types of amphipathic molecules, wherein said
- 30 amphipathic molecules are selected from one or more of lipids, surfactants, and block copolymer amphiphiles, and are preferably lipids, most preferably phospholipids.

26. The power unit according to any one of claims 14 to 25, wherein the volume of each droplet is from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1
5 nL to 2 nL.

27. The power unit according to any one of claims 14 to 26, wherein at least one droplet within the power unit of the invention comprises magnet particles.

10 28. A method for producing a power unit according to any one of claims 1 to 27, the method comprising the steps of:

- providing one or more amphipathic molecule-coated first droplets, and one or more amphipathic molecule-coated second droplets; and
- contacting said one or more amphipathic molecule-coated first droplets and said
15 one or more amphipathic molecule-coated second droplets in series to provide a power unit according to any one of claims 1 to 27.

29. The method according to claim 28, wherein the method is for producing a power unit according to any one of claims 4 to 13, the method comprising the steps of:

- 20 • providing:
 - (a) one or more amphipathic molecule-coated droplets of one or more high salt fluids,
 - (b) one or more amphipathic molecule-coated droplets of one or more cation selective fluids,
 - 25 (c) one or more amphipathic molecule-coated droplets of one or more salt diffusion target fluids, and
 - (d) one or more amphipathic molecule-coated droplets of one or more anion selective fluids; and
- contacting said one or more amphipathic molecule-coated droplets of the above
30 (a), one or more amphipathic molecule-coated droplets of the above (b), one or more amphipathic molecule-coated droplets (c), and one or more amphipathic

molecule-coated droplets of the above (d) in series to provide a power unit according to any one of claims 4 to 13.

30. The method according to claim 29, wherein said one or more high salt fluids, one or more cation selective fluids, one or more salt diffusion target fluids, and one or more anion selective fluids are each solutions or suspensions (preferably solutions) in a droplet medium, and each droplet is prepared by depositing a volume of fluid in a suspension medium that is immiscible with the droplet medium, wherein:

- 10 (i) said suspension medium contains amphipathic molecules, and/or
- (ii) said droplet medium contains amphipathic molecules, and/or
- (iii) amphipathic molecules are added to the suspension medium after the volume of solution is deposited into the suspension medium.

15 31. The method according to claims 29 or claim 30, wherein:

- the one or more high salt fluids, the one or more cation selective fluids, the one or more salt diffusion target fluids, and the one or more anion selective fluids are as defined in any one of claims 6 and 8 to 11; and/or
- the suspension medium is as defined in claim 7; and/or
- 20 - the amphipathic molecules are as defined in claim 12; and/or
- the volume of each droplet is as defined in claim 13.

32. The method according to claim 28, wherein the method is for producing a power unit according to any one of claims 14 to 27, the method comprising the steps of:

- 25 • providing:
 - (a) one or more amphipathic molecule-coated droplets of one or more discharge cathodic fluids containing a first ion donor/acceptor material,
 - (b) one or more amphipathic molecule-coated droplets of one or more separator fluids, and
 - 30 (c) one or more amphipathic molecule-coated droplets of one or more discharge anodic fluids containing a second ion donor/acceptor material,

- contacting said one or more amphipathic molecule-coated droplets of the above (a), one or more amphipathic molecule-coated droplets of the above (b), and one or more amphipathic molecule-coated droplets (c) in series to provide a power unit according to any one of claims 14 to 27.

5

33. The method according to claim 32, wherein said one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids are each solutions or suspensions in a droplet medium, and each droplet is prepared by depositing a volume of fluid in a suspension medium that is

10 immiscible with the droplet medium, wherein:

- (i) said suspension medium contains amphipathic molecules, and/or
- (ii) said droplet medium contains amphipathic molecules, and/or
- (iii) amphipathic molecules are added to the suspension medium after the volume of solution is deposited into the suspension medium.

15

34. The method according to claims 32 or claim 33, wherein:

- the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids are as defined in any one of claims 16 and 18 to 24; and/or
- 20 - the suspension medium is as defined in claim 17; and/or
- the amphipathic molecules are as defined in claim 25; and/or
- the volume of each droplet is as defined in claim 26.

35. A method for activating a power unit according to any one of claims 1 to 27, the method comprising the step of transforming the series of droplets into a series of compartments wherein each compartment is diffusively continuous with its one or more neighbouring compartments.

36. The method according to claim 35, wherein the step of transforming the series of series of droplets into the series of compartments comprises disassembling or permeabilising the amphiphilic membranes, preferably disassembling the amphiphilic membranes, wherein, further preferably

the amphiphilic membranes are disassembled by introducing the power unit into a disassembling medium and/or by washing the power unit with a disassembling medium, wherein the disassembling medium is a medium that is that is immiscible with the droplet medium, and is preferably oil or an organogel.

5

37. The method according to claim 35 or claim 36, wherein the power unit is a power unit according to claim 8 or 18, wherein the step of transforming the series of droplets into the series of compartments comprises gelling the one or more gelling agents such that the series of droplets becomes a series of gel compartments wherein each gel compartment is
10 diffusively continuous with its one or more neighbouring gel compartments.

38. An active power unit obtainable by the method of any one of claims 35 to 37.

39. An active power unit comprising a series of biocompatible gel compartments,
15 wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

- (a) one or more high salt biocompatible gel compartments,
- (b) one or more cation selective biocompatible gel compartments,
- (c) one or more salt diffusion target biocompatible gel compartments,
- 20 (d) one or more anion selective biocompatible gel compartments, and
- (e) one or more high salt biocompatible gel compartments;

wherein the one or more high salt biocompatible gel compartments of the above (a) may be the same one or more high salt biocompatible gel compartments as the one or more high salt biocompatible gel compartments of the above (e); and wherein

25 each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.

40. The active power unit according to claim 39, wherein:

- said series of biocompatible gel compartments further comprises, between the one
30 or more biocompatible gel compartments of the above (a) and the one or more biocompatible gel compartments of the above (b), an optionally repeating sub-series of biocompatible gel compartments comprising, in this order:

- (i) one or more cation selective biocompatible gel compartments,
 - (ii) one or more salt diffusion target biocompatible gel compartments,
 - (iii) one or more anion selective biocompatible gel compartments, and
 - (iv) one or more high salt biocompatible gel compartments; and/or
- 5 • the active power unit comprises a plurality of said series of biocompatible gel compartments, wherein the plurality of series of biocompatible gel compartments are arranged in parallel such that biocompatible gel compartments of the same type within each series of biocompatible gel compartments are positioned adjacent to one another.
- 10
41. The active power unit according to claim 39 or claim 40, wherein:
- the one or more high salt biocompatible gel compartments, one or more cation selective biocompatible gel compartments, one or more salt diffusion target biocompatible gel compartments, and one or more anion selective biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the compartment medium is water; and/or
 - the one or more high salt biocompatible gel compartments, one or more cation selective biocompatible gel compartments, one or more salt diffusion target biocompatible gel compartments, and one or more anion selective biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the one or more biocompatible gels are selected from gels derived from a polymer selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum, isubgol, carrageenan, tragacanth, pectin, starch, sodium aginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably ligin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer
- 15
- 20
- 25
- 30

- (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide, particularly preferably agarose or silk fibroin; and/or
- said one or more high salt biocompatible gel compartments each contain one or more salts, and the total concentration of the one or more salts in each of the one or more high salt fluids is independently from 10 M to 0.2 M, preferably from 5 M to 0.5 M, more preferably from 4 M to 1 M, even more preferably from 2.5 to 1.5 M; and/or
 - said one or more salt diffusion target biocompatible gel compartments each contain no salt or contain one or more salts, wherein, preferably, said one or more salt diffusion target biocompatible gel compartments each contain one or more salts, and further preferably:
 - the total concentration of the one or more salts in each of the one or more salt diffusion target biocompatible gel compartments is independently from 0.05 M to 0.001 M, preferably from 0.03 M to 0.002 M, more preferably from 0.02 M to 0.005 M, even more preferably from 0.015 to 0.005 M; and/or
 - the total concentration of the one or more salts in each of the one or more high salt biocompatible gel compartments is independently from 2000 to 1.1 times, preferably 1000 to 10 times, preferably from 800 to 50 times, more preferably from 500 to 100 times, even more preferably from 300 to 150 times, higher than the total concentration of the one or more salts in each of the salt diffusion target fluids; and/or
 - said one or more high salt biocompatible gel compartments, and optionally said one or more salt diffusion target biocompatible gel compartments, each contain one or more salts, wherein the one or more salts are each independently salts of the formula $A^{p+}_n X^{q-}_m$, wherein:
 - A is selected from metal cations and organic cations;
 - X is selected from halogen anions, inorganic anions, and organic anions;
 - and
 - p, q, n and m are each integers from 1 to 4, wherein $p \times n = q \times m$; and wherein, preferably the one or more salts are each independently selected from

lithium chloride, sodium chloride, potassium chloride, calcium chloride, pyronine Y chloride or GABA chloride, most preferably calcium chloride; and/or

- said cation selective biocompatible gel compartments contain a polymer having anionic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having anionic groups attached to, or forming part of, the polymer backbone is poly(sodium 4-styrenesulfonate); and/or
- said cation selective biocompatible gel compartments contain a polymer having cationic groups attached to, or forming part of, the polymer backbone, wherein, preferably, the polymer having cationic groups attached to, or forming part of, the polymer backbone is poly(allylamine hydrochloride); and/or
- the volume of each biocompatible gel compartment is from 10 pL to 10 μ L, preferably from 50 pL to 1 μ L, further preferably from 100 pL to 500 nL, more preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL.

15

42. The active power unit according to any one of claims 38 to 41, wherein the active power unit is contained in a gel, preferably an organogel.

43. An active power unit comprising a series of biocompatible gel compartments, wherein said series of biocompatible gel compartments comprises, in this order or the reverse thereof:

- (a) one or more discharge cathodic biocompatible gel compartments containing a first ion donor/acceptor material,
- (b) one or more separator biocompatible gel compartments, and
- (c) one or more discharge anodic biocompatible gel compartments containing a second ion donor/acceptor material, wherein
 - the first ion donor/acceptor material and the second ion donor/acceptor material each donate/accept the same ions,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion acceptor material,
 - one of the first ion donor/acceptor material and the second ion donor/acceptor material is a discharge ion donor material; and wherein

30

each biocompatible gel compartment is diffusively continuous with its one or more neighbouring biocompatible gel compartments.

44. The active power unit according to claim 43, wherein:

- 5 • said series of biocompatible gel compartments further comprises, between the one or more biocompatible gel compartments of the above (a) and the one or more biocompatible gel compartments of the above (b), an optionally repeating sub-series of biocompatible gel compartments comprising, in this order:
 - (i) one or more separator biocompatible gel compartments,
 - 10 (ii) one or more discharge anodic biocompatible gel compartments containing a second ion donor/acceptor material,
 - (iii) one or more separator biocompatible gel compartments, and
 - (iv) one or more discharge cathodic biocompatible gel compartments containing a first ion donor/acceptor material; and/or
- 15 • the active power unit comprises a plurality of said series of biocompatible gel compartments, wherein the plurality of series of biocompatible gel compartments are arranged in parallel such that biocompatible gel compartments of the same type within each series of biocompatible gel compartments are positioned adjacent to one another.

20

45. The active power unit according to claim 43 or claim 44, wherein:

- the one or more discharge cathodic biocompatible gel compartments, one or more separator biocompatible gel compartments, and one or more discharge anodic biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the compartment medium is water; and/or
- 25 • the one or more discharge cathodic biocompatible gel compartments, one or more separator biocompatible gel compartments, and one or more discharge anodic biocompatible gel compartments are each compartments of one or more biocompatible gels within a compartment medium, wherein, preferably, the one or more biocompatible gels are selected from gels derived from a polymer selected from a polysaccharide (preferably agar, gellan gum, xanthan gum, guar gum,
- 30

- isubgol, carrageenan, tragacanth, pectin, starch, sodium alginate, alginate gum, chitosan, hydroxyethylcellulose and agarose, most preferably agarose), a polynucleic acid (preferably DNA and RNA), a polyamide (preferably collagen, gelatin, and silk fibroin), a polyphenol (preferably lignin), a polyester (preferably polycaprolactone and polylactic acid), a polyether (preferably polyethyleneglycol), a vinyl polymer (preferably polyvinylpyrrolidone, polyvinyl alcohol and polyvinyl acetate), an acrylate polymer (preferably polyacrylic acid), and an acrylamide polymer (preferably polyacrylamide); wherein the polymer is most preferably a polysaccharide or polyamide, particularly preferably agarose or silk fibroin; and/or
- said discharge cathodic biocompatible gel compartments, one or more separator biocompatible gel compartments, and one or more discharge anodic biocompatible gel compartments each contain mobile ions, wherein the mobile ions are the same ions as are donated/accepted by the first ion donor/acceptor material and the second ion donor/acceptor material, and wherein, preferably, the mobile ions are present in the form a soluble salt of the mobile ion with a mobile counterion; and/or
 - said discharge cathodic biocompatible gel compartments and discharge anodic biocompatible gel compartments each contain one or more electron-conducting materials (preferably one electron-conducting material, further preferably the same one electron-conducting material), wherein, further preferably, each electron-conducting material is selected from a carbon nanomaterial (such as carbon nanotubes, graphene, carbon nanodiamonds, carbon nanohorns, carbon nanofibers, preferably carbon nanotubes), nanowires (such as nickel, platinum, gold and silver nanowires, preferably silver nanowires) and a conductive polymer (such as poly(acetylene), poly(p-phenylenevinylene), poly(pyrrole), poly(aniline), poly(thiophene), poly(3,4-ethylenedioxythiophene), and poly(p-phenylene sulfide), preferably poly(3,4-ethylenedioxythiophene)), preferably a carbon nanomaterial; and/or
 - in the discharge cathodic biocompatible gel compartments and discharge anodic biocompatible gel compartments:
 - said first ion donor/acceptor material is a discharge ion acceptor material, and

- said second ion donor/acceptor material is a discharge ion donator material, wherein preferably:
 - (a) said first ion donor/acceptor material is a first Li ion donor/acceptor material and said discharge ion acceptor material is a discharge Li ion acceptor material, and
 - 5 (b) said second ion donor/acceptor material is a second Li ion donor/acceptor material and said discharge ion donator material is a discharge Li ion donator material, and, further preferably
 - said one or more discharge Li ion acceptor materials are each independently selected from lithium nickel cobalt aluminium oxide, lithium
 - 10 nickel manganese cobalt oxide, lithium nickel cobalt manganese aluminium oxide, lithium manganese oxide, lithium manganese nickel oxide, lithium vanadium oxide, lithium iron phosphate, lithium nickel oxide and lithium cobalt oxide, preferably lithium manganese oxide, lithium manganese nickel oxide, lithium iron phosphate, and lithium cobalt oxide, more preferably
 - 15 lithium manganese oxide, most preferably LiMn_2O_4 ; and/or
 - said one or more discharge Li ion donator materials are each independently selected from graphite, hard carbon, silicon, silicon/carbon, tin/cobalt alloy, copper/tin alloy, copper/antimony alloy, manganese/tin alloy, molybdenum sulfide, lithium titanate, niobates, preferably
 - 20 molybdenum sulfide, lithium titanate, and niobates, more preferably molybdenum sulfide, and lithium titanate, more preferably still lithium titanate, most preferably $\text{Li}_4\text{Ti}_5\text{O}_{12}$; and/or
 - (c) the one or more discharge cathodic fluids, one or more separator fluids, and one or more discharge anodic fluids each contain mobile Li ions, wherein, preferably,
 - 25 the mobile Li ions are present in the form a soluble salt of the Li ion with a mobile counterion such as LiCl , LiBr , LiPF_6 , LiBF_4 , LiClO_4 , Li_2SO_4 and LiNO_3 , preferably LiCl , LiBr , Li_2SO_4 and LiNO_3 , most preferably LiCl ; and/or
 - the volume of each biocompatible gel compartment is from 10 pL to 10 μL , preferably from 50 pL to 1 μL , further preferably from 100 pL to 500 nL, more
 - 30 preferably from 500 pL to 100 nL, even more preferably from 1 nL to 50 nL, even more preferably still from 1 nL to 10 nL, most preferably from 1 nL to 2 nL.

46. The active power unit according to any one of claims 38 and 43 to 45, wherein the active power unit is surrounded by amphipathic molecules, wherein the amphipathic molecules are preferably as defined in claim 25.
- 5 47. A device comprising:
(a) the power unit according to any one of claims 1 to 27, or an active power unit according to any one of claims 38 to 46, and
(b) one or more electronic components.
- 10 48. A method of generating an electric current, said method comprising the steps of either:
(i) providing a power unit according to any one of claims 1 to 27, connecting two droplets within the series of droplets with electronically conductive means, and activating the power unit by the method for activating a power unit according to any one of claims 35 to 37, or
15 (ii) providing an active power unit according to any one of claims 38 to 46, and connecting two compartments within the series of compartments with electronically conductive means.
- 20 49. A method of modulating the activities of one or more cells or tissues, the method comprising a step of either:
(i) providing a power unit according to any one of claims 3 to 27 and activating the power unit by the method for activating a power unit according to any one of claims 35 to 37, or
25 (ii) providing an active power unit according to any one of claims 38 to 46, wherein one or more cells or tissues are contained within, or are in the presence of, the power unit according to any one of claims 3 to 27, or the active power unit according to any one of claims 38 to 46; and wherein, preferably,
- when the power unit is a power unit according to any one of claims 3 to 13, or the
30 active power unit is an active power unit according to any one of claims 38 to 42, the one or more cells are neurons and/or the one or more tissues are brain tissues, or

- when the power unit is a power unit according to any one of claims 14 to 27, or the active power unit is an active power unit according to any one of claims 38 and 43 to 46, the one or more cells are cardiomyocytes and/or the one or more tissues are heart tissues.

5