

## HIGHLY STRETCHABLE ENERGY STORAGE DEVICES

### Field of Invention

- 5 The present disclosure generally relates to energy storage devices, and more particularly relates to highly stretchable energy storage devices.

### Background

- 10 The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

- Wearable electronics have developed toward miniaturisation, multifunctionality, and convenience compared to other electronic equipment. Wearable electronics must be flexible and stretchable to resist mechanical deformation produced by human movements without performance deterioration. To reach the goal of a completely autonomous system, the energy storage devices (ESDs) used to power wearable electronics must also withstand deformation. For developing a stretchable energy storage device (SESD), each component including the electrode and electrolyte must be stretchable.
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- The ESD electrodes comprise a current collector and an active material which is generally coated on the surface of the current collector. The introduction of stretchability in electrodes poses two major problems: the loss/break of conductive pathways/networks; and the delamination of active material from the current collector during deformation. In the past, research has focused on developing SESDs based on modifying the geometric structure to generate stretchability from a flexible material, or fabricating intrinsically stretchable electrodes. In the first approach, the stretchable structure is made using flexible material into wavy/wrinkled, spiral, serpentine, and woven configurations. For example, the wavy/wrinkled geometry is achieved by first isotropically buckling a circular acrylic elastomer to 200% strain and then depositing the polyaniline (PANI)@CNT film onto the pre-strained elastomer substrate (J. Yu *et al.*, *ACS Nano* **2016**, *10*, 5204-5211). In these geometrically modified structures, the contact between the electrode and the electrolyte is difficult to maintain, and the assembly process is complicated and expensive; all of which impede the steady output of electrochemical performance and their practical use.
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To overcome the above issues, intrinsically stretchable electrodes were developed. At present, intrinsically stretchable electrodes are generally prepared by loading or compounding the active materials with the substrate composed of the conductive filler and the polymer elastic matrix. Among the widely studied elastic matrices such as polyacrylamide, fluororubber, poly(dimethyl siloxane), poly(vinyl alcohol), and polyurethane, there is still a need to improve interface compatibility between the components of electrodes as there is often a tradeoff between the active material loading and the amount of stretchability attained. Previously, a highly stretchable current collector using gallium-based liquid metal particles, carboxylated polyurethane (CPU) and nickel flakes was developed to be stretched to 700% (S. Park *et al.*, *Adv. Mater.* **2019**, *31*, 1805536). However, some unaddressed issues may include compatibility between the electrode and electrolyte and between the active material and its adhesion with the current collector.

Therefore, to overcome at least one of the aforementioned problems, there exists a need for new highly stretchable energy storage devices.

### Summary of Invention

It has been surprisingly found that an intrinsically stretchable electrode may be prepared through sedimenting the active material, liquid metal particles, in a stretchable conductive matrix. This technique resulted in an integrated single-layer electrode that combines current collector and active material. These liquid metal-based electrodes may be utilised to develop stretchable supercapacitors, upon curing the ionogel (of a similar polymer matrix) between the electrodes.

Aspects and embodiments of the invention are provided in the following numbered clauses.

1. An elastomeric electrode film material, comprising:
  - an elastomeric polymer matrix;
  - a conductive filler material; and
  - a plurality of liquid metal particles, wherein the elastomeric electrode film material has a first surface and a second surface, and the plurality of liquid metal particles are dispersed on or adjacent to the first surface.
2. The elastomeric electrode film material according to Clause 1, wherein the elastomeric polymer matrix is selected from one or more of the group consisting of thermoplastic polyurethane (TPU), polyester TPU, polyether TPU, polycaprolactone TPU, blends thereof

and copolymers thereof, optionally wherein the elastomeric polymer matrix is a thermoplastic polyurethane.

3. The elastomeric electrode film material according to Clause 1 or Clause 2, wherein the  
5 conductive filler material is selected from one or more of the groups consisting of single-walled carbon nanotubes, acetylene black, graphite powder, graphene, and, more particularly multiwalled carbon nanotubes, and carbon black.

4. The elastomeric electrode film material according to Clause 3, wherein the conductive  
10 filler material is multiwalled carbon nanotubes and carbon black.

5. The elastomeric electrode film material according to Clause 4, wherein one or both of the following apply:  
the multiwalled carbon nanotubes are present in an amount of from 2 to 10 wt% (e.g.  
15 about 5 wt%) of the weight of the elastomeric polymer matrix; and  
the carbon black is present in an amount of from 10 to 30 wt% (e.g. about 20 wt%) of the weight of the elastomeric polymer matrix.

6. The elastomeric electrode film material according to any one of the preceding clauses,  
20 wherein the liquid metal is a gallium alloy with one or more metals selected from indium, tin and zinc, for example, GaInSn or eutectic gallium indium (EGaIn).

7. The elastomeric electrode film material according to any one of the preceding clauses,  
wherein the liquid metal particles are present in an amount that is from 100 to 300 wt% (e.g.  
25 200 wt%) of the weight of the elastomeric polymer matrix.

8. The elastomeric electrode film material according to any one of the preceding clauses, wherein the elastomeric electrode film material has one or more of the following properties:  
(a) a maximum stretchability of from 900 to 2000% (e.g. about 1600%) of its original size  
30 in at least one dimension when subjected to a strain;  
(b) a conductivity that is higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state, optionally wherein the conductivity is from 300 to 500% (e.g. 400%) higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state; and  
(c) a conductivity that is about the same as the film in a non-strained state when the film  
35 is subjected to a strain of from 400 to 600%, such as about 500%.

9. A liquid metal-based solid-state supercapacitor, comprising:  
a first electrode comprising an elastomeric electrode film material as described in any one of Clauses 1 to 8;  
a second electrode comprising an elastomeric electrode film material as described in any one of Clauses 1 to 8; and  
an ionogel sandwiched between the first and second electrodes.
10. The liquid metal-based solid-state supercapacitor according to Clause 9, wherein the ionogel comprises:  
a crosslinked elastomeric polymeric matrix; and  
an ionic liquid.
11. The liquid metal-based solid-state supercapacitor according to Clause 10, wherein the ionic liquid is present in an amount of from 100 to 300 wt% (e.g. 200 wt%) relative to the weight of the crosslinked elastomeric polymeric matrix.
12. The liquid metal-based solid-state supercapacitor according to Clause 10 or Clause 11, wherein the crosslinked elastomeric polymeric matrix is an aliphatic polyurethane acrylate (e.g. CN990 or, more particularly, CN9021).
13. The liquid metal-based solid-state supercapacitor according to any one of Clauses 10 to 12, wherein the ionic liquid is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.
14. A method of forming an elastomeric electrode film material as described in any one of Clauses 1 to 8, the method comprising the steps of:
- (i) providing:  
a first mixture comprising a first solvent, an elastomeric polymer matrix and a conductive filler material; and  
a second mixture comprising a second solvent and a plurality of liquid metal particles;  
and
- (ii) mixing the first and second mixtures together, drop-casting the resulting mixture into a mold and evaporating off the first and second solvents to provide the elastomeric electrode film material.
15. The method according to Clause 14, wherein the first and second solvents are dimethylformamide.

16. A method of forming a liquid metal-based solid-state supercapacitor as described in any one of Clauses 9 to 13, the method comprising the steps of:

(aa) providing a mixture comprising:

one or more urethane acrylate oligomers;

5 a photoinitiator; and

an ionic liquid; and

(ab) sandwiching the mixture between a first elastomeric electrode film and a second elastomeric electrode film and subjecting the mixture to a photocuring step to provide the liquid metal-based solid-state supercapacitor, wherein

10 the first and second elastomeric electrode films are as described in any one or Clauses 1 to 8.

17. The method according to Clause 16, wherein the photoinitiator is (2,4,6-trimethylbenzoyl) phosphine oxide.

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### Drawings

Fig. 1 depicts scanning electron microscopy (SEM) images of a liquid metal-based electrode surface at different magnifications: (a) low magnification; and (b) high magnification.

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Fig. 2 depicts stress-strain curves of a liquid metal-based electrode (eutectic gallium indium (EGaIn)/carbon black (CB)/carbon nanotubes (CNT)/ thermoplastic polyurethane (TPU)).

Fig. 3 depicts the conductivity versus tensile strain for the liquid metal-based electrode.

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Fig. 4 depicts the cyclic voltammogram (CV) of a liquid metal-based electrode in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI) electrolyte.

Fig. 5 depicts the CVs of a liquid metal-based electrode in BMIM TFSI electrolyte after different strains (%).

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Fig. 6 depicts the fabrication procedure of liquid metal-based supercapacitors with the ionogel.

Fig. 7 depicts the CV of a liquid metal-based supercapacitor.

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Fig. 8 depicts the CVs of a liquid metal-based supercapacitor after different strains (%).

Fig. 9 depicts the CV of a liquid metal-based supercapacitor after 500 stretching cycles (strain variation: 0%-50%).

5 Figs. 10A and 10B relate to differing perspective views of a liquid metal-based solid-state supercapacitor according to the current invention.

Figs. 11A and 11B show a top (or bottom) view and a cross-sectional view, respectively, of the method of manufacturing a liquid metal-based solid-state supercapacitor according to the current invention.

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### Description

A highly intrinsically stretchable electrode may be prepared by sedimenting liquid metal particles in a conductive stretchable matrix to form a liquid metal-based electrode. The liquid metal-based electrode can be stretched to at least approximately 900% strain (possibly higher), and its conductivity increases with stretching up to at least 250% and resumes its initial conductivity at 500% strain. Without wishing to be bound by theory, it is believed that the liquid metal particles possess a thin metallic oxide shell that prevents the leaching of the liquid metal and provides a high surface area for electrochemical reactions. Benefitting from these properties, an assembled all-solid-state-supercapacitor provides high stretchability and electrochemical performance during and after mechanical strain. Again, without wishing to be bound by theory, it is believed that this core-shell morphology of the liquid metal particles helps increase the electrical conductivity and preserves the amount of active material during mechanical deformation as the shell (liquid metal oxide) breaks and the flow of liquid metal provides a continuous conductive network.

In a first aspect of the invention, there is provided an elastomeric electrode film material, comprising:

- an elastomeric polymer matrix;
  - 30 a conductive filler material; and
  - a plurality of liquid metal particles, wherein
- the elastomeric electrode film material has a first surface and a second surface, and the plurality of liquid metal particles are dispersed on or adjacent to the first surface.

35 In embodiments herein, the word "comprising" may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word "comprising" may also relate to the situation where only the components/features listed are intended to be

present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the  
5 phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure,  
10 such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As noted below, the elastomeric electrode film material is formed through taking a homogeneous mixture of the components in a solvent and drop-casting the components to  
15 form the film. As such, the liquid metal particles tend to sediment towards the bottom of the drop-casted material and thus, the liquid metal particles are clustered on the bottom surface (i.e. are at least partly embedded within the elastomeric polymer matrix) or are close thereto, and these liquid metal particles close to, but not in contact with, the surface are therefore entirely encapsulated within the polymer matrix. As will be appreciated, the loading amount of  
20 the liquid metal particles will affect how close each of the liquid metal particles is to the surface of the elastomeric electrode film material to which they are clustered. At relatively low loading values, almost all of the liquid metal particles may be on the surface of the elastomeric electrode film material (i.e. at least partly embedded in the elastomeric polymer matrix), while at higher loading values, more of the liquid metal particles may not be in contact with the  
25 surface directly, while at much higher loading values, a higher proportion of the liquid metal particles (relative to the liquid metal particles in contact with the surface) will not be in contact with the surface to which they are clustered at all.

The elastomeric polymer matrix may be formed from any suitable material. For example, the  
30 elastomeric polymer matrix may be formed from any elastomeric polymeric material that do not requires UV or thermal curing. In particular embodiments of the invention that may be mentioned herein, the elastomeric polymer matrix may be selected from one or more of the group consisting of thermoplastic polyurethane (TPU), polyester TPU, polyether TPU and polycaprolactone TPU, blends thereof and copolymers thereof. For example, the elastomeric  
35 polymer matrix may be a thermoplastic polyurethane. As will be appreciated, the term “thermoplastic polyurethane” refers to any suitable thermoplastic polyurethane material that meets the generally discussed properties set out herein.

The conductive filler material may be any suitable material. For example, the conductive filler material may be selected from one or more of the group consisting of single-walled carbon nanotubes, acetylene black, graphite powder, graphene, and, more particularly multiwalled carbon nanotubes, and carbon black. In particular embodiments of the invention that may be mentioned herein, the conductive filler material may be a combination of multiwalled carbon nanotubes and carbon black. In such latter embodiments, one or both of the following may apply:

the multiwalled carbon nanotubes may be present in an amount of from 2 to 10 wt% (e.g. about 5 wt%) of the weight of the elastomeric polymer matrix; and

the carbon black may be present in an amount of from 10 to 30 wt% (e.g. about 20 wt%) of the weight of the elastomeric polymer matrix. As will be appreciated, any suitable ratio of the multiwalled carbon nanotubes to carbon black may be used in embodiments of the current invention.

When used herein, the term "liquid metal" is intended to refer to elemental metals or metallic alloys with very low melting points. The metallic alloys may form a eutectic that is liquid at room temperature. Examples of elemental metals that may be used as liquid metals include caesium, rubidium, francium and gallium. It will be appreciated that the use of metals that present less risk to health is preferred. As such, stable isotopes of the radioactive metals may be used. When an alloy is used as the liquid metal it may be any suitable alloy, such as a galinstan alloy, which components are gallium, indium and tin in proportions suitable for forming a eutectic alloy at room temperature (e.g. 68 wt% Ga, 22 wt% In, and 10 wt% Sn). In particular embodiments of the current invention, the liquid metal may be a gallium alloy with one or more metals selected from indium, tin and zinc. For example, the gallium alloy may be GaInSn or eutectic gallium indium (EGaIn).

The liquid metal particles may be present in any suitable amount. For example, the liquid metal particles may be present in an amount that is from 100 to 300 wt% (e.g. 200 wt%) of the weight of the elastomeric polymer matrix.

The elastomeric electrode film material disclosed herein, may have one or more of the following properties:

- (a) a maximum stretchability of from 900 to 2000% (e.g. about 1600%) of its original size in at least one dimension when subjected to a strain;
- (b) a conductivity that is higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state, optionally wherein the conductivity is from 300 to 500% (e.g.

400%) higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state; and

(c) a conductivity that is about the same as the film in a non-strained state when the film is subjected to a strain of from 400 to 600%, such as about 500%.

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Also disclosed herein is a liquid metal-based solid-state supercapacitor, which makes use of the elastomeric electrode film material disclosed hereinbefore. Thus, in a second aspect of the invention, there is provided a liquid metal-based solid-state supercapacitor, comprising:

a first electrode comprising an elastomeric electrode film material as described  
10 hereinbefore;

a second electrode comprising an elastomeric electrode film material as described  
hereinbefore; and

an ionogel sandwiched between the first and second electrodes.

15 While the first and second electrodes and the ionogel are not bound together by covalent bonds, they are held together by physical interactions. In the first instance, the ionogel includes a polymeric material that has adhesive properties, which helps attach/bind the first and second electrodes to the ionogel's surfaces. Secondly, the first surfaces (i.e. the surface of the first and second electrodes that carry the liquid metal particles) face into the ionogel. This provides  
20 mechanical interlocking between the liquid metal particles that extend out of the electrode surfaces and the ionogel (where the ionogel will fill in grooves and pores in the first surface of the electrodes). As such, it will be appreciated that in embodiments of the current invention, the first surface of the first and second electrodes is in direct contact with the ionogel. This is illustrated in Fig. 10, where the liquid metal-based solid-state supercapacitor 100 is composed  
25 of a first electrode 110 and a second electrode 120 comprising an elastomeric electrode film material as described hereinbefore, where the inner surfaces of the electrodes include the liquid metal particles 130, which surfaces sandwich the ionogel 140.

In certain embodiments, the ionogel may comprise:

30 a crosslinked elastomeric polymeric matrix; and  
an ionic liquid.

The ionic liquid may be present in any suitable amount. For example, the ionic liquid may be present in an amount of from 100 to 300 wt% (e.g. 200 wt%) relative to the weight of the  
35 crosslinked elastomeric polymeric matrix. Any suitable ionic liquid may be used herein. In particular embodiments of the invention that may be mentioned herein, the ionic liquid may be 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

The crosslinked elastomeric polymeric matrix may be any suitable material. For example, it may be formed from oligomers that are suitable to undergo crosslinking/polymerisation under UV or thermal conditions. In particular embodiments that may be mentioned herein, the crosslinked elastomeric polymeric matrix may be an aliphatic polyurethane acrylate (e.g. CN990 or, more particularly, CN9021).

Also disclosed herein are methods to make the two products of the first and second aspects of the invention. Thus, in a third aspect of the invention, there is provided a method of forming an elastomeric electrode film material as described hereinbefore (i.e. with respect to the first aspect of the invention), the method comprising the steps of:

- (i) providing:
  - a first mixture comprising a first solvent, an elastomeric polymer matrix and a conductive filler material; and
  - a second mixture comprising a second solvent and a plurality of liquid metal particles; and
- (ii) mixing the first and second mixtures together, drop-casting the resulting mixture into a mold and evaporating off the first and second solvents to provide the elastomeric electrode film material.

The elastomeric polymer matrix, conductive filler material, and liquid metal particles are as described hereinbefore and a further discussion of them is omitted to avoid repetition. The first and second solvents may be any suitable solvents. For example, the first and second solvents may be the same solvent. In particular embodiments of the invention, the first and second solvents may be dimethylformamide.

In a fourth aspect of the invention, there is provided a method of forming a liquid metal-based solid-state supercapacitor as described hereinbefore (i.e. with respect to the second aspect of the invention), the method comprising the steps of:

- (aa) providing a mixture comprising:
  - one or more urethane acrylate oligomers;
  - a photoinitiator; and
  - an ionic liquid; and
- (ab) sandwiching the mixture between a first elastomeric electrode film and a second elastomeric electrode film and subjecting the mixture to a photocuring step to provide the liquid metal-based solid-state supercapacitor, wherein

the first and second elastomeric electrode films are as described hereinbefore (i.e. with respect to the first aspect of the invention).

It will be appreciated that the mixture used herein is ideally a homogeneous mixture. This may  
5 be obtained by dissolving the mixture in a suitable solvent (e.g. acetone) and subjecting the mixture to agitation before removal of the solvent before use in step (aa).

In order to achieve a good formation of the liquid metal-based solid-state supercapacitor, a suitable material may be used as a spacer material. The function of the spacer material is to  
10 help maintain the constant thickness of the ionogel between the electrodes. This may be, for example, the use of VHB tape and an example of this is shown in Fig. 11. In this figure, VHB tape 210 is used as a spacer to maintain the constant thickness of the ionogel between the electrodes. As a mixture (e.g. of CN9021 resin, ionic liquid and photoinitiator) is injected between the electrodes 220 and 230, the VHB tape 210 helps to prevent leakage. After UV  
15 curing, the VHB tape may be removed.

Any suitable photoinitiator may be used herein. For example, the photoinitiator may be (2,4,6-trimethylbenzoyl) phosphine oxide.

20 Further embodiments of the invention will be described by reference to the following numbered clauses.

1. Preparation of liquid metal-based electrode

a. The stretchable conductive matrix was prepared by dissolving the thermoplastic polyurethane (TPU, relative density: 1.15-1.20 g/cm<sup>3</sup>, 0.3 g) with the conductive filler, multiwalled carbon nanotubes (MWCNT, 5 wt%, 15 mg) and carbon black (CB, 20 wt%, 60 mg), in 2.5 ml dimethylformamide (DMF) solvent. This mixture (MWCNT/CB/TPU) is stirred at 50 degrees Celsius and 600 rpm for 48 hours to achieve a viscous, shiny, paste-like slurry. Scale up accordingly to the respective ratio if needed.

30 b. The eutectic gallium indium (EGaIn, density - 6.25 g/cm<sup>3</sup>, 0.6 g) bulk particle in 20 ml acetone having the weight percentage of liquid metal is up to 300 wt% of the TPU polymer. The liquid metal particles, microparticles, and submicron particles (e.g. particles) are prepared by probe sonicating the EGaIn solution for 3 minutes at 100 W power or, in some cases, for  
35 30 minutes at 300 W power. The liquid metal particle solution is allowed to stand for 10 minutes to sediment the particles, and acetone is removed through evaporation at room temperature.

- c. The liquid metal particles obtained are mixed in 0.5 ml DMF for transferring to the MWCNT/CB/TPU mixture. The EGaIn/MWCNT/CB/TPU mixture is stirred at 50 degrees Celsius and 600 rpm for 48 hours to achieve a homogenous distribution of liquid metal particles. This attained mixture is drop cast on the square Teflon mould at 50 degrees Celsius.
- 5 After the evaporation of the DMF solvent, a free-standing, stretchable, conductive film is formed with the liquid metal particles sedimented at the bottom of the electrode.
2. Preparation of liquid metal-based all-solid-state supercapacitor
- a. The ionogel for the supercapacitor was prepared by mixing polyurethane acrylate (PUA, CN9021, 1 g) and diphenyl (2,4,6- trimethylbenzoyl) phosphine oxide (TPO, 10 mg) in 4 ml of acetone. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI, 200 wt%, 2g), was added to the CN9021/TPO mixture. The obtained CN9021/BMIM TFSI/TPO solution was stirred at 500 rpm for 6 hours and sonicated for 10 minutes. This mixture was drop casted on the Teflon mould to evaporate the acetone solvent. The obtained
- 15 viscous mixture was injected between the two liquid metal-based electrodes. The constant distance between the electrode was maintained by using the VHB tape spacer. This was followed by five minutes of curing under 395 nm light exposure. In this way, the symmetric liquid metal-based all-solid-state supercapacitor device was assembled.
- 20 The advantages of the presently prepared liquid metal-based electrode for stretchable supercapacitors include, but are not limited to:
- a. Highly stretchable, e.g. up to 900% (and possibly higher);
  - b. Increased conductivity during deformation;
  - c. Preservation of the amount of active material on the surface during deformation;
  - 25 d. Prevention of leaching of liquid metal;
  - e. High stretching cycle stability; and
  - f. Enhanced electrochemical performance during/after deformation.
- Further aspects and embodiments of the invention will now be discussed by reference to the
- 30 following non-limiting examples.

## Examples

### 35 Materials

Eutectic gallium indium (EGaIn, Smart Memories Pte. Ltd.), multiwalled carbon nanotubes (MWCNT, Nanocyl, NC7000), thermoplastic polyurethane (TPU) (Usof, BTE-75A),

[BMIM][TFSI] (Sigma-Aldrich, 98%), CN9021 (Sartomer), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) (Sigma-Aldrich, 97%), acetone (ACS reagent,  $\geq 99.5\%$ ) and N, N-dimethylformamide (DMF) (Sigma-Aldrich,  $> 99.9\%$ ) were purchased and used as received.

#### 5    **Example 1. Preparation of liquid metal-based electrode**

The stretchable conductive matrix was prepared by dissolving the TPU (relative density: 1.15-1.20 g/cm<sup>3</sup>, 0.3 g) with conductive filler, MWCNT (5 wt%, 15 mg) and CB (20 wt%, 60 mg), in 2.5 mL dimethylformamide (DMF) solvent. This mixture (MWCNT/CB/TPU) was stirred at  
10    50 °C and 600 rpm for 48 hours to achieve a viscous, shiny, paste-like slurry. The reaction may be scaled up accordingly to the respective ratio if needed.

The EGaln (density: 6.25 g/cm<sup>3</sup>) bulk particle has a weight percentage of liquid metal that was up to 300 wt% of the TPU polymer. The liquid metal microparticles (up to 200 wt% of the TPU  
15    polymer) were prepared by probe sonicating the EGaln in 20 mL acetone for 3 minutes at 100 W power. The liquid metal sub-microparticles (up to 100 wt% of the TPU polymer) were prepared by probe sonicating the EGaln in 20 mL acetone for 30 minutes at 300 W power. The liquid metal particle solution was composed of both microns and submicron particles. The liquid metal particle solution was allowed to stand for 10 minutes to sediment the particles,  
20    and acetone was removed through evaporation at room temperature.

The liquid metal particles obtained were mixed in 0.5 mL DMF for transferring to the MWCNT/CB/TPU mixture. The EGaln/MWCNT/CB/TPU mixture was stirred at 50 °C and 600 rpm for 48 hours to achieve a homogenous distribution of liquid metal particles. This attained  
25    mixture was drop cast on the square Teflon mould at 50 °C. After the evaporation of the DMF solvent, a free-standing, stretchable, conductive film was formed with the liquid metal particles sedimented at the bottom of the electrode.

#### **Example 2. Characterization of liquid metal-based electrode**

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The liquid metal-based electrode prepared in Example 1 was characterised.

#### *SEM*

Field Emission Scanning Electron Microscopy (FE-SEM) was performed using JOEL 7600F  
35    to examine the surface morphology of the liquid metal electrodes at different levels of magnifications. The FE-SEM images were captured using secondary electron imaging (SEI) mode with an electron beam energy of 5 kV to obtain highly resolution images.

### *Tensile tests*

The mechanical properties of the samples were measured by a universal testing machine (MTS criterion model 43) using the 10kN load cell and pneumatic clamps to hold the sample.

- 5 The stress–strain curves were obtained at a 5 mm/min strain rate. The Young's modulus of the materials was computed by examining the slope of the curve within the range of 0 to 5% strain.

### *CV*

- 10 The Autolab PGSTAT128N was utilized for carrying out of Cyclic voltammetry (CV) analysis. Cyclic Voltammetry are employed for analysing the redox behaviour of the electrodes and quantifying the capacitance. The CV was performed in a 3-electrode configuration to investigate the redox behavior of the liquid metal-based electrode as working electrode with BMIM TFSI electrolyte, Platinum sheet as counter electrode and Ag/AgCl as reference  
15 electrode.

### Results and discussion

- The SEM images, as shown in Fig. 1a, depict the liquid metal particles' average diameter of ~5 microns sedimented at the bottom surface of the conductive matrix. At a higher magnification  
20 level (Fig. 1b), the network of carbon nanotubes around the liquid metal particles could be observed. The mechanical property of liquid metal-based electrodes was evaluated using a tensile tester, as shown in Fig. 2. The stress-strain curve shows that this material's maximum stretchability was ~1600%, and the average value was ~900%. The conductivity was measured during stretching (Fig. 3). It was observed that with an increase in strain to 250%,  
25 the conductivity increased by approximately 400%, and at 500% strain, the electrode had the same conductivity as without strain.

- The electrochemical performance of liquid metal-based electrodes was analysed through the CV technique, as shown in Fig. 4. The CV was conducted in a three-electrode configuration  
30 at a scan rate of 20 mV/s with the platinum sheet as a counter electrode, the Silver/Silver chloride (Ag/AgCl) electrode as the reference electrode and the liquid metal-based electrode as the working electrode in BMIM TFSI ionic liquid. The redox peaks observed during oxidation in the CV were due to the interaction of BMIM cation with the liquid metal oxide layer at ~1 V and TFSI anion with the liquid metal, Ga, at ~-0.45 V. Similarly, the counter peaks were  
35 observed in at 0 V and -0.45 V.

The electrochemical performance was also measured after and during the mechanical deformation (Fig. 5). The liquid metal-based electrode showed that for strain up to 900%, there was almost no decrease in the capacitance; above 500%, there is a trend of capacitance increase due to the breaking of nanoparticles at higher strain%.

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### **Example 3. Preparation of liquid metal-based all-solid-state supercapacitor**

The fabrication steps of a liquid metal-based supercapacitor are depicted in Fig. 6, in which ionogel was cured between two liquid metal-based electrodes.

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The ionogel for the supercapacitor was prepared by mixing polyurethane acrylate (PUA, CN9021, 1 g) and diphenyl (2,4,6- trimethylbenzoyl) phosphine oxide (TPO, 10 mg) in 4 mL of acetone. The ionic liquid, BMIM TFSI (200 wt%, 2g), was added to the CN9021/TPO mixture. The obtained CN9021/BMIM TFSI/TPO solution was stirred at 500 rpm for 6 hours and sonicated for 10 minutes. This mixture was drop casted on the Teflon mould to evaporate the acetone solvent. The obtained viscous mixture was injected between the two liquid metal-based electrodes. The constant distance between the electrode was maintained by using a VHB tape spacer. This was followed by five minutes of curing under 395 nm light exposure. In this way, the symmetric liquid metal-based all-solid-state supercapacitor device was assembled.

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### **Example 4. Performance of liquid metal-based supercapacitor**

The liquid metal-based supercapacitor (prepared in Example 3) and its performance were investigated by following the protocols in Example 2.

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#### Results and discussion

The CV of the device shows stability over a large potential window of 3 V (Fig. 7). The redox peak during oxidation around 2 V is related to liquid metal oxide interaction with the BMIM cation in the ionogel. The electrochemical performance was compared using CV under different strains, as shown in Fig. 8. There is no significant variation in the capacitance up to 150%, and the device could endure 500 stretching cycles without significant change in the performance (Fig. 9).

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Therefore, in the present disclosure, a highly intrinsically stretchable electrode was prepared through sedimenting the active material, liquid metal particles, in a stretchable conductive matrix. This technique resulted in an integrated single-layer electrode that combines current

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collector and active material. The liquid metal-based electrode can be stretched to approximately 900% strain, and its conductivity increases with stretching up to 250% and resumes its initial conductivity at 500% strain. The liquid metal particles possess a thin metallic oxide shell preventing the leaching of the liquid metal and providing a high surface area for electrochemical reactions. These liquid metal-based electrodes were utilised to develop stretchable supercapacitors, upon curing the ionogel (of a similar polymer matrix) between the electrodes. Benefitting from the properties of the liquid metal-based electrode, the assembled all-solid-state-supercapacitor provides high stretchability and electrochemical performance during and after mechanical strain. This core-shell morphology of liquid metal particles helps to increase the electrical conductivity and preserve the amount of active material during mechanical deformation as the shell (liquid metal oxide) breaks and the flow of liquid metal provides a continuous conductive network.

## Claims

1. An elastomeric electrode film material, comprising:  
an elastomeric polymer matrix;  
a conductive filler material; and  
a plurality of liquid metal particles, wherein  
the elastomeric electrode film material has a first surface and a second surface, and  
the plurality of liquid metal particles are dispersed on or adjacent to the first surface.
2. The elastomeric electrode film material according to Claim 1, wherein the elastomeric polymer matrix is selected from one or more of the group consisting of thermoplastic polyurethane (TPU), polyester TPU, polyether TPU, polycaprolactone TPU, blends thereof and copolymers thereof, optionally wherein the elastomeric polymer matrix is a thermoplastic polyurethane.
3. The elastomeric electrode film material according to Claim 1 or Claim 2, wherein the conductive filler material is selected from one or more of the group consisting of single-walled carbon nanotubes, acetylene black, graphite powder, graphene, and, more particularly multiwalled carbon nanotubes, and carbon black.
4. The elastomeric electrode film material according to Claim 3, wherein the conductive filler material is multiwalled carbon nanotubes and carbon black.
5. The elastomeric electrode film material according to Claim 4, wherein one or both of the following apply:  
the multiwalled carbon nanotubes are present in an amount of from 2 to 10 wt% (e.g. about 5 wt%) of the weight of the elastomeric polymer matrix; and  
the carbon black is present in an amount of from 10 to 30 wt% (e.g. about 20 wt%) of the weight of the elastomeric polymer matrix.
6. The elastomeric electrode film material according to any one of the preceding claims, wherein the liquid metal is a gallium alloy with one or more metals selected from indium, tin and zinc, for example, GaInSn or eutectic gallium indium (EGaIn).
7. The elastomeric electrode film material according to any one of the preceding claims, wherein the liquid metal particles are present in an amount that is from 100 to 300 wt% (e.g. 200 wt%) of the weight of the elastomeric polymer matrix.

8. The elastomeric electrode film material according to any one of the preceding claims, wherein the elastomeric electrode film material has one or more of the following properties:

- (a) a maximum stretchability of from 900 to 2000% (e.g. about 1600%) of its original size in at least one dimension when subjected to a strain;
- (b) a conductivity that is higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state, optionally wherein the conductivity is from 300 to 500% (e.g. 400%) higher when the film is subjected to a strain of 250% as compared to the film in a non-strained state; and
- (c) a conductivity that is about the same as the film in a non-strained state when the film is subjected to a strain of from 400 to 600%, such as about 500%.

9. A liquid metal-based solid-state supercapacitor, comprising:

- a first electrode comprising an elastomeric electrode film material as described in any one of Claims 1 to 8;
- a second electrode comprising an elastomeric electrode film material as described in any one of Claims 1 to 8; and
- an ionogel sandwiched between the first and second electrodes.

10. The liquid metal-based solid-state supercapacitor according to Claim 9, wherein the ionogel comprises:

- a crosslinked elastomeric polymeric matrix; and
- an ionic liquid.

11. The liquid metal-based solid-state supercapacitor according to Claim 10, wherein the ionic liquid is present in an amount of from 100 to 300 wt% (e.g. 200 wt%) relative to the weight of the crosslinked elastomeric polymeric matrix.

12. The liquid metal-based solid-state supercapacitor according to Claim 10 or Claim 11, wherein the crosslinked elastomeric polymeric matrix is an aliphatic polyurethane acrylate (e.g. CN990 or, more particularly, CN9021).

13. The liquid metal-based solid-state supercapacitor according to any one of Claims 10 to 12, wherein the ionic liquid is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

14. A method of forming an elastomeric electrode film material as described in any one of Claims 1 to 8, the method comprising the steps of:

- (i) providing:
  - a first mixture comprising a first solvent, an elastomeric polymer matrix and a conductive filler material; and
  - a second mixture comprising a second solvent and a plurality of liquid metal particles;and
- (ii) mixing the first and second mixtures together, drop-casting the resulting mixture into a mold and evaporating off the first and second solvents to provide the elastomeric electrode film material.

15. The method according to Claim 14, wherein the first and second solvents are dimethylformamide.

16. A method of forming a liquid metal-based solid-state supercapacitor as described in any one of Claims 9 to 13, the method comprising the steps of:

- (aa) providing a mixture comprising:
  - one or more urethane acrylate oligomers;
  - a photoinitiator; and
  - an ionic liquid; and
- (ab) sandwiching the mixture between a first elastomeric electrode film and a second elastomeric electrode film and subjecting the mixture to a photocuring step to provide the liquid metal-based solid-state supercapacitor, wherein
  - the first and second elastomeric electrode films are as described in any one or Claims 1 to 8.

17. The method according to Claim 16, wherein the photoinitiator is (2,4,6-trimethylbenzoyl) phosphine oxide.