

TACTILE SENSOR

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore Patent Application No. 10202004802U, filed 22 May 2020, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] An aspect of the disclosure relates to an electrochemical transistor. Another aspect of the disclosure relates to a process for making an electrochemical transistor. Another aspect of the disclosure relates to a pressure sensor including the electrochemical transistor as described herein.

BACKGROUND

[0003] The development of highly sensitive flexible pressure sensors is particularly attractive for new and disruptive technologies such as cyber-physical systems, soft robotics and wearable healthcare devices. Current flexible tactile sensors consist of organic/polymeric thin films that exploit three main pressure sensing mechanisms - piezoresistive, capacitive and piezoelectric. Although they allow for good pressure sensitivity ($0.7\text{--}100\text{ kPa}^{-1}$), simple device architecture and readout, they are still subjected to the limitation of high voltages/power consumption, inherent charge leakage, or parasitic noise from body and environmental sources. Although state-of-the-art pressure sensitivities have been demonstrated in organic field effect transistors (OFET) with a microstructured gate dielectric, the high driving voltages required (30-200V) limit their integration and portability.

[0004] Therefore, there remains a need to provide improved electrochemical transistors. There also remains a need to provide improved pressure sensors.

SUMMARY

[0005] In a first aspect, there is provided an electrochemical transistor including a solid polymer electrolyte layer including an ionic conductive polymer and an ionic liquid incorporated into the ionic conductive polymer; a gate electrode that is deposited on a first main side of the solid polymer electrolyte layer; a source electrode and a drain electrode; and a channel comprising a semiconducting material facing a second main side of the solid polymer

electrolyte layer and connecting the source electrode with the drain electrode, the second main side being opposite to the first main side.

[0006] In a second aspect, there is provided a process for making an electrochemical transistor, the process including: providing a first transistor part including a source electrode and a drain electrode disposed on a substrate, a channel connecting the source electrode with the drain electrode; wherein the channel includes a semiconducting material; providing a second transistor part including providing a solid polymer electrolyte layer including an ionic conductive polymer and an ionic liquid incorporated into the ionic conductive polymer; disposing the solid polymer electrolyte layer on a gate electrode; assembling the electrochemical transistor by disposing the second transistor part on the first transistor part such that the solid polymer electrolyte layer is on one side facing the gate electrode and on the other side facing the channel comprising the semiconducting material.

[0007] In a third aspect, there is provided a pressure sensor including the electrochemical transistor as defined herein or obtained from a process of as defined herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

- **FIG. 1** shows an example of an all-solid-state OECT device architecture, which includes a conjugated polymer as the channel, with the source and drain metal electrodes and the solid polymer electrolyte on top of the channel layer;
- **FIG. 2** is a schematic view of the solid polymer electrolyte (also referred to as polymeric solid electrolyte) by blending polymer matrix (ionic conductive polymer) with ionic liquids and structures of polymers, cations and anions used for studies of ionic conductivity and mechanical properties in solid polymer electrolyte;
- **FIG. 3** is a schematic view showing the poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) solid polymer electrolyte, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([EMIM][TFSI]) ionic liquid; and polymer structures of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and poly(3-hexyothiophene-2,5-diyl) (P3HT);

- **FIG. 4** is a schematic view showing the counter-ion exchange being manipulated by modulating the electrostatic interactions (dashed bond shown in above figure) between charged components. The disassembly and subsequent self-assembly process between the positively charged PEDOT⁺ and the negatively charged poly(styrenesulfonate) (PSS)⁻ reorganizes the ordering of the conducting poly(3,4-ethylenedioxythiophene) (PEDOT) molecules;
- **FIG. 5A** shows the output performance for PEDOT:PSS based OECTs;
- **FIG. 5B** shows the transfer performance for PEDOT:PSS based OECTs;
- **FIG. 5C** shows the transconductance (g_m) performance for PEDOT:PSS based OECTs where the measurements for g_m were taken at $V_D = -0.5$ V;
- **FIG. 5D** shows the switching response performance for PEDOT:PSS based OECTs;
- **FIG. 6A** shows the transfer characteristics of the all-solid-state OECT based on PEDOT:PSS operate well after heating up to 100 °C for 10 mins in the air, which shows excellent temperature stability;
- **FIG. 6B** shows the output characteristics of the all-solid-state OECT based on PEDOT:PSS operate well after heating up to 100 °C for 10 mins in the air, which shows excellent temperature stability;
- **FIG. 6C** shows that the transfer characteristics of all-solid-state OECT based on PEDOT:PSS operate well after multiple lamination and delamination processes and stored in the air after one week, which therefore allows reuse and practical applications;
- **FIG. 6D** shows that the transfer characteristics of all-solid-state OECT with P3HT operate well after multiple lamination and delamination processes and stored in the air after one week, which therefore allows reuse and practical applications;
- **FIG. 7A** shows the output performance for P3HT based OECTs (width/length/thickness (W/L/d) of P3HT channel is 1000 μm /200 μm /81.0 nm);
- **FIG. 7B** shows the transfer performance for P3HT based OECTs;
- **FIG. 7C** shows the transconductance (g_m) performance for P3HT based OECTs where the measurements for g_m were taken at $V_D = -0.5$ V;
- **FIG. 7D** shows the switching response performance for P3HT based OECTs;
- **FIG. 8A** shows the chemical structure of the poly[(5-fluoro-2,1,3-benzothiadiazole-4,7-diyl)(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)(6-fluoro-

2,1,3-benzothiadiazole-4,7-diyl)(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)] (PCDTFBT) polymer;

- **FIG. 8B** shows the transfer characteristics of the PCDTFBT all-solid-state OECT with different thickness of channel;
- **FIG. 8C** shows the output characteristics of the PCDTFBT all-solid-state OECT with thickness of 109 nm;
- **FIG. 8D** shows the transconductance of the PCDTFBT all-solid-state OECT with different thickness of channel;
- **FIG. 8E** shows the maximum transconductance of the PCDTFBT all-solid-state OECT as a function of channel thickness;
- **FIG. 8F** shows the temporal response of the drain current (I_{ds}) of the PCDTFBT all-solid-state OECT with different thickness of the channel, wherein it is shown that the response time increased while increasing the thickness of channel, presumably because it needs more anions to dope the PCDTFBT channel layer;
- **FIG. 8G** shows the cycling stability of the all-solid-state OECT based on PCDTFBT, where successive gate voltage pulse was applied (with V_G switches from 0 V to -0.8 V, and constant $V_D = -0.5$ V), the results showed a high switching stability, where the drain current retained ~90.7% of the original value after 500 cycles;
- **FIG. 9A** shows the chemical structure of the [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₀BM) small molecule;
- **FIG. 9B** shows the transfer characteristics of the PC₇₀BM all-solid-state OECTs;
- **FIG. 9C** shows the transconductance (g_m) of the PC₇₀BM all-solid-state OECTs; wherein the active channel thickness was controlled by spin-coating different concentration of solutions (1 mg/ml, 5 mg/ml, 10 mg/ml) at a same speed;
- **FIG. 9D** shows the output characteristics of the all-solid-state OECT with PC₇₀BM concentration of 10 mg/ml;
- **FIG. 9E** shows the cycling stability of the all-solid-state OECT based on PC₇₀BM, where successive gate voltage pulses are applied (with V_G switches from 0 V to +1 V, and constant $V_D = 0.5$ V), wherein the result exhibited high switching stability, where the drain current retained above 95% of the original value after 500 cycles;

- **FIG. 10A** is a schematic illustration of in-situ spectro-electrochemistry measurements of PEDOT:PSS or P3HT films as semiconducting material which is interfaced with solid polymer electrolyte;
- **FIG. 10B** shows the optical switching behaviour under different gate voltages for the PEDOT:PSS films interfaced with solid polymer electrolyte;
- **FIG. 10C** shows the optical switching behaviour under different gate voltages for the P3HT films interfaced with solid polymer electrolyte;
- **FIG. 11** is a device schematic of a pressure sensor (also referred to as tactile sensor) based on all-solid-state OECT with pyramid structures on polymer electrolyte layer;
- **FIG. 12A** is a SEM image of solid polymer electrolyte with pyramids array in a side view, showing that a membrane with a thickness of about 40 μm shows a high flexibility under applied deformation;
- **FIG. 12B** is a top-view of the micro-structured solid polymer electrolyte, for which the length, width and height are obtained to be 10.5 μm , 10.5 μm , and 8.0 μm , respectively;
- **FIG. 12C** shows the optic images of solid polymer electrolyte on polyimide substrate, showing that the solid polymer electrolyte with pyramidal structure owns a high transparency and flexibility;
- **FIG. 12D** shows the optic images of the flexible OECT-based pressure sensor on polyimide substrate; showing that the solid polymer electrolyte with pyramidal structure owns a high transparency and flexibility;
- **FIG. 13** is a schematic illustration of the ionic doping mechanism for pressure sensor;
- **FIG. 14A** shows the transfer performance of the PEDOT:PSS-based tactile sensor under different pressure;
- **FIG. 14B** shows the output performance of the PEDOT:PSS-based tactile sensor under different pressure;
- **FIG. 15** shows the leakage current (I_{GS}) under different pressure stimuli at $V_{\text{G}} = 0.5 \text{ V}$;
- **FIG. 16** shows pulse measurements (V_{G} vary from -0.6 V to 0.6 V, pulse length = 0.5 s, $V_{\text{D}} = -0.5 \text{ V}$) with over 1000 cycles of continuous operation for the all-solid-state OECT under a constant pressure (15 kPa), the inset is the transient response of drain current to gate pulse after 1000 cycles;
- **FIG. 17A** shows the sensitivity of the device to pressure in 4-15 kPa;
- **FIG. 17B** shows the sensitivity of the device to pressure in 0.1-4 kPa;

- **FIG. 17C** shows the sensitivity of the device to pressure in a very low pressure region (< 100 Pa);
- **FIG. 17D** is a top-view of solid polymer electrolyte before and after applying pressure, wherein a transparent cover slip was used to apply pressure on the top of pyramids;
- **FIG. 18A** shows the limit of detection with a flower and a grain of rice where the limit of detection of the OECT-based pressure sensor was performed at $V_D = -0.5$ V and $V_G = 0.6$ V;
- **FIG. 18B** shows the device stability over time;
- **FIG. 18C** shows the stability test of sensor over 300 cycles at 10 kPa;
- **FIG. 18D** shows the top-view of optical images of solid polymer electrolyte before and after 300 pressure cycles;
- **FIG. 19** is a schematic illustration of the doping mechanism in P3HT-based pressure sensor;
- **FIG. 20A** shows the absorption spectra of polarized ultraviolet-visible spectroscopy from P3HT films with the micro-structured solid polymer electrolyte under different gate voltage before applying pressure;
- **FIG. 20B** shows the absorption spectra of polarized ultraviolet-visible spectroscopy from P3HT films with the micro-structured solid polymer electrolyte under different gate voltage after applying pressure;
- **FIG. 21A** shows the transfer performance under different pressure;
- **FIG. 21B** shows the sensitivity to pressure of the P3HT device at different pressure region, whereby the error bars represent the sample variation and measurement uncertainty;
- **FIG. 22A** shows plots of extracted capacitance values as a function of active volume of P3HT films;
- **FIG. 22B** shows the volumetric capacitance of P3HT film as a function of the applied pressures;
- **FIG. 22C** are color-coded contour plots of absorption spectra of polarized ultraviolet-visible spectroscopy from P3HT films with the solid polymer electrolyte before and after applying pressure;
- **FIG. 22D** is a comparison of sensitivity to pressure and operating voltage for different types of pressure sensors;

- **FIG. 22E** shows the current-voltage (CV) curves of the P3HT films at various applied pressure using solid polymer electrolyte with microstructures, wherein the scan rate was fixed at 10 mV/s, and two strong redox peaks can be observed in each curve, indicating that the capacitance characteristics are mainly due to Faradaic redox reactions, it is observed that the redox peaks are becoming stronger while increasing the applied pressure, due to the ionic doping effect;
- **FIG. 23A** shows the tunability of sensitivity by gate voltage;
- **FIG. 23B** shows the relative change of resistance under 4 kPa at $V_{DS} = -0.5$ V as a function of applied gate voltage;
- **FIG. 24A** shows the pressure sensor exposed to radial artery pulse;
- **FIG. 24B** shows electrical signals induced by radial artery pulse under different gate voltages;
- **FIG. 24C** shows electrical signals induced by radial artery pulse under different gate voltages;
- **FIG. 24D** shows the pulse signals with environmental interference (continuous air flow from human breath) at high ($V_G = 0.6$ V) and low ($V_G = 0.4$ V) sensitivity states, respectively;
- **FIG. 24E** shows the device stability over time;
- **FIG. 24F** shows the results of a stability test of sensor over 300 cycles at 1 kPa;
- **FIG. 25A** shows a schematic diagram of the 6×6 pressure sensor array;
- **FIG. 25B** shows a circuit schematic of the 6×6 pressure sensor array;
- **FIG. 26A** is a photograph of a fully fabricated flexible sensor array, wherein the fabricated sensors array consists of a 6×6 pixel matrix with an active area of 3.9×2.2 cm², the inset image is the optical microscope image of a single sensor pixel in the array, depicting an OECT-based pressure sensor (channel length ~ 150 μ m and width ~ 2000 μ m) covered with microstructured solid polymer electrolyte.
- **FIG. 26B** shows the result of a static test for the pressure sensor array to demonstrate the ability to mapping the pressure stimuli distribution and tract the finger's movement;
- **FIG. 26C** shows the result of a dynamic test for the pressure sensor array to demonstrate the ability to mapping the pressure stimuli distribution and tract the finger's movement;

- **FIG. 26D** shows the result of a dynamic test for the pressure sensor array to demonstrate the ability to mapping the pressure stimuli distribution and tract the finger's movement;
- **FIG. 27** shows the transfer curves for OECT devices based on different types of electrolytes at $V_D = -0.5$ V;
- **FIG. 28** shows the transfer curves for all-solid-state OECT devices at $V_D = -0.5$ V, using pristine PVDF-HFP and PVDF-HFP/[EMIM][TFSI] as solid electrolytes, respectively, wherein the device with pristine PVDF-HFP without ionic liquid in electrolyte showed no transistor characteristics, indicating that the ions are responsible for the electrochemical doping effect;
- **FIG. 29** shows the transfer curves for all-solid-state OECT devices with different treatment of electrolyte to minimize the hysteresis, wherein for the OECT with DMF-treated electrolyte, the obvious hysteresis may be caused by the existence of dimethyl formamide (DMF) in electrolyte, which has a high boiling point (~ 153 °C) and is difficult to remove under low temperature fabrication process;
- **FIG. 30** illustrates the temporal response of the drain current (I_{ds}) of OECT with different types of electrolyte;
- **FIG. 31A** shows the cycling stability of the OECT based on PEDOT:PSS using ionic liquid, where successive gate voltage pulse are applied with V_G switches from 0 V to 0.6 V for PEDOT:PSS and constant $V_D = -0.5$ V, wherein the PEDOT:PSS channel exhibited high switching stability, where the drain current retained 91.2% of the original value after 13000 cycles, which is comparable to the retention ($\sim 91.8\%$) for PEDOT:PSS channel using liquid electrolyte ([EMIM][TFSI]);
- **FIG. 31B** shows the cycling stability of the OECT based on PEDOT:PSS using solid polymer electrolyte, where successive gate voltage pulse are applied with V_G switches from 0 V to 0.6 V for PEDOT:PSS, and constant $V_D = -0.5$ V, wherein the PEDOT:PSS channel exhibited high switching stability, where the drain current retained 91.2% of the original value after 13000 cycles, which is comparable to the retention ($\sim 91.8\%$) for PEDOT:PSS channel using liquid electrolyte ([EMIM][TFSI]),
- **FIG. 31C** shows the cycling stability of the OECT based on P3HT using solid polymer electrolyte, where successive gate voltage pulse are applied with V_G switches from 0 V to -0.7 V for P3HT, and constant $V_D = -0.5$ V, wherein, the P3HT channel using solid

polymer electrolyte exhibited good switching stability, where the drain current retained 91.5% of the original value after 500 cycles;

- **FIG. 32A** shows absorption spectra of polarized ultraviolet-visible spectroscopy from PEDOT:PSS with the solid polymer electrolyte under different gate voltage;
- **FIG. 32B** shows absorption spectra of polarized ultraviolet-visible spectroscopy from P3HT films with the solid polymer electrolyte under different gate voltage;
- **FIG. 33** shows the change of active channel resistance ($\Delta R/R_0$) and I_{GS} response to the cyclic pressure, proving that the ions are much easier to move between channel and electrolyte for the doping/de-doping with PEDOT:PSS under pressure;
- **FIG. 34** shows the transient response of drain current with V_G switches from 0.6 V to -0.6 V for pulse width of 0.5 s and constant $V_D = -0.5$ V for 1000 cycling pulses;
- **FIG. 35** shows the transfer curves for PEDOT-based OECT device with no microstructures (in this case, pyramids) on solid polymer electrolyte under different pressure stimuli;
- **FIG. 36** shows the transfer characteristic of solid OECT under high pressure regions (above 15 kPa), wherein the transfer curves showed a little degradation under high pressure state, maybe because little cations stayed in the PEDOT:PSS polymer under effect of pressure injection;
- **FIG. 37** shows the drain current response to high and low region of pressures;
- **FIG. 38** shows the output characteristic of P3HT-based all-solid state OECT touch sensor under the pressure of 15 kPa;
- **FIG. 39** shows the relationship of sensitivity to gate voltage to prove the tunable sensitivity via bias conditions in PEDOT-based pressure sensor;
- **FIG. 40** shows the manipulation of the counter-ion exchange by modulating the electrostatic interactions (dashed bond shown in **FIG. 40**) between charged components, the disassembly and subsequent self-assembly process reorganizes the ordering of the conducting PEDOT molecules;
- **FIG. 41** shows the transfer characteristic of solid OECT with different gate electrodes wherein the gate electrode modified with a non-polarizable PEDOT:PSS/[EMIM]Cl film (PEDOT:PSS/ILs) reduces the electrochemical impedance and potential drop between gate electrode and electrolyte interface and hence leading to a large modulation of source-drain current and a lower operating voltage; and

- **FIG. 42** shows a side-gate OECT construction, wherein the gate electrode is coplanar with the source-drain electrodes, and the solid polymer electrolyte is positioned across the gate electrode and channel layer; the gate electrode can be modified with a non-polarizable layer, e.g. PEDOT:PSS.

DETAILED DESCRIPTION

[0009] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the disclosure may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the disclosure. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the disclosure. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0010] In a first aspect, the present disclosure refers to an electrochemical transistor. The electrochemical transistor may include a solid polymer electrolyte layer. The solid polymer electrolyte layer may include an ionic conductive polymer. The solid polymer electrolyte layer may include an ionic liquid incorporated into the ionic conductive polymer. The electrochemical transistor may include a gate electrode. The gate electrode may be deposited on a first main side of the solid polymer electrolyte layer. The electrochemical transistor may include a source electrode. The electrochemical transistor may include a drain electrode. The electrochemical transistor may include a channel. The channel may comprise a semiconducting material. The semiconducting material may be facing a second main side of the solid polymer electrolyte layer. The semiconducting material may connect the source electrode with the drain electrode. The second main side may be opposite to the first main side.

[0011] The electrochemical transistor disclosed herein can be classified as an organic electrochemical transistor (OECT), having a channel comprising a semiconducting material (also referred to as the active polymer channel or the active channel) on which an electrolyte is disposed, which is the source of ions. Reversible ionic insertion/extraction from the semiconducting material is modulated through the applied gate voltage. The electrochemical transistor may have a strong signal amplification since the ionic doping occurs over the entire volume of the semiconducting material, and thus significant modulations in the current can be achieved under low gate voltages. Surprisingly, the employment of a solid polymer electrolyte layer as described herein improves long-term operation, reproducibility, scalability and

integration of the OECT, which was limited in traditional devices due to usage of a liquid electrolyte. The employment of a solid polymer electrolyte layer as described herein also allows for independent gating, which was not possible in traditional devices since the ions in the liquid electrolyte are shared between all the fabricated transistors. The employment of a solid polymer electrolyte layer also enables the electrochemical transistor disclosed herein to be used for a wide variety of sensing applications including tactile input. The employment of a solid polymer electrolyte layer also demonstrated to produce superior results than OECTs with other electrolytes such as hydrogels, ion-gels which incorporate aqueous electrolytes, or ionic liquids within an organic matrix, since said hydrogels allow operation only in a narrow temperature range, while poorly miscibility of the ionic liquids within polymers at concentrations required for realizing high ionic conductivity result in viscous, thick gel electrolytes that are not convenient for use in flexible applications. The employment of a solid polymer electrolyte layer advantageously demonstrates a high ionic conductivity, resulting in efficient ion transport and fast switching response. The demonstration of this high performance flexible OECT, utilising a solid state polymer electrolyte, is therefore significant for a wide variety of applications.

[0012] Specifically, the electrochemical transistor disclosed herein provides for pressure-sensing modalities, wherein the applied pressure modulates the electrochemical doping process in the semiconducting material under a low operation voltage of less than 1V and ultralow power consumption ($<5 \mu\text{W}$). Accordingly, a pressure sensor comprising the electrochemical transistor exhibits the highest sensitivity ever measured ($\sim 10000 \text{ kPa}^{-1}$), which is about 10,000 times higher as compared with capacitive pressure sensors and 100 times higher than resistive sensors. It is postulated that the high sensitivity is caused by that the pressure sensing mechanism being based on an ionic migration for the doping/de-doping of the semiconducting material in the channel. This advantageous pressure sensing mechanism may be due to the employment of the solid polymer electrolyte layer as described herein, causing the ion migration to occur from the solid polymer electrolyte layer for doping/de-doping of the channel upon application of pressure.

[0013] The term “solid polymer electrolyte layer”, as used herein, refers to a layer having a composition wherein an ionic liquid is incorporated into an ionic conductive polymer. The ionic conductive polymer may act in this composition as an electrolyte matrix for an ionic liquid. Optionally, the ionic conductive polymer in the solid polymer electrolyte layer does not

participate in the electrical or ionic conduction mechanisms, but allows for the cations and ions of the ionic liquid to migrate through the solid polymer electrolyte layer.

[0014] As used herein, the term “solid” when used in the phrase “solid polymer electrolyte layer” takes its normal meaning, and therefore includes references to compositions or substances demonstrating (significant) structural rigidity and resistance to changes of shape or volume (e.g. substances which exhibit no flow). In particular, the term “solid” may refer to substances characterised by their resistance to penetration. The term “solid” is understood not to include a hydrogel.

[0015] The solid polymer electrolyte layer may have a first main side and a second main side, wherein the second main side is opposite to the first main side. The first main side and the second main side of the solid polymer electrolyte layer refer to the two largest surfaces of the layer. In particular, a layer typically extends into two directions (perpendicular to each other), while having a thickness in a direction which is perpendicular to the two directions in which the layer extends. The two surfaces that extend into the two directions are referred to herein as the first main side and a second main side. The distance between the two surfaces of the first main side and a second main side may refer to the thickness of the solid polymer electrolyte layer.

[0016] The electrochemical transistor according to the disclosure may be arranged in such a configuration that the solid polymer electrolyte layer is facing (e.g., being in contact with) a gate electrode with a first main side thereof and facing a channel, connecting the source electrode with the drain electrode, with a second main side thereof. The electrochemical transistor of such a configuration may be termed a layered electrochemical transistor, since the solid polymer electrolyte layer divides the channel with the source electrode and the drain electrode from the gate electrode. Such a configuration may also be seen in contrast to an in-plane transistor, wherein the gate electrode, source electrode and the drain electrode are all interconnected in one plane along one extending direction. In contrast, the gate electrode in the transistor disclosed herein is “stacked”, with reference to the source electrode and the drain electrode, due to the solid polymer electrolyte layer being disposed there between, meaning that the gate electrode is perpendicularly arranged to the largest extending direction of the solid polymer electrolyte layer.

[0017] Advantageously, when the electrochemical transistor is arranged in such configuration that the solid polymer electrolyte layer faces a gate electrode with a first main side thereof and faces a channel, connecting the source electrode with the drain electrode, with

a second main side thereof, the layered electrochemical transistor is particularly well suited as a pressure sensor, since a surface area of the gate electrode would be maximized in such a configuration.

[0018] The term “ionic conductive polymer” as used herein refers to a polymer that functions as an electrolyte and may exhibit limited electrical conductivity. The ionic conductive polymer may comprise an organic polymer. The ionic conductive polymer may be selected from a fluoropolymer-copolymer, an organosilicon, polyether and a polyacrylate. In particular, the ionic conductive polymer may be a material formed from vinylene-based, vinylidene fluoride-based, methacrylate-based, ethylene oxide-based, vinyl alcohol-based, ethylene carbonate-based, vinyl pyrrolidone-based monomers. The ionic conductive polymer may be selected from the group consisting of poly(vinylidene difluoride) (PVDF), PVDF-HFP, poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(ethylene carbonate) (PEC), poly(vinyl pyrrolidone) (PVP), a sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion), or a combination thereof.

[0019] The term “ionic liquid” as used herein refers to salts that are liquid over a wide temperature range, including room temperature. The ionic liquid used herein may be an organically based salt. The ionic liquid may further be a monomer, i.e. it does not contain covalently linked repeating units. Preferably, these salts may be, for example, imidazole derivatives and pyridine derivatives. In a preferred embodiment, the ionic liquid may have a dialkylsubstituted imidazole derivative as cation, wherein the alkyl substituents are positioned at the nitrogen atoms. The alkyl substituents may be alkyl units selected from C₁-C₅. In another embodiment, the ionic liquid may have an inorganic cation. The cation may also be selected from 1-ethyl-3-methylimidazolium [EMIM]⁺, 1-butyl-3-methylimidazolium [BMIM]⁺, 1-octyl-3-methyl [OMIM]⁺, 1-decyl-3-methyl-[DMIM], Mg²⁺, Ca²⁺, Zn²⁺, Ni²⁺, Cu²⁺, Pb²⁺, Ba²⁺, or a combination thereof. The anion may be selected from tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), hexafluoroantimonate (SbF₆⁻), nitrate, bisulphate (hydrogen sulphate), tetraphenylborate [B(C₆H₅)₄⁻], dicyanamide [DCA]⁻, thiocyanate, acetate, hexyltriethylborate, nonafluorobutanesulfonate, bis(fluorosulfonyl)imide ([FSI]⁻), bis[(trifluoromethyl)sulfonyl]imide ([TFSI]⁻), tris[(trifluoromethyl)sulphonyl]methide, trifluoroacetate and heptafluorobutylate, as well as anions based on chlorides and other halides of aluminum, copper, manganese, lead, cobalt, nickel or gold, e.g. tetrachloroaluminate (AlCl₄⁻), heptachlorodialuminate (Al₂Cl₇⁻) and tetrachlorocuprate (CuCl₄²⁻ and CuCl₄³⁻),

trifluoromethanesulfonate [OTF]⁻, diethyl phosphate [DEP]⁻, ethyl sulphate [EtOSO₃]⁻, perchlorate [ClO₄]⁻, lactate, halogen anions, for example fluoride, chloride and bromide. In one example, the ionic liquid is [EMIM][TFSI].

[0020] The ionic liquid together with the ionic conductive polymer may form the solid polymer electrolyte layer by being mixed together and molded into a layered shape. This solid polymer electrolyte layer may be characterized in that there is no covalent bond between the ionic liquid and the ionic conductive polymer. Accordingly, the association between the ionic liquid and the ionic conductive polymer may be an attractive interaction that does not involve sharing of electrons, while resulting in adherence of the two materials. For example, such non-covalent interaction may include hydrophobic interaction, hydrophilic interaction, ionic interaction, hydrogen bonding, and/or *van der Waals* interaction.

[0021] According to various embodiments, a weight ratio of the ionic liquid to the ionic conductive polymer may be from 10:1 to 1:30, or from 5:1 to 1:1, or from 5:1 to 1:15, from 4:1 to 1:10, from 3:1 to 1:5, or about 2:1. The range from 5:1 to 1:1 may be working particularly well because of the sufficient ion numbers inside the solid polymer electrolyte layer and its good mechanical behaviors.

[0022] According to various embodiments, the gate electrode may be in contact with a first main side of the solid polymer electrolyte layer. "Being in contact" may refer to a direct contact between the materials.

[0023] According to various embodiments, the channel comprising a semiconducting material may be in contact with a second main side of the solid polymer electrolyte layer.

[0024] While in some embodiments, the solid polymer electrolyte layer may be substantially flat, in other embodiments, the solid polymer electrolyte layer may comprise microstructures. The microstructures may be protruding from a surface of the solid polymer electrolyte layer. Said surface may be on the second main side. Advantageously, the microstructures may enhance the sensitivity of the pressure sensor. In particular, the microstructures may enhance the detection and discrimination of spatiotemporal tactile stimuli such as static and dynamic pressure.

[0025] The average distance between two neighboring microstructures may be between about 0.1 μm and about 1000 μm, or between about 0.2 μm and about 600 μm, or between about 0.3 μm and about 300 μm, or between about 0.4 μm and about 100 μm, or between about 0.5 μm and about 60 μm, or between about 0.8 μm and about 10 μm, or about 1.0 μm to about 5.0 μm. Decreasing the average distance between two neighboring microstructures may be

advantageous in enhancing the pressure sensitivity. On the other hand, increasing the average distance between two neighboring microstructures may be advantageous to broaden the sensing range.

[0026] According to various embodiments, the microstructures may be tapered, e.g. having a narrowing (optionally gradual) towards one end facing away from the solid polymer electrolyte layer. According to various embodiments, the microstructures may be selected from the group consisting of micro-pyramids, micro-domes, micro-pillars, micro-fibers, micro-cones, or a combination thereof. Preferably, the microstructures include micro-pyramids. By using micro-pyramids as microstructures, the contact area between the solid polymer electrolyte and the channel, upon the application of pressure, is progressively increased.

[0027] The electrochemical transistor can be modeled as an ionic circuit consisting of an electrolyte/channel capacitor (C_{CH}), gate/electrolyte capacitor (C_G) and electrolyte resistor (R_E). Under no applied pressure, there is negligible ion penetration from the solid polymer electrolyte layer to the channel since the contact area between the micro-pyramids and the semiconducting material may be minimal (exemplified in **FIG. 13**). This may translate to an impedance mismatch at the tip of the micro-pyramids, thereby limiting the ion flow from the solid polymer electrolyte layer to the channel. In this configuration, the area of the gate electrode of capacitor C_G may be invariable, whereas its opposite electrode area (ΔA), and the distance between these two electrodes, defined by the height of the solid polymer electrolyte layer comprising the micro-pyramids ($\Delta \delta$), may be variable with respect to applied pressure. Therefore, under no pressure load, ΔA is minimum and $\Delta \delta$ is maximum causing the value of effective C_G to be exceptionally low compared to C_{CH} . Hence, the charging is limited by C_G , resulting in negligible change in I_{DS} with respect to V_{GS} . Hence, most of the applied gate voltage may drop at the pyramidal tips of solid polymer electrolyte layer due to the highest impedance, resulting in $C_{CH} > C_G$. Under applied pressure, the effective interface and contact area between solid polymer electrolyte layer with micro-pyramids and channel increases, more ions are induced to transfer from the solid polymer electrolyte layer into the channel under positive gate bias, generating a significant electrochemical switching from highly conducting state to neutral semiconducting state, thus modulating the source-drain current.

[0028] The microstructures may protrude from the surface of the solid polymer electrolyte layer. The microstructures may protrude, measured from the surface of the solid polymer electrolyte layer to the tip of the microstructures, up to a height of 1000 μm , optionally up to a

height of 500 μm , optionally up to a height of 100 μm , optionally up to a height of 30 μm , optionally up to a height of 20 μm , optionally up to a height of 10 μm .

[0029] The solid polymer electrolyte layer may have an approximate thickness in the range of from about 0.1 micrometer (μm) to about 1000 μm , or from about 0.2 μm to about 600 μm , or from about 0.3 μm to about 200 μm , or from about 0.4 μm to about 100 μm , or from about 0.5 μm to about 60 μm , or from about 0.8 μm to about 10 μm , or from about 1.0 μm to about 5.0 μm . The approximate thickness described herein describes the distance from the first main side to the second main side. Advantageously, a thinner solid polymer electrolyte layer may increase flexibility and/or softness of the electrochemical transistor. A solid polymer electrolyte layer including microstructures may have a higher thickness (which includes the height of the microstructures) than a solid polymer electrolyte layer without microstructures. Accordingly, the solid polymer electrolyte layer including microstructures may have a thickness of from about 0.1 μm to 1000 μm , or less than about 1000 μm , or less than about 800 μm , or less than about 500 μm , or less than about 100 μm , or less than about 80 μm , or less than about 50 μm , or less than about 30 μm , or less than about 10 μm .

[0030] The solid polymer electrolyte layer may be disposed on a channel comprising a semiconducting material. The channel may be a pathway for connecting the source electrode with the drain electrode. The channel may comprise, or be filled with, a semiconducting material. The semiconducting material may be an n-type or a p-type semiconducting material. When the electrochemical transistor works in depletion mode, p-type semiconducting materials are used in the channel. When the electrochemical transistor works in accumulation mode, p-type or n-type semiconducting materials are used in the channel. The semiconducting material may be an organic material. In some embodiments, the semiconducting material may be selected from the group consisting of poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), PEDOT:PSS, P3HT, PCDTFBT, fullerene, fullerene derivatives, for example, fullerene derivatives with glycolated side chains, PC₇₀BM, or a combination thereof.

[0031] According to some embodiments, the channel may include an additional additive selected from the group consisting of an additional ionic liquid, ethylene glycol, poly(ethylene oxide), Triton X-100, dimethyl sulfoxide, and x-sorbitol or a combination thereof. Additionally or alternatively, the channel may include additional surfactants, such as GOPS, to reduce the surface energy. The additional ionic liquid may be defined as the ionic liquid comprised in the solid polymer electrolyte layer. Advantageously, when the channel includes an additional additive, this may increase the ionic conductivity.

[0032] In particular, when the semiconducting material is PEDOT:PSS or any derivative thereof, and the additive is an ionic liquid, this combination results in a synergistic effect. Specifically, the anions from an ionic liquid can disrupt the PEDOT:PSS attraction and bring the PEDOT chains together to induce a more closely packed order of PEDOT units and fibrillar morphology, which allows an efficient pathway for hole transport and advantageously provides more interface and surface area for ions penetration and doping/de-doping. In **FIG. 40**, this effect is exemplified with PEDOT:PSS as the semiconducting material that was modified with a water-soluble ionic liquid, namely [EMIM][Cl].

[0033] According to some embodiments, a ratio (WdL^{-1}) of a channel width (W) times channel thickness (d) to a channel length (L) is between about 20 nanometer to about 20000 nanometer, or between about 50 nanometer to about 10000 nanometer, or between about 100 nanometer to about 1000 nanometer, or between about 200 nanometer to about 800 nanometer.

[0034] According to some embodiments, a transconductance of the electrochemical transistor is within about 0.1 milli-Siemens to about 50 milli-Siemens, or within about 0.1 milli-Siemens to about 40 milli-Siemens, or within about 1.0 milli-Siemens to about 20 milli-Siemens, or within about 5.0 milli-Siemens to about 10 milli-Siemens. The transconductance may refer to the current through the output of the electrochemical transistor to the voltage across the input of the electrochemical transistor.

[0035] The channel including the semiconducting material and the solid polymer electrolyte layer may render the source and drain electrode into contact with the gate electrode. A material for each of the electrodes may be independently selected from metals, such as gold, silver, nickel, titanium, platinum. Alternatively, a material for each of the electrodes may be independently selected from conducting polymers including poly(3,4-ethylenedioxythiophene), poly(thiophene)s, polyaniline, polypyrrole. Other materials with high electrical conductivity including carbon, indium tin oxide (ITO), fluorine doped tin oxide (FTO), aluminum oxide-doped zinc oxide (AZO) may also be used. The metal electrodes may be deposited by thermal evaporation. Alternatively, conducting polymers or carbon ink as electrodes may be printed by screen printing or inkjet printing.

[0036] According to various embodiments, the gate electrode may be modified with a non-polarizable layer, comprising a non-polarizable material. "Non-polarizable", as used herein, may refer to a material that may cause no, or very minor, charge separation at the electrode-electrolyte boundary. In other words, a Faradic current may freely pass through the system and

the electrode reaction may be very fast. A conventional example for a non-polarizable electrode would be a silver/silver chloride electrode. The meaning of the term “non-polarizable” is contrasted herein with “polarizable”. A polarizable material may refer to a material that may cause charge separation at the electrode-electrolyte boundary. In other words, no Faradic current, or only very little, may pass through the system and the electrode reaction may be very slow. A conventional example for a polarizable electrode would be a platinum electrode.

[0037] The non-polarizable layer may be facing the first main side of the solid polymer electrolyte layer. The non-polarizable material may comprise a conducting polymer, e.g. PEDOT:PSS, or carbon, or composite materials, e.g. Ag/AgCl. The non-polarizable material may additionally comprise a further additive including a further additional ionic liquid, e.g. [EMIM][Cl], or an adhesive agent, e.g. (3-glycidyloxypropyl)trimethoxysilane (GOPS), or a modifier, e.g. ethylene glycol. The further additional ionic liquid may be defined as the ionic liquid comprised in the solid polymer electrolyte layer.

[0038] According to various embodiments, the source electrode and the drain electrode are disposed on a substrate. The substrate may include silicon oxide, glass, quartz, polymers, metal foil, cellulose, or a combination thereof. Where it is necessary to have a flexible electrochemical transistor, flexible substrates may also be used, selected from the group consisting of polyimide, polyethylene terephthalate, parylene-C, polydimethylsiloxane (PDMS), polyethylene naphthalate, paper, cellulose, polyacrylonitrile, or a combination thereof.

[0039] According to various embodiments, a flexible layer including an organic layer is disposed on a side of the gate electrode that is not facing the solid polymer electrolyte layer. Said flexible layer may be used for encapsulation. Accordingly, disposing a flexible layer including an organic layer on a side of the gate electrode that is not facing the solid polymer electrolyte layer, or using said flexible layer as an encapsulation of the electrochemical transistor, may increase long-term stability of the electrochemical transistor. The organic layer may be selected from the group consisting of polyimide, polyethylene terephthalate, parylene-C, polydimethylsiloxane, polyethylene naphthalate, cellulose, polyacrylonitrile, carbon paper or a combination thereof. The thickness of the encapsulation layer may be about 0.1 μm to about 10 μm , or about 1 μm to about 5 μm .

[0040] In a second aspect, there is provided a process for making an electrochemical transistor. The process may include providing a first transistor part including a source electrode and a drain electrode disposed on a substrate, and a channel connecting the source electrode

with the drain electrode; wherein the channel includes a semiconducting material. The process may include providing a second transistor part including providing a solid polymer electrolyte layer including an ionic conductive polymer and an ionic liquid incorporated into the ionic conductive polymer; and disposing the solid polymer electrolyte layer on a gate electrode. The process may include assembling the electrochemical transistor by disposing the second transistor part on the first transistor part such that the solid polymer electrolyte layer is on one side facing the gate electrode and on the other side facing the channel comprising the semiconducting material.

[0041] The process may include a step of providing the solid polymer electrolyte layer by mixing the ionic conductive polymer and the ionic liquid, optionally in a solvent. The ionic liquid may be dry before the addition. Said differently, the ionic liquid may be pre-dried before usage.

[0042] According to various embodiments, the solvent may have a boiling point below 120 °C. Hence, the solvent may be selected from the group consisting of acetone, chloroform, ethanol, tetrahydrofuran, toluene, water, isopropanol, dichloromethane, ethyl acetate, diethyl ether, or a combination thereof. The amount of ionic conductive polymer to the solvent required may vary depending on the ionic conductive polymer and the solvent used. As an example, a mass ratio of ionic conductive polymer to solvent may range from 1:4 to 1:20, or 1:6 to 1:10, such as 1:7.

[0043] By “mixing” is meant contacting one component with another component. The mixing step may involve dissolving one or both components in the solvent. As used herein, the term “dissolved” refers to a state where none of the substance being dissolved is visible as a solid in the solution. The order of mixing the components is dissolving the ionic conductive polymer in the solvent before adding the ionic liquid. The solution obtained after mixing may be allowed to stand substantially without agitation (e.g. no active stirring step was conducted). Advantageously, such process step may improve the quality of the solid polymer electrolyte layer by decreasing the amount of bubbles (air) in the solution obtained after mixing.

[0044] According to various embodiments, the solution obtained after mixing may be deposited on a substrate. The deposition may include dip-coating, drop-casting, spin-coating, screen printing, inkjet printing or spray printing. Hence, the solid polymer electrolyte layer may be formed by at least one method selected from the group consisting of: spin-coating, screen-printing, and inkjet-printing. For example, spin-coating may be carried out, optionally

at 1500 rpm for 60 s. After the deposition, the obtained solid polymer electrolyte layer may be dried.

[0045] The solid polymer electrolyte layer may be formed by being spin-coated on a template. In other words, the deposition may include depositing the solution obtained after mixing on a template (e.g., a mold). The template may comprise a pattern. The pattern may be the template for the microstructures. Accordingly, using a templating method and drying the obtained solid polymer electrolyte layer may result in the solid polymer electrolyte layer to comprise microstructures.

[0046] In a third aspect, there is provided a pressure sensor including the electrochemical transistor as defined above or obtained from a process of as defined above.

[0047] In a further aspect, the present disclosure refers to an electrochemical transistor. The electrochemical transistor may include a solid polymer electrolyte layer. The solid polymer electrolyte layer may include an ionic conductive polymer. The solid polymer electrolyte layer may include an ionic liquid incorporated into the ionic conductive polymer. The electrochemical transistor may include a gate electrode. The electrochemical transistor may further include a source electrode. The electrochemical transistor may include a drain electrode. The electrochemical transistor may include a channel. The channel may include a semiconducting material. The solid polymer electrolyte layer may connect the gate electrode with the channel. The channel may connect the source electrode with the drain electrode. The gate electrode may be modified with a non-polarizable layer (e.g. including PEDOT:PSS). The non-polarizable layer may be disposed between the gate electrode and the solid polymer electrolyte layer. Materials used for the solid polymer electrolyte layer, the channel, the semiconducting material, the non-polarizable layer and the electrodes may be the same as those described for the first aspect.

[0048] As described for the solid polymer electrolyte layer of the first aspect, the solid polymer electrolyte layer may have a first main side and a second main side. According to various embodiments illustrated in FIG. 42, the gate electrode may be facing the second main side of the solid polymer electrolyte layer. The semiconducting material may be facing the second main side of the solid polymer electrolyte layer. In other words, in these embodiments, the gate electrode may be disposed in a coplanar arrangement with the source electrode and the drain electrode. Such a configuration may be considered as an in-plane transistor, wherein the gate electrode, source electrode and the drain electrode are all interconnected in one plane along one extending direction.

[0049] There is also provided a process for making an electrochemical transistor with a coplanar arrangement. The process may include providing a substrate and disposing a source electrode and a drain electrode disposed on the substrate. The process may include disposing a channel connecting the source electrode with the drain electrode on the substrate; wherein the channel includes a semiconducting material. The process may include disposing a gate electrode on the substrate. The source electrode, drain electrode, channel and gate electrode may be disposed on the substrate in a coplanar arrangement. The process may include disposing a solid polymer electrolyte layer including an ionic conductive polymer and an ionic liquid incorporated into the ionic conductive polymer on the coplanar arrangement of the source electrode, drain electrode, channel and gate electrode. Additionally or alternatively, the process may include providing a first transistor part including a source electrode and a drain electrode disposed on a substrate, and a channel connecting the source electrode with the drain electrode; wherein the channel includes a semiconducting material. The process may include providing a second transistor part including providing a solid polymer electrolyte layer including an ionic conductive polymer and an ionic liquid incorporated into the ionic conductive polymer; and disposing the solid polymer electrolyte layer on a gate electrode. The process may include assembling the electrochemical transistor by disposing the second transistor part on the first transistor part such that the solid polymer electrolyte layer faces both the gate electrode and the channel comprising the semiconducting material on the same side. The process may involve that the source electrode and the drain electrode together with the channel are only provided on a part of the substrate. The process may also involve that the whole gate electrode or only a part of the gate electrode is disposed on the solid polymer electrolyte layer. Hence, when the first transistor part is assembled with the second transistor part, the gate electrode may be disposed such that it faces the substrate, without facing the source electrode and the drain electrode together with the channel. Likewise, the source electrode and the drain electrode together with the channel may be facing the solid polymer electrolyte layer without facing the gate electrode. Such a process may result in an electrochemical transistor as shown in FIG. 42.

[0050] By “about” in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[0051] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or

combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments. In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0052] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

EXAMPLES

[0053] Some embodiments of this disclosure are directed to a solid polymer electrolyte exhibiting high ionic conductivity and high mechanical strength. Examples of such ionic conductive solid polymer electrolyte can facilitate good electrochemical response in ion-permeable conjugated polymers. Other examples of different conjugated polymers and small molecules may be used as active channel materials for the OECT of the disclosure. Examples of these conjugated polymers and small molecules are used herein to further assess the use of solid polymer electrolytes.

[0054] Ionic-electronic coupling across the entire volume of conjugated polymer films endows OECTs with high transconductance and low operating voltage. However, OECTs utilize liquid electrolytes, which limit their long-term operation, reproducibility, and integration while solid electrolytes typically result in inefficient ion transport. In one embodiment, a solid polymer electrolyte is present to facilitate good electrochemical response in conjugated polymers and yield high OECT performance. This allows for the OECT based pressure sensors, modulated through a pressure sensitive ionic doping process. The pressure sensor exhibits the highest sensitivity ever measured ($\sim 10000 \text{ kPa}^{-1}$) and excellent stability. Flexible sensor arrays realize a static capture of spatial pressure distribution and enable monitoring of dynamic pressure stimuli. The examples demonstrate that all-solid-state OECTs are good candidates for providing rich tactile information, enabling applications for soft robotics, health monitoring and human-machine interfaces.

[0055] Traditional OECTs operate in liquid electrolytes, resulting in some limitations such as the long-term operation, reproducibility, scalability and integration. A shift to the utilization of solid polymer electrolytes is essential to solve these limitations. The device architecture of an all-solid-state OECT includes an active conjugated polymer as the channel, with the source and drain metal electrodes and the solid polymer electrolyte on top of the channel layer (**FIG. 1**).

[0056] Blending of ionic liquids with ionic conductive polymer to form a chemically or physically crosslinked network with excellent mechanical properties is an efficient method to construct solid polymer electrolyte. This polymeric electrolyte system should be solvent-free during operation, and the conduction mechanisms are directly tied to interactions between the ions and polymer matrix, retaining a large fraction of the ionic conductivity. The solid multivalent ionic conductive polymers, including homopolymers, PEO, PVA, PVDF and their blend copolymers, PVDF-co-HFP, poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-co-TrFE) are possible choices as these polymers can be easily processed to build uniform films and 3D framework with high flexibility and robustness. Other homopolymers and/or copolymers with backbone chain comprising repeating ion-coordinating functional groups may be used as the ionic conductive polymer. For example, backbone chains comprising oxygen such as in ether group, alkoxy group and carbonyl group. Other examples include backbone chains having carbonate side group and ester side group. Further examples include backbone chains having (poly)ester group, nitrile group, pendant hydroxyl group and carbon-fluorine group. PEO as a polymer host shows enhanced ionic conductivity for solid polymer electrolyte system, because of the highly percolated network connecting nearby solvation sites for the ionic motion. The PVDF-co-HFP copolymer network with high chain dipole moment can interact with mobile ionic liquid to form an elastomeric ionic gel with great physical robustness and allow ion migration freely under applied electric field (**FIG. 2**). Other polymers such as PEC and PVP can coordinate with divalent salts (Mg^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Ba^{2+}) of the ionic liquid via their carbonyl oxygen. Control of the ionic concentration in polymers can induce strong and conformal adhesion on three-dimensional surface. Other ionic sources with weak binding affinity and good plasticizing ability for the polymer backbone are also appropriate for this system such as $[\text{EMIM}]^+$, $[\text{BMIM}]^+$, $[\text{FSI}]^-$, $[\text{TFSI}]^-$, dicyanamide ($[\text{DCA}]^-$), hexafluorophosphate ($[\text{PF}_6]^-$), tetrafluoroborate ($[\text{BF}_4]^-$), ClO_4^- , Cl^- . The mentioned anions and cations can be combined with each other freely to form ionic liquids, such as $[\text{EMIM}][\text{TFSI}]$, $[\text{BMIM}][\text{PF}_6]$, $[\text{EMIM}][\text{DCA}]$, etc.

[0057] **Example 1: Synthesis of solid polymer electrolyte**

[0058] Firstly, copolymer PVDF-co-HFP was dissolved in acetone (110 mg/ml) and followed by vigorous stirring at room temperature for 12 hours. Then, the pre-dried ionic liquid $[\text{EMIM}][\text{TFSI}]$ was added into the above solution with a weight ratio of 1:2 and followed by vigorous vibration for 30 minutes. After the removal of bubbles in solution by standing still,

the prepared solution was spin-coated on a smooth surface to fabricate the solid polymer electrolyte at 1500 rpm for 60 s. Then the film on substrate was transferred into the vacuum oven to remove the solvent under 70 °C for 24 hours. The obtained solid polymer electrolyte could be peeled off from the substrate and used to assemble the OECT device.

[0059] **Example 2: Synthesis of all-solid-state OECT**

[0060] The polyimide substrate was pre-cleaned in a sonicated bath using soap water, deionized water, acetone and ethanol one after another. The cleaned substrate was deposited with source and drain electrodes (Ni/Au, 10/90 nm) using a shadow mask by thermal evaporation. A thin layer of PMMA (5 wt.% in toluene) was spin-coated on the substrate as a sacrificial layer and then irradiated with ultraviolet-ozone (UVO) through a shadow mask for 2 hours to pattern the channel. To prepare the active channel solution, the PEDOT:PSS aqueous solution was filtered by 0.45 µm hydrophilic PVDF filters and then mixed with [EMIM][Cl] (14.662 mg/ml) and GOPS (0.5 wt.%), followed by a magnetic stirring for 1 hour. Then the solution was spin-coated onto the patterned PMMA substrate at 4000 rpm for 40 s, followed by annealing at 140 °C for 20 mins. After that, the device was dipped into toluene for 20 s and rinsed with DI water to remove the PMMA layer. To prepare the gate electrode, 100 nm gold (Au) was deposited on polyimide film and was then modified by non-polarizable PEDOT:PSS/[EMIM][Cl] film instead of conventional Ag/AgCl pellet. Then, the solid polymer electrolyte was transferred onto the gate electrode and the all-solid-state device was assembled as an architecture of PI/gate electrode/solid polymer electrolyte/channel/source-drain electrodes/PI.

[0061] For P3HT-based OECTs, pristine P3HT was dissolved in analytical grade chloroform, respectively, followed by magnetic stirring at 50 °C for 30 mins. The active channel layers were prepared by spin-coating on the source-drain electrodes at 3000 rpm for 30 s using the above solutions. The channel thickness of the P3HT film was controlled by varying the concentration from 1 mg/ml to 10 mg/ml. The solution preparation and spin-coating were carried out in a N₂ glovebox. The transfer of solid polymer electrolyte and lamination with gate electrode were similar with the process to fabricate PEDOT:PSS-based OECTS.

[0062] **Example 3: Device characterization**

[0063] The output and transfer characteristics and other electrical properties were tested by Keysight Precision Source/Measure Unit (B2900A Series) and a probe station (Karl Suss PM5). For the measurement of UV-VIS Spectroelectrochemistry, the PEDOT:PSS solution was spin-coated on ITO glass substrates in air and subsequently annealed at 140 °C for 20 mins.

The P3HT film on ITO glass was prepared in glovebox. Then the solid polymer electrolyte with/without pyramids was transferred onto the ITO glass to cover the PEDOT:PSS or P3HT film, followed by the encapsulation of another ITO glass which acted as gate electrode. A Keysight precision source/measure unit (B2912A) was chosen to apply biasing between gate electrode and ITO glass. The absorption spectra were recorded using a UV-vis-NIR spectrophotometer (SHIMADZU, UV-3600) over the wavelength range from 300-1500 nm as sample was biased.

[0064] **Example 4: Performance results of all-solid-state OECTs**

[0065] Firstly, demonstration is made of the prototypical PEDOT:PSS as the organic conducting materials in channel (i.e. active channel). In this example, ionic liquid additive ([EMIM][Cl]) was introduced in the PEDOT:PSS system to achieve better electronic and ionic transport properties in OECTs (**FIG. 4**). The anions from the ionic liquid could disrupt the PEDOT:PSS attraction and bring the PEDOT chains together to induce a more closely packed order of PEDOT units and fibrillar morphology, which allowed an efficient pathway for hole transport and provided more interface and surface area for ions penetration and doping/de-doping. In this example, the PEDOT:PSS solution was modified with a water-soluble ionic liquid, namely, 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]), and GOPS as surfactant to reduce surface energy. In this example, the PEDOT:PSS/[EMIM][Cl] active channel has a thickness (d) of ~ 68.97 nm with a width/length (W/L) of $1000\text{ }\mu\text{m}/200\text{ }\mu\text{m}$.

[0066] In the case of PEDOT:PSS channel, the OECT was conducting at zero gate bias owing to the highly doped PEDOT⁺ state, and could be switched off at positive gate voltages, exhibiting a depletion mode of operation. The transfer and output characteristics of the PEDOT:PSS based all-solid-state OECT (**FIG. 5A and FIG. 5B**) demonstrated that the decrease in drain current (I_D) upon the application of a positive gate bias (V_G) was consistent with the injection of [EMIM]⁺ cations from the polymer electrolyte into the PEDOT:PSS film, to reduce the conducting PEDOT from highly conducting state to neutral semiconducting state. The device shows a high peak transconductance (g_m) of ~ 2.8 mS at $V_G = 0.15$ V and a desirable on/off ratio of $\sim 10^3$ at $V_D = -0.5$ V. For device using pristine PVDF-co-HFP (without [EMIM][TFSI]), no transistor characteristics could be observed under low gate biasing, thus proving that the ions are responsible for the electrochemical doping effect. As a result of the entire volumetric doping process with mobile ions, the transconductance (g_m) increased proportionally to the channel geometry (Wd/L) (**FIG. 5C**). The large transconductance and low voltage operation make the all-solid-state OECT device ideal ion-to-electron transducers. The

rise time for the all-solid-state OECT is calculated to be 3.87 ms from the transient response, which is only slightly slower but within similar timescales to that of NaCl aqueous electrolyte (~ 0.5 ms) and ionic liquid electrolyte (~ 1.1 ms) based OECTs. These results indicate that the use of PVDF-co-HFP polymer electrolyte has sufficient ion mobility to allow fast doping and dedoping of the channel. Notably, when compared to reported solid-state OECTs, the response speed is significantly faster (~ 46 ms to ~ 1.82 s).

[0067] The solid polymer electrolyte can also support OECT operation at high temperatures (for example, 100°C in ambient atmosphere) in which conventional liquid electrolytes would have evaporated, and it was observed that both I_D and g_m remain unaffected (**FIG. 6A** and **FIG. 6B**). The OECTs with PVDF-HFP/[EMIM][TFSI] polymer electrolyte also operate well after multiple lamination and delamination processes, which therefore allows reuse and extends practical applications (**FIG. 6C**).

[0068] To further assess the use of PVDF-co-HFP polymer as a solid polymer electrolyte, OECTs with 2 other p-type conjugated polymers, P3HT and PCDTFBT as well as n-type PC₇₀BM molecule were fabricated. In the case of all solid-state P3HT-based OECT, the transfer characteristic also showed a low gate operation (< -1.3 V), high on/off ratio ($\sim 5 \times 10^5$) and large g_m of ~ 4.62 mS at $V_G = -1$ V and $V_D = -0.5$ V (**FIG. 7**). The current modulation with gate voltage was consistent with an accumulation mode operation where the current increases with increasing V_G . When a negative bias was applied to the gate, the [TFSI]⁻ anions penetrate the P3HT semiconductor layer, resulting in an increase in the channel current. A linear correlation was found between g_m and channel geometry, proving that the mechanism for P3HT-device is electrochemical doping by anions, with more anions in the polymer inducing more holes in the channel. A slow rise time (~ 0.95 s) was obtained for anion doping in P3HT.

[0069] Moreover, another library of materials such as PCBM, PCDTFBT as channel for the all-solid-state OECT were also tested (**FIG. 8** and **FIG. 9**). These devices also showed a low operating gate biasing (< -1 V for p-type and < 1 V for n-type), a high transconductance, and a linear correlation between g_m and channel geometry. The results demonstrated that the solid polymer electrolyte is a universal choice for various p-type or n-type conjugated polymers and small molecules to construct all-solid-state OECT.

[0070] The spectro-electrochemical response of the films to gain insights on the operation of the device were further investigated. The change in optical absorption spectra of the PEDOT:PSS and P3HT films interfaced with the solid polymer electrolyte under biasing was monitored (**FIG. 10**). For PEDOT:PSS, upon application of positive voltage at $V_g = +0.5$ V, the

film switches from oxidized to neutral state since the injected cations from the electrolyte dedope PEDOT. As a result, a new absorption peak between 650 nm and 700 nm was observed, which is attributed to the π - π^* transition of neutral PEDOT, while the intensity of the polaronic and bipolaronic optical transitions at near IR region decreased correspondingly. The intensity of the new absorption feature increased while the intensity of initial polaron-induced transition decreased with higher positive gate voltages, consistent with the depletion mode in PEDOT:PSS based OECT.

[0071] For P3HT, at 0 V, its neutral state exhibits an absorption band in the visible region from ~350 nm to ~700 nm, corresponding to π - π^* transitions. With increasing negative bias, the first oxidation state of P3HT is initiated, and appears as an increase in absorption band centered at ~800 nm with a concurrent decrease in the neutral absorption band with an isosbestic point at ~624 nm. Beyond -0.7 V bias, a second oxidation state is initiated, emerging as an absorption band beyond 1000 nm. This is in agreement with accumulation of charges in the P3HT layer through the [TFSI]⁻ anion doping effect. Further, the electrochemistry was fully reversible.

[0072] **Example 5: All-solid-state OECT based soft tactile sensor**

[0073] There are therefore many combinations of conjugated polymers, ion-coordinating polymers (also referred to as ionic conductive polymers), ionic liquids and solid polymer electrolyte microstructures that would allow the development of higher performing all-solid-state OECTs for tactile perception in soft robotic applications.

[0074] The architecture of the all-solid-state OECT-based pressure sensor includes source-drain electrodes, gate electrode, active channel, substrate and solid polymer electrolyte with microstructures (**FIG. 11**). Here, the solid polymer electrolyte comprises ionic conductive polymer (PVDF-co-HFP) and ionic liquid ([EMIM][TFSI]). The incorporation of microstructures on the surface of the solid polymer electrolyte as pressure-sensing component enhanced the detection and discrimination of spatiotemporal tactile stimuli such as static and dynamic pressure.

[0075] The microstructures on solid polymer electrolyte could be realized by the facile nano-imprinting technique or template method, easily forming various kinds of microstructures, such as micro-pyramids, micro-pillars, micro-dome and hierarchical structure. For example, using template method, the PVDF-co-HFP/[EMIM][TFSI] mixed solution in acetone was spin-coated on a micro-pyramidal silicon mold to fabricate the patterned solid polymer electrolyte at 1500 rpm for 60 s. Then the film on mold was transferred into the vacuum oven to remove

the solvent under 70 °C for 24 hours. The obtained solid polymer electrolyte with microstructures could be peeled off from the molds and used to assemble the OECT-based tactile sensors (**FIG. 12C and FIG. 12D**). The SEM images of the solid polymer electrolyte revealed that the shape of each pyramids holds a square base with a length of 10.5 μm , and tapered to a tip with a height of 8.0 μm (**FIG. 12A and FIG. 12B**). Generally, the pyramidal structures may have a dimension (length, width, height) ranging from 1 μm to 100 μm for tactile sensors. The distance between two pyramidal structures may range from 1 μm to 100 μm .

[0076] The following examples describe specific aspects of some embodiments of this disclosure to illustrate and provide a description for those of ordinary skill in the art. The examples should not be construed as limiting this disclosure, as the examples merely provide specific methodology useful in understanding and practicing some embodiments of this disclosure.

[0077] **Example 6: PEDOT:PSS based all-solid-state OECT working in depletion mode for soft tactile sensor**

[0078] According to Bernards model, the OECT can be modeled as an ionic circuit consisting of an electrolyte/channel capacitor (C_{CH}), gate/electrolyte capacitor (C_{G}) and electrolyte resistor (R_{E}). Under no applied pressure, there is negligible ion penetration from the solid electrolyte to the PEDOT:PSS channel since the contact area between the electrolyte pyramids and polymer is minimal (see **FIG. 13**). This is translated to a huge impedance mismatch at the tip of the pyramidal structure, thereby limiting the ion flow from the electrolyte to the channel. In this configuration, area of the top electrode of capacitor C_{G} is invariable, whereas its opposite electrode area (ΔA), and the distance between these two electrodes, defined by the height of the pyramidal solid electrolyte ($\Delta\delta$), are variable with respect to applied pressure. Therefore, under no pressure load, ΔA is minimum and $\Delta\delta$ is maximum causing the value of effective C_{G} to be exceptionally low compared to C_{CH} . Hence, the charging is limited by C_{G} , resulting in negligible change in I_{DS} with respect to V_{GS} . Hence, most of the applied gate voltage dropped at the pyramidal tips of solid polymer electrolyte due to the highest impedance, resulting in $C_{\text{CH}} > C_{\text{G}}$. Under applied pressure, the effective interface and contact area between solid polymer electrolyte with micro-pyramids and channel increased, more EMIM⁺ ions were induced to transfer from electrolyte into channel under positive gate bias, generating a significant electrochemical switching from highly conducting state to neutral semiconducting state, thus modulating the source-drain current. In this case, the solid polymer

electrolyte was activated like the nanochannel of mechanoreceptors in human skin, inducing an ion-squeezing effect from the mechanical loads.

[0079] **Device characterization**

[0080] The output and transfer characteristics and other electrical properties were tested by Keysight Precision Source/Measure Unit (B2900A Series) and a probe station (Karl Suss PM5). For the pressure measurement, a highly configurable force tester (ESM 303, Mark-10 Corporation) with a force gauge (Mark-10 025/012) for tension and compression measurement applications were used to apply an external pressure. The instrument can carry out a dynamic pressure measurement at adjustable speeds of 0.5-1100 mm/min. For the stability test, a piece of elastic PDMS with a contact area of $\sim 1 \times 1 \text{ cm}^2$ was attached on the pressing tip of force gauge to provide a buffer force and used to calculate the applied pressure.

[0081] **Performance results of PEDOT:PSS-based soft tactile sensor**

[0082] The transfer characteristics at $V_D = -0.5 \text{ V}$ revealed that the source-drain current changes significantly in response to different pressures, indicating successful detection of pressure stimuli (**FIG. 14**). In the absence of pressure loading, the OECT showed negligible current change, where a high drain current of more than 1.8 mA was observed due to the low resistance of the intrinsic PEDOT:PSS channel.

[0083] The leakage current (I_{GS}) increased with increasing applied pressure (**FIG. 15**) at a constant gate voltage, which implied the increase in ion migration events to the channel. Therefore, it can be postulated that the pressure sensing mechanism was based on the ionic migration for the doping/de-doping of conjugated polymer in the active channel, unlike the other existing types of pressure sensors.

[0084] Under applied pressure of 15 kPa and for continuous pulse test, source-drain current was monitored under a periodical variation of V_G between -0.6 V to 0.6 V with a pulse width of 0.5 s. The device shows stable on- and off-state I_{DS} values (maintained $\sim 90\%$ of I_{on}/I_{off}) upon successive V_G pulse for 1000 cycles, implying a negligible performance degradation (**FIG. 16**). The results present a highly reversible ion doping/de-doping process in all-solid-state OECT operation.

[0085] To characterize the performance of the all-solid-state OECT-based pressure sensor, the sensitivity (S) is defined as: $S = (\Delta R/R_0)/\Delta P$, where R_0 is the initial source-drain resistance under no pressure, ΔR is the variation of source-drain resistance after loading pressure, ΔP is the variation of the applied pressure. By deriving the slope of calibration curve in linear sensing

regions, the sensitivity is obtained to be $\sim 71.9 \text{ kPa}^{-1}$ in high pressure region (5-15 kPa) with bias condition of $V_D = -0.6 \text{ V}$ and $V_G = 0.6 \text{ V}$ (**FIG. 17A**).

[0086] The different sensitivity in different pressure regimes represented different deformation stages of micro-pyramids with pressure. In low pressure region ($< 4 \text{ kPa}$), the sensing mechanism in this region can be owing to the increase of contact points between the tip of micro-pyramidal electrolyte and active channel layer (**FIG. 17B**). However, in high pressure region ($> 5 \text{ kPa}$), the interface of micro-pyramids and channel layer turned from point-to-face contact to face-to-face contact (**FIG. 17D**), which gave rise to a dramatic increase of available pathways for ions migration, thus achieving the highest sensitivity of $\sim 71.9 \text{ kPa}^{-1}$. For pressures beyond 15 kPa, the micro-pyramidal shape tended to a flat plane due to the almost entire compression, and the contact area reached its maximum limitation.

[0087] Compared with previous FET-based pressure sensors, the operating voltage in this example is substantially lower, which is significant for practical application. In addition, the limit of detection of the OEET-based pressure sensor was performed at $V_D = -0.6 \text{ V}$ and $V_G = 0.6 \text{ V}$ by placing a flower ($\sim 11 \text{ mg}$, 1.1 Pa) and a grain of rice ($\sim 20 \text{ mg}$, 2.0 Pa) on the sensor to test the signal response (**FIG. 18A**). The results exhibit the limit of pressure that can be measured as low as 1.1 Pa and the sensing to very low pressure presents good repeatability.

[0088] The stability over time is a key parameter for organic electronic devices in the practical applications. The source-drain current showed no obvious degradation under different pressure over almost 70 days, confirming a high operational stability of the solid-state OEETs (**FIG. 18B**). To further investigate the repeatability and stability of device, a continuously cyclic stability test was performed under 10 kPa over 300 cycles and showed a retention of 80.6% (**FIG. 18C**). Despite the slight performance degradation, the device could still work well at low operating voltage of $V_D = -0.5 \text{ V}$, $V_G = 0.6 \text{ V}$. The solid polymer electrolyte also remained intact and showed no significant microstructure deformation after cyclic pressures (**FIG. 18D**). The good reproducibility and durability of this OEET-based pressure sensor indicated a potential candidate in flexible electronics.

[0089] **Example 7: P3HT based all-solid-state OEET working in accumulation mode for soft tactile sensor**

[0090] In another embodiment, an unprecedentedly higher sensitivity at both high and low pressure regimes could be observed when the OEET operated in the accumulation mode using P3HT as active channel polymer.

[0091] **Device characterization**

[0092] The output and transfer characteristics and other electrical properties were tested by Keysight Precision Source/Measure Unit (B2900A Series) and a probe station (Karl Suss PM5). For the pressure measurement, a highly configurable force tester (ESM 303, Mark-10 Corporation) with a force gauge (Mark-10 025/012) for tension and compression measurement applications were used to apply an external pressure. The cyclic voltammetry measurements of the films were recorded using a potentiostat/galvanostat (Autolab, PGSTAT302N, Metrohm). The working electrode was a P3HT film with various geometries cast on top of an ITO-coated substrate.

[0093] In this example, P3HT based OECT and the pressure sensing is also modulated by the micro-structured solid polymer electrolyte. The loading pressure could open the pathways for the migration of the $[\text{TFSI}]^-$ anions from solid polymer electrolyte to the P3HT channel, thus a large number of holes were induced under the effect of doped anions in the entire volumetric polymer (**FIG. 19**).

[0094] The electrochemical doping process with applied pressure was also monitored through in-situ spectro-electrochemistry. There was no change in the absorption spectrum while adjusting the gate bias (from 0.1 V to -1.4 V) before applying pressure and an obvious difference was observed after applying pressure (**FIG. 20**). The P3HT could be completely and reversibly doped at -1.4 V, with a decline of peak of absorption spectrum between 500 and 550 nm and rise of peak between 700-900 nm. The results demonstrated that the applied pressure and gate bias both induce electrochemical doping effect in P3HT.

[0095] The transfer and output characteristics exhibited a dramatic increasing of $-I_{\text{ds}}$ with the increase of applied pressure from 0 to 15 kPa (**FIG. 21A**). The sensitivity was up to 10828.2 kPa^{-1} in the very low pressure regime ($< 100 \text{ Pa}$), 5468.3 kPa^{-1} in the pressure regime (0.1-5 kPa) and 1671.2 kPa^{-1} in the pressure regime above 5 kPa, which is, to the author's knowledge, the highest ever reported sensitivity.

[0096] The volumetric capacitance (C^*) of P3HT film could be estimated from the slope of the film capacitance vs. volume plot. Here the C^* using solid polymer electrolyte without microstructures was achieved to be $\sim 35.86 \text{ F/cm}^3$. At high pressures ($> 15 \text{ kPa}$), when the contact area between the electrolyte and P3HT was maximised, the volumetric capacitance (C_{P}^*) approached the volumetric capacitance of P3HT film using a planar solid polymer electrolyte (without microstructures) (**FIG. 22**), indicating efficient pressure induced doping.

[0097] The performance of the all-solid-state OECT-based pressure sensors hold the highest reported sensitivity, while operating only at low voltages ($V_{\text{d}} = -0.5 \text{ V}$ and $V_{\text{G}} = -1.3 \text{ V}$), which

is almost a factor of 100 smaller than OFET-based devices and therefore beneficial for various wearable electronic applications. In addition, the power consumption was as low as $<1 \mu\text{W}$ - 1 mW from 15 kPa pressure to no-pressure loading state ($I_D < 2 \mu\text{A}$ - 1.8 mA ; $V_D = 0.5 \text{ V}$, $V_G = 0.6 \text{ V}$) for depletion mode PEDOT:PSS device. For accumulation mode P3HT device, the ultralow power consumption of $< 28 \text{ nW}$ at no-pressure loading can be achieved ($I_D < 56 \text{ nA}$; $V_D = -0.5 \text{ V}$), while the power consumption at 15 kPa pressure can be varied from $<5 \mu\text{W}$ - 1.1 mW with $V_G = -0.3$ - 1.3 V ($I_D < 9.6 \mu\text{A}$ - 2.2 mA ; $V_D = -0.5 \text{ V}$). The few μW in power consumption is several dozen times lower than that of reported transistor-type pressure sensors ($< 1 \text{ mW}$; $I_D = 10 \mu\text{A}$, $V_G = -100 \text{ V}$) and piezoresistive-type pressure sensors ($< 0.5 \text{ mW}$).

[0098] **Application of soft tactile sensor in health monitoring**

[0099] The OECT-based sensors are able to show a large tunable sensitivity range through the modulation of gate bias (**FIG. 23A**). For instance, the pressure sensitivity for PEDOT:PSS device changed from 4.47 kPa^{-1} to 2.18 kPa^{-1} to 0.59 kPa^{-1} as the V_G was changed from 0.55 V to 0.5 V and to 0.4 V respectively. Similarly, the electrical signal response to same pressure level can be tuned with applied gate bias (**FIG. 23B**).

[00100] By selecting different gate voltages to tune various sensitivity of the pressure sensor, typical pulse pressure waveforms with clearly distinguishable peaks were achieved and the heart rate of the volunteer was calculated to be 72 bpm (beats per minute) (**FIG. 24B**). The flexible pressure sensors are useful for precise detection of the wrist artery pulse (**FIG. 24C**) with the characteristic peaks (P1, P2, P3) which represent percussion wave, tidal wave, and diastolic wave, clearly distinguishable from the enlarged curve. Generally, the radial augmentation index $AI_r = P2/P1$ and $\Delta T_{DVP} = T_{P2} - T_{P1}$ can reflect arterial stiffness, which are highly related to human health. The average value of $P2/P1$ and ΔT_{DVP} are calculated to be ~ 0.52 and $\sim 250 \text{ ms}$, respectively, which is consistent with a healthy adult-male status. The ability to tune sensitivity can allow selection of conditions such that noise does not cause interference. The advantage of the tunable sensitivity is apparent when the pulse signals are monitored under environmental interference of continuous air flow from human breath. To assess this ability, the device with high sensitivity at $V_G = 0.6 \text{ V}$ exhibited messy pulse signals, while good signals were obtained for device with relatively low sensitivity at $V_G = 0.4 \text{ V}$ (**FIG. 24D**).

[00101] **Application of soft tactile sensor arrays**

[00102] Having established the basic processing parameters for high resolution sensor arrays patterning, a flexible pressure sensor array consisting of 6×6 pixels was fabricated to realize a

capture of spatial and temporal pressure information distribution. The device array was made with a similar architecture as the above pressure sensor unit and each pixel acted as an electrically independent sensor due to the non-electrical crosstalk (**FIG. 25**).

[00103] The highly flexible 6×6 device array was fabricated on flexible polyimide substrate (**FIG. 26A**). All devices presented typical OECT behavior at $V_{DS} = -0.6$ V and $V_G = 0.6$ V and response to pressure stimuli. To test the spatially resolved mapping with subtle pressure stimuli, several pieces of patterned PDMS with a thickness of about 1.5 mm were placed on the top of device array (**FIG. 26B**). Only those device units under pressure loading by the patterned PDMS could show response to pressure and output signal changes. The electric signals of each sensor unit in the device array as one pixel was recorded, then used to reconstruct the color map, which reflected the pressure distribution applied on the device array. The color of each pixel corresponded to the relative signal change caused by applied pressure on the sensing array. It was demonstrated that legible N, T, U-shaped patterns can be observed from the mapping results, proving the feasibility to precisely detect and recognize external pressure stimuli with patterned distribution in a static method.

[00104] Notably, the device array also enabled to monitor dynamic pressure stimuli such as the pressure track caused by finger's motion on device arrays. When finger sliding along the device array from pixel #1 (C1, R6) to pixel #16 (C6, R1) (**FIG. 26C**), the motion path was achieved by collecting and analyzing the signal changes of corresponding pixels. A clear shape "Z" was identified in the mapping image, where the area without finger's motion showed no obvious change in electric signal, indicating the excellent dynamic pressure monitoring of flexible sensor array. The real-time signal changes of sensor units in one cycle of finger's motion were recorded (**FIG. 26D**). When the finger passed through the pixel slowly and gently, the corresponding sensor unit exhibited an obvious signal change and then returned to its original state after the finger separated from this sensor unit and kept on moving. A motion speed of about 1 cm/s was calculated from the curves of real-time signal response, which is in accord with finger's actual motion speed. In the future, there are several aspects to be improved for the further applications, such as to optimize the pixel density and the response/recovery times and apply the devices to integrated multifunctional devices. These results provide a novel concept to mimic human tactile perception and promoting flexible all-solid-state OECT-based sensors in the applications of future wearable devices and E-skin, etc.

[00105] **Discussion**

[00106] The examples have presented high performance all solid-state OECTs based on solid polymer electrolytes with high ionic conductivity which facilitate excellent electrochemical response in a variety of ion-permeable conjugated polymers. The all solid-state OECTs also reveal a new strategy for ultrasensitive tactile sensors based on a pressure induced ionic doping mechanism. Notably, the all-solid-state OECT-based pressure sensors exhibited a high sensitivity, excellent stability over time, a low limit of detection, a low operating voltage and ultra-low power consumption. The pressure induced electrochemical doping throughout the bulk of organic semiconductor and use of micro-pyramidal structure to regulate alterable pathways for ions migration contribute to the high sensitivity of OECT-based pressure sensor. Spatial pressure information distribution as well as dynamic pressure monitoring was mapped and monitored on a flexible sensor array. These all solid-state OECTs reveal a new pathway towards ultrasensitive tactile sensors and will broaden the applications areas for OECT device, towards more solid-state applications such as human-machine interfaces, medical health monitoring and soft robots. Critically, it would also allow for a wider variety of organic semiconductors (developed for OFETs) to be now explored in the OECT configuration. The low operating voltages and the ability of these OECTs to be printed also opens avenues for easier assimilation into large area electronic skin applications powered by small integrated power sources.

[00107] **Advantages and improvements over existing methods, devices or materials**

[00108] An all-solid-state OECT in particular for tactile perception with high sensitivity and low power consumption has been demonstrated. The pressure sensing is modulated through the ionic doping process from the solid polymer electrolyte to the conjugated polymer channel. High pressure sensitivity is achieved owing to the intrinsic functionality of signal conversion and high amplification of OECTs. Other advantages of this OECT-based tactile sensor include low power consumption, low-cost printing processes, adaptable on any active surfaces and use of environmentally friendly organic materials.

[00109] In comparison to current flexible sensor technology, high performance touch sensors based on new sensing mechanism were fabricated. The touch sensors were also easily fabricated by solution-processing method, low-cost and show good flexibility and robustness. The organic materials are biocompatible, which are safe for the contact with human and food. High sensitivity (above 10^3 kPa^{-1}) has been demonstrated and the pressure sensor is tunable by applied voltage. Sensors on soft robots often require a tethered connection to support electrical hardware, or bulky on-board components such as batteries and microprocessors. The tactile

sensors require very low operating voltage ($<1V$), hence it will enable large area sensor arrays or higher spatial density with low power consumption, which is a great challenge in other touch sensor technologies.

[00110] **Commercial applications of the Disclosure**

[00111] The development of conformable, flexible and bendable pressure or touch sensors is an emerging technological goal in a variety of fields, including electronic skin, soft robotics and wearables, which are relevant to advanced manufacturing and engineering (AME). This disclosure has advantages in commercialization of pressure or touch sensors to meet the application needs of human-computer user interfaces, robotics, and industrial monitoring and therefore will be attractive to industrial subscriptions.

[00112] Ionic-electronic coupling across the entire volume of conjugated polymer films endows OECTs with high transconductance and low operating voltage. However, OECTs utilize liquid electrolytes, which limit their long-term operation, reproducibility, and integration while solid electrolytes typically results in inefficient ion transport. Herein, it is shown that a solid polymer electrolyte can facilitate a good electrochemical response in conjugated polymers and yield high OECT performance. This allows for the OECT based pressure sensors, modulated through a pressure sensitive ionic doping process. The pressure sensor exhibits the highest sensitivity ever measured ($\sim 10000 \text{ kPa}^{-1}$) and excellent stability. Flexible sensor arrays realize a static capture of spatial pressure distribution and enable monitoring of dynamic pressure stimuli. Herein it is demonstrated that all-solid-state OECTs are good candidates for providing rich tactile information, enabling applications for soft robotics, health monitoring and human-machine interfaces.

[00113] High performance OECTs (e.g., peak transconductance of $2.8 - 4.6 \text{ mS}$ or thickness-normalized transconductance of 386.0 to 711.5 S cm^{-1}) are demonstrated herein employing a solid polymer electrolyte that facilitates good electrochemical response in four different ion-permeable conjugated polymers and molecules. Pressure sensing through OECTs fabricated using the prototypical (PEDOT:PSS as well as P3HT are demonstrated herein at dramatically low voltages ($<1V$) and ultralow power consumption ($<5 \mu W$). It is assumed that the pressure sensing is modulated through the ionic doping process from the solid polymer electrolyte to the conjugated polymer channel, however the disclosure is not limited thereto. High pressure sensitivity is achieved owing to the intrinsic functionality of signal conversion and high amplification of OECTs; about 10^4 times better than capacitive pressure sensors, about 10^2 times higher than resistive sensors, and about 10 times better than OFET-type sensors.

[00114] **Electrical performance of all-solid-state OECTs**

[00115] **FIG. 1** shows the device architecture of the OECT with a solid polymer electrolyte comprising PVDF-co-HFP ionic conductive polymer and ionic liquid, [EMIM][TFSI] (**FIG. 3**). The high chain dipole moment of the PVDF-co-HFP copolymer interacts with the ionic liquid to form an elastomeric ionic gel that allows for facile ion migration under applied electric field. Transfer and output characteristics of the all-solid-state PEDOT:PSS OECT (**FIG. 5A, FIG. 5B, FIG. 5C, FIG. 5D**) show a decrease in drain current (I_D) upon application of positive gate bias (V_G), consistent with the injection of [EMIM]⁺ cations from the solid polymer electrolyte into the PEDOT:PSS film, where the conducting PEDOT is reduced to neutral state. The device shows a high peak transconductance (g_m) of ~2.8 mS at $V_G = 0.15$ V and a desirable on/off ratio of $\sim 10^3$ at $V_D = 0.5$ V, comparable to operation under aqueous NaCl or ionic liquid electrolytes (**FIG. 27**). Devices utilizing pristine PVDF-co-HFP (without [EMIM][TFSI], **FIG. 28**), showed no transistor characteristics at these voltages, indicating that the ions are responsible for the electrochemical doping effect. Due to the entire volumetric doping in OECTs, the transconductance (g_m) increased with channel geometry (Wd/L) (**FIG. 5C**). The large transconductance and low voltage operation make the all-solid-state OECT device ideal ion-to-electron transducers. Drain current hysteresis was negligible, attributable to the high ionic conductivity and solvent choices (**FIG. 29**). The all-solid-state OECTs had a rise time of 3.87 ms (**FIG. 30**), comparable to devices in aqueous (~0.5 ms) and ionic liquid (~1.1 ms) electrolytes. These results indicate that the PVDF-co-HFP polymer electrolyte has sufficient ion mobility to allow fast doping and dedoping of the channel. Notably, when compared to previously reported solid-state OECTs (~46 ms to ~1.82 s), the response speed is significantly faster. Excellent switching stability is also observed, where the drain current retained 91.2% of the original value after 13,000 cycles, comparable to (~91.8%) liquid-state PEDOT:PSS OECTs (**FIG. 31**). It is also shown herein that the solid polymer electrolyte can support OECT operation at high temperatures (for example, 100 °C in ambient atmosphere) in which conventional liquid electrolytes would have evaporated, and observed that both I_D and g_m remain unaffected (**FIG. 6A, FIG. 6B**). Furthermore, the devices operate well after multiple lamination and delamination processes, which therefore allow reuse (**FIG. 6C, FIG. 6D**).

[00116] To further assess the suitability of the solid polymer electrolyte, the studies were extended to P3HT, which is a widely used accumulation mode OECT material, as well as

typical OFET materials such as p-type PCDTFBT and n-type PC₇₀BM (**FIG. 7** and **FIG. 8** and **FIG. 9**). The results demonstrated that the solid polymer electrolyte is a universal choice to construct highly performing and stable OEECTs. In the case of all solid-state P3HT-based OEECT, the transfer characteristic also shows a low gate operation (< -1.3 V), high on/off ratio ($\sim 5 \times 10^5$), large g_m of ~ 4.62 mS at $V_G = -1$ V and $V_D = -0.5$ V (**FIG. 7B**) and good device stability after multiple lamination and delamination processes and 1 week storage in the air (**FIG. 6D**). A rise time of ~ 0.95 s is obtained for anion doping in P3HT, which is considerably faster than previous reports.

[00117] **Operating Mechanism**

[00118] The spectrochemical response of the films was investigated to confirm the doping and de-doping processes of the conjugated systems. **FIG. 10** and **FIG. 32A**, **FIG. 32B** show the change in optical absorption of the conjugated polymer films interfaced with the solid polymer electrolyte under bias. Upon application of $V_g = +0.5$ V, the film switches from oxidized to neutral state since the injected cations de-dope PEDOT. As a result, a new absorption feature between 650 nm and 700 nm was observed, attributable to the π - π^* transition of neutral PEDOT, while the intensity of the polaronic and bipolaronic optical transitions at near IR region decreased correspondingly. At higher positive gate voltages, the intensity of the new absorption feature increased while the intensity of initial polaron-induced transition decreased, consistent with the depletion mode in PEDOT:PSS based OEECT. For P3HT, its neutral state exhibited an absorption band from ~ 350 nm to ~ 700 nm, corresponding to π - π^* transitions. With increasing negative bias, the first oxidation state appeared as an increase in absorption centered at ~ 800 nm with a concurrent decrease in the neutral absorption band (350-700 nm) with an isosbestic point at ~ 624 nm. Beyond -0.7 V bias, a second oxidation state emerges with an absorption band beyond 1000 nm. This is in agreement with accumulation of charges in the P3HT layer through the $[\text{TFSI}]^-$ anion doping effect.

[00119] **OEECT-based pressure sensors**

[00120] With the demonstration of a high performance solid state OEECT, the pressure sensing capability of such a device (**FIG. 11**) was explored. For this, the polymer electrolyte, which acts as the active pressure-sensing layer, is patterned as micro-pyramid arrays using a silicon mold, followed by the peel-off and lamination process to assemble an OEECT-based pressure sensor (**FIG. 12C** and **FIG. 12D**). Unlike most ion-gels which are viscous and thick, the solid polymer electrolyte is easy to pattern to form micro-pyramid arrays on surfaces. Each

of these pyramids has a square base of 10.5 μm side, and tapers to a tip with a height of 8.0 μm (SEM images, **FIG. 12A** and **FIG. 12B**). As shown in the transfer characteristics (**FIG. 14A**, **FIG. 14B**), the source-drain current changed significantly in response to different pressures, indicating successful detection of pressure stimuli. At a constant gate voltage, the leakage current (I_{GS}) increased with increasing applied pressure (**FIG. 15**), which implies the increase in ion migration events to the channel. It is therefore hypothesized that the pressure sensor exploits a pressure sensing mechanism which is based on ionic migration for doping/de-doping of conjugated polymer in the active channel, unlike other existing types of pressure sensors.

[00121] According to Bernards model, the OECT can be modeled as an ionic circuit consisting of an electrolyte/channel capacitor (C_{CH}), gate/electrolyte capacitor (C_G) and electrolyte resistor (R_E) (**FIG. 13**). For no applied pressure, there is negligible ion penetration from the solid polymer electrolyte to the PEDOT:PSS channel since the contact area between the electrolyte pyramids and polymer is minimal. Hence, most of the applied gate voltage drops at the gate/electrolyte interface, resulting in $C_{CH} > C_G$. Under applied pressure, the effective interface and contact area between solid polymer electrolyte with micro-pyramids and channel increased, and most of the applied voltage drops at the electrolyte/channel interface ($C_{CH} < C_G$), more EMIM⁺ ions are transferred from electrolyte into channel under positive gate bias, generating a significant electrochemical switching from highly conducting state to neutral semiconducting state, thus modulating the source-drain current (see **FIG. 13**). The deformed pyramidal structure under pressure can also reduce the resistance of electrolyte (R_E), due to the compression effect which induces a higher ionic concentration in the channel. The decreased electrolyte resistance thus leads to a higher effective gate potential to modulate the source-drain current. This also corroborates well with **FIG. 33** which shows similar dependence of leakage current (I_{GS}) and source-drain current (I_{DS}) response to cyclic pressure stimuli. In this case, the solid ionic electrolyte is activated like the nanochannel of mechanoreceptors in human skin, inducing an ion-squeezing effect from the mechanical loads. The device shows stable on- and off-state I_{DS} values (maintained ~90% of I_{on}/I_{off}) upon successive V_G pulse (between -0.6 V to 0.6 V with a pulse width of 0.5 s) and under applied pressure of 15 kPa, for 1000 cycles, implying negligible performance degradation (**FIG. 16**, **FIG. 34**). While the theory on ion transfer is explained herein, the disclosure is not necessarily limited thereto.

[00122] The sensitivity of the all-solid-state OECT-based pressure sensor is shown in **FIG. 17A**. By deriving the slope in linear sensing regions, the sensitivity up to ~71.9 kPa⁻¹ in high pressure region (5-15 kPa) was obtained, which is much higher than previously reported

values using capacitive-type (0.55 kPa^{-1}), piezoresistive-type (27.9 kPa^{-1}) or micro-structured PDMS dielectric transistor-type (8.2 kPa^{-1}), **Table 1**. The device also exhibits a response to very low pressure ($< 100 \text{ Pa}$) with a sensitivity of $\sim 1.74 \text{ kPa}^{-1}$ (see **FIG. 17B**, **FIG. 17C**). As shown in **FIG. 18A**, a flower ($\sim 11 \text{ mg}$; 1.1 Pa) and a grain of rice ($\sim 20 \text{ mg}$; 2.0 Pa) was placed on the sensor to test the signal response. The results exhibited the limit of pressure can be obtained as low as 1.1 Pa and the sensing to very low pressure presents good repeatability.

[00123] **Table 1.** Comparison of the pressure sensitivity, pressure range, operating voltage and limit of detection of some pressure sensors.

Types of devices	Device structures	Sensitivity / Pressure region	Operating voltage	Limit of detection
Capacitive	Patterned microstructured composite rubber dielectric	0.831 kPa ⁻¹ / 0-0.5 kPa	1 V	1.4 Pa
	Porous nylon netting and graphene	0.33 kPa ⁻¹ / 0-1 kPa	1 V	3.3 Pa
	E-textile based on functionalized silkworm fiber coiled yarns	0.136 kPa ⁻¹ / 0-2 kPa	1 V	50 Pa
	Double layer PDMS microstructure	0.055 kPa ⁻¹ / 2-10 kPa	1 V	500 Pa
	A pyramid microstructured dielectric layer along with a lamination layer	0.022 kPa ⁻¹ / 0-10 kPa	5 V	-
Piezoresistive	Hollow nanosphere microstructure	31.6 kPa ⁻¹ / 0-250 Pa	1 V	0.6 Pa
	Two-Dimensional Titanium Carbide (MXene)/ Natural Microcapsule	24.63 kPa ⁻¹ / 0-200 Pa	1 V	8 Pa
	PEDOT@PVDF double-layer nanofiber woven fabric	18.4 kPa ⁻¹ / 0-100 Pa	1 V	2 Pa
	Hierarchical ZnO nanowires	6.8 kPa ⁻¹ / 0-2 kPa	10 V	0.6 Pa
	Microstructure-frame-supported organic thermoelectric materials	4.6 kPa ⁻¹ / 0-1 kPa	0.1 V	100 Pa

	Self-Assembled Polystyrene Microspheres	2.49 kPa ⁻¹ / 4-200 kPa	1 V	4 kPa
	Uniform micro-patterned PDMS films with SWNT ultrathin films	1.80 kPa ⁻¹ / 0-300 Pa	2 V	0.6 Pa
	Knitted fabric with carbon black particles and polyvinylidene fluoride	1.50 kPa ⁻¹ / 10-60 kPa	1 V	-
	Ultrathin gold nanowire-impregnated tissue paper	1.14 kPa ⁻¹ / 0-5 kPa	1.5 V	13 Pa
	Reduced graphene oxide intercalated by covalently tethered molecular pillars	0.82 kPa ⁻¹ / 0-0.6 kPa	0.2 V	7 Pa
OFET	Microstructured PDMS dielectric	8.2 kPa ⁻¹ / 0-8 kPa	V _G = -200 V V _D = -200 V	< 100 Pa
	Microstructured drain-source electrode	514 kPa ⁻¹ / 0-250 Pa	V _G = -10 V V _D = -60 V	10 Pa
	3D self-organized organic semiconductor microstructures	1.07 kPa ⁻¹ / 0-1 kPa	V _G = -80 V V _D = -80 V	80 Pa
	Suspended gate	192 kPa ⁻¹ / 0-5 kPa	V _G = -60 V V _D = -60 V	0.5 Pa
	Microstructured P(VDF-TrFE) gate dielectric layer	1.02 kPa ⁻¹ / 0-80 Pa	V _G = -100 V V _D = -100 V	20 Pa
	Bilayer dielectric of PAA with PMMA polyelectrolytes	56.15 kPa ⁻¹ / 0-5 kPa	V _G = -5 V V _D = -5 V	100 Pa

OEET	All-solid-state-OEET based on PEDOT:PSS	71.9 kPa ⁻¹ / 5-15 kPa	V _G = 0.6V V _D = -0.5 V	1.1 Pa
	All-solid-state-OEET based on P3HT	10828.2 kPa ⁻¹ / 0-100 Pa	V _G = -1.3 V V _D = -0.5 V	< 10 Pa

[00124] The microstructured solid polymer electrolyte greatly enhanced the pressure sensitivity of the sensor relative to that of an unstructured film which does not present obvious response to pressure stimuli (see **FIG. 35**). The different sensitivity at the various pressure regimes represented different deformation stages of micro-pyramids with pressure. At low pressures (< 4 kPa), the sensing mechanism is due to the increased contact between the micro-pyramidal tip and active channel layer. However, at higher pressures (>5 kPa), the interface turns from point-to-face contact to face-to-face contact, which increased the available pathways for ions migration, resulting in the highest sensitivity of ~ 71.9 kPa⁻¹. For pressures beyond 15 kPa, the micro-pyramidal shape tended to a flat plane due to almost complete compression, and the contact area reached its maximum limit (**FIG. 36**). The transient response (**FIG. 37**) of the current to high (> 5 kPa)/low (<1 kPa) pressure regions showed stable stepped and cyclic response supporting the high pressure-sensitive resolution and reproducibility of the pressure sensor.

[00125] Significantly, an unprecedentedly higher sensitivity at both high and low pressure regimes was observed when the OEET operated in the accumulation mode. A P3HT based OEET was demonstrated where the transfer and output characteristics exhibited a dramatic increasing of I_{ds} with the increase of applied pressure from 0 to 15 kPa or with the increase in V_G under the pressure of 15 kPa (**FIG. 21A** and **FIG. 38, respectively**). The sensitivity is up to 10828.2 kPa⁻¹ in the very low pressure regime (< 100 Pa), 5468.3 kPa⁻¹ in the pressure regime (0.1-5 kPa) kPa⁻¹ and 1671.2 kPa⁻¹ in the pressure regime above 5 kPa, which is, to the author's knowledge, the highest ever reported sensitivity. The electrochemical doping process with applied pressure was also monitored through in-situ spectro-electrochemistry. As shown in **FIG. 22C** and **FIG. 20**, there was no change in the absorption spectrum while adjusting the gate bias (from 0.1 V to -1.4 V) before applying pressure and an obvious difference after applying pressure. The P3HT can be completely and reversibly doped at -1.4 V, with a decline of peak of absorption spectrum between 500 and 550 nm and rise of peak between 700-900 nm. The results demonstrated that the applied pressure and gate bias both induced

electrochemical doping effect in P3HT (**FIG. 19**). At high pressures ($>15\text{ kPa}$), when the contact area between the electrolyte and P3HT was maximised, the volumetric capacitance (C_P^*) approached the volumetric capacitance of P3HT film using a planar solid polymer electrolyte (without microstructures) (**FIG. 22A to FIG. 22E**), indicating efficient pressure induced doping.

[00126] The performance of the all-solid-state OECT-based pressure sensors held the highest reported sensitivity (**FIG. 22D**), while operating only at low voltages ($V_d = -0.5\text{ V}$ and $V_G = -1.3\text{ V}$), which is almost a factor of 100 smaller than OFET-based devices and therefore beneficial for various wearable electronic applications. In addition, the power consumption was as low as $<1\text{ }\mu\text{W} - 1\text{ mW}$ from 15 kPa pressure to no-pressure loading state ($I_D < 2\text{ }\mu\text{A} - 1.8\text{ mA}$; $V_D = -0.5\text{ V}$, $V_G = 0.6\text{ V}$) for depletion mode PEDOT:PSS device. For accumulation mode P3HT device, the ultralow power consumption of $<28\text{ nW}$ at no-pressure loading can be achieved ($I_D < 56\text{ nA}$; $V_D = -0.5\text{ V}$), while the power consumption at 15 kPa pressure can be varied from $<5\text{ }\mu\text{W} - 1.1\text{ mW}$ with $V_G = -0.3 - 1.3\text{ V}$ ($I_D < 9.6\text{ }\mu\text{A} - 2.2\text{ mA}$; $V_D = -0.5\text{ V}$). The few μW in power consumption is several dozen times lower than that of reported transistor-type pressure sensors ($<1\text{ mW}$; $I_D = 10\text{ }\mu\text{A}$, $V_G = -100\text{ V}$) and piezoresistive-type pressure sensors ($<0.5\text{ mW}$).

[00127] The OECT-based sensors are able to show large tunable sensitivity range through the modulation of gate bias (**FIG. 23A, FIG. 39**). For instance, the pressure sensitivity for PEDOT:PSS device changed from 4.47 kPa^{-1} to 2.18 kPa^{-1} to 0.59 kPa^{-1} as the V_G is changed from 0.55 V to 0.5 V and to 0.4 V respectively. Similarly, the electrical signal response to same pressure level can be tuned with applied gate bias (**FIG. 23B**). The ability to tune sensitivity can allow selection of conditions such that noise does not cause interference. The flexible pressure sensors are useful for precise detection of the wrist artery pulse (**FIG. 24A, FIG. 24B, FIG. 24C**) with the characteristic peaks (P1, P2, P3) which represent percussion wave, tidal wave, and diastolic wave, clearly distinguishable. The advantage of the tunable sensitivity is apparent when the pulse signals are monitored under environmental interference of continuous air flow from human breath. As shown in **FIG. 24D**, the device with high sensitivity at $V_G = 0.6\text{ V}$ exhibits messy pulse signals, while good signals are obtained for device with relatively low sensitivity at $V_G = 0.4\text{ V}$.

[00128] The source-drain current showed no obvious degradation under different pressure over almost 70 days, confirming a high operational stability of the solid-state OECTs (**FIG. 24E**). To further investigate the repeatability and stability of device, a continuously cyclic

stability test was performed under 1 kPa over 300 cycles and showed a retention of 91.9% (**FIG. 24F**). Despite the slight performance degradation, the device could still work well at low operating voltage of $V_D = -0.5$ V, $V_G = 0.6$ V (**FIG. 17D and FIG. 18D**). The good reproducibility and durability of this OECT-based pressure sensor indicate a potential candidate in flexible electronics. The OECTs are easily scalable and, a flexible pressure sensor array of 6×6 pixels was fabricated to capture spatial and temporal pressure distribution (**FIG. 25A, FIG. 25B**). **FIG. 26A** shows the highly flexible device array on polyimide substrate while **FIG. 26B** shows several legible pieces of PDMS placed on the device array with the corresponding pressure map. The device array also enables dynamic pressure stimuli monitoring such as the pressure track caused by finger's motion on device arrays (**FIG. 26C, FIG. 26D**).

[00129] **Outlook**

[00130] A high performance all solid-state OECTs was developed based on solid polymer electrolytes with high ionic conductivity which facilitate excellent electrochemical response in a variety of ion-permeable conjugated polymers. The all solid-state OECTs also reveal a new strategy for ultrasensitive tactile sensors based on a pressure induced ionic doping mechanism. Notably, the all-solid-state OECT-based pressure sensors exhibited a high sensitivity of up to 10828.2 kPa⁻¹ (for P3HT accumulation mode), excellent stability over time (more than 2 months), a low limit of detection of 1.1 Pa, a low operating voltage ($\sim \pm 1$ V) and ultra-low power consumption (< 5 μ W). The pressure induced electrochemical doping throughout the bulk of organic semiconductor and use of micro-pyramidal structure to regulate alterable pathways for ions migration contribute to the high sensitivity of OECT-based pressure sensor. Spatial pressure information distribution as well as dynamic pressure monitoring was mapped and monitored on a flexible sensor array. It is believed that these all solid-state OECTs reveal a new pathway towards ultrasensitive tactile sensors and will broaden the applications areas for OECT device, towards more solid-state applications such as human-machine interfaces, medical health monitoring and soft robots. Critically, it would also allow for a wider variety of organic semiconductors (developed for OFETs) to be now explored in the OECT configuration. The low operating voltages and the ability of these OECTs to be printed also opens avenues for easier assimilation into large area electron skin applications powered by small integrated power sources.

[00131] **Experimental Section**

Materials. PEDOT:PSS, Clevios PH1000) were purchased from Heraeus. P3HT, PC₇₀BM molecule, PVDF-co-HFP, Mw= 400,000 g/mol, [EMIM][TFSI], 1-Ethyl-3-methylimidazolium chloride ([EMIM][Cl]), (3-glycidyloxypropyl)trimethoxysilane (GOPS), poly(methylmethacrylate) (PMMA, Mw= 100,000), and all the processing solvents including acetone, ethanol, chloroform and toluene were purchased from Sigma-Aldrich and used as received. Regio-regular PCDTFBT was purchased from 1-material inc., Canada.

Fabrication of solid polymer electrolyte. Firstly, copolymer PVDF-co-HFP was dissolved in acetone (110 mg/ml) and followed by vigorous stirring at room temperature for 12 hours. Then, the pre-dried ionic liquid [EMIM][TFSI] was added into the above solution with a weight ratio of 1:2 and followed by vigorous vibration for 30 minutes. After the removal of bubbles in solution by standing still, the prepared solution was spin-coated on a micro-pyramidal silicon mold to fabricate the patterned solid polymer electrolyte at 1500 rpm for 60 s. Then the film on mold was transferred into the vacuum oven to remove the solvent under 70 °C for 24 hours. The obtained solid polymer electrolyte could be peeled off from the molds and used to assemble the OECT device. The cleaned silicon wafer was used as substrate to fabricate solid polymer electrolyte without microstructures under same experiment parameters.

Fabrication of all-solid-state OECT. The silicon substrates were pre-cleaned in a sonicated bath using soap water, deionized water, acetone and ethanol one after another. The cleaned substrate was deposited with source and drain electrodes (Ni/Au, 10/90 nm) using a shadow mask by thermal evaporation. A thin layer of PMMA (5 wt.% in toluene) was spin-coated on the substrate as a sacrificial layer and then irradiated with ultraviolet-ozone (UVO) through a shadow mask for 2 hours to pattern the channel. To prepare the active channel solution, the PEDOT:PSS aqueous solution was filtered by 0.45 µm hydrophilic PVDF filters and then mixed with [EMIM][Cl] (14.662 mg/ml) and GOPS (0.5 wt.%), followed by a magnetic stirring for 1 hours. Ionic liquid additive was introduced in PEDOT:PSS system to achieve better electronic and ionic transport properties in OECTs as reported in our previous work. Then the PEDOT:PSS solution was spin-coated onto the patterned PMMA substrate at 4000 rpm for 40 s, followed by annealing at 140 °C for 20 mins. After that, dipping the device into toluene for 20 s and rinsed with DI water to remove the PMMA layer. To prepare the gate electrode, 100 nm Au was deposited on polyimide film and then was modified by non-polarizable PEDOT:PSS/[EMIM][Cl] film. Then, the solid polymer electrolyte without micro-pyramids was transferred onto the gate electrode to complete the all-solid-state device.

For P3HT, PC₇₀BM and PCDTFBT-based OECTs, pristine P3HT, PC₇₀BM and PCDTFBT were dissolved in analytical grade chloroform, respectively, followed by magnetic stirring at 50 °C for 30 mins. The active channel layers were prepared by spin-coating on the source-drain electrodes at 3000 rpm for 30s using the above solutions. The channel thickness of the P3HT, PC₇₀BM and PCDTFBT film was controlled by varying the concentration from 1 mg/ml to 10 mg/ml. The solution preparation and spin-coating were carried out in a N₂ glovebox. The transfer of solid polymer electrolyte and lamination with gate electrode were similar with the process to fabricate PEDOT:PSS-based OECTS.

For OECTs with liquid electrolytes (0.1 M NaCl aqueous solution and pure ionic liquid [EMIM][TFSI]), a drop of NaCl solution or ionic liquid were placed on top of the channel of transistor and an Ag/AgCl gate electrode is dipped into the liquid.

To fabricate OECT-based pressure sensor, flexible polyimide film was used as substrate and for the gate electrode, another polyimide film was coated with a layer of 100 nm gold and another layer of PEDOT:PSS/[EMIM]Cl to reduce the electrochemical impedance and potential drop between gate electrode and electrolyte interface. The solid polymer electrolyte with micro-pyramids was transferred as sensitive layer from the mold and used for the lamination on the gate electrode, wherein the side without pyramidal shapes is in contact with the gate electrode. Then the patterned solid electrolyte with gate electrode was laminated on the channel layer to complete the flexible pressure sensor. For the flexible sensor array with 6×6 pixels, the fabrication processes are similar as mentioned above using different shadow masks.

Device characterization. The output and transfer characteristics and other electrical properties were tested by Keysight Precision Source/Measure Unit (B2900A Series) and a probe station (Karl Suss PM5). The scan rate was 5 mV s⁻¹ during the measurements of transfer and output characteristics. The measurements of typical performance of OECTs with unpatterned solid electrolyte were carried out without applying any pressure. For the pressure measurement, a highly configurable force tester (ESM 303, Mark-10 Corporation) with a force gauge (Mark-10 025/012) for tension and compression measurement applications were used to apply an external pressure. The instrument can carry out a dynamic pressure measurement at adjustable speeds of 0.5-1100 mm/min. For the stability test, a piece of elastic PDMS with a contact area of ~1×1 cm² was attached on the pressing tip of force gauge to provide a buffer force and used to calculate the applied pressure. The spatial and temporal pressure distributions were plotted by calculating the normalized difference of resistances between the measurement before and

after applying pressure. PDMS pieces with legible N, T, U-shaped patterns with a thickness of about 1.5 mm were placed on the device array to test the corresponding pressure map. Each sensor unit in the device array as one pixel was recorded, then used to reconstruct the color map, which could reflect the pressure distribution applied on the device array. The SEM morphology of solid polymer electrolyte was measured using field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7600F). The cyclic voltammetry measurements of the films were recorded using a potentiostat/galvanostat (Autolab, PGSTAT302N, Metrohm). The working electrode was a P3HT film with various geometries cast on top of an ITO-coated substrate.

[00132] **UV-VIS Spectroelectrochemistry.** The PEDOT:PSS solution was spin-coated on ITO glass substrates in air and subsequently annealed at 140 °C for 20 mins. The P3HT film on ITO glass was prepared in glovebox. Then the solid polymer electrolyte with/without pyramids is transferred onto the ITO glass to cover the PEDOT:PSS or P3HT film, followed by the encapsulation of another ITO glass which can be acted as gate electrode. To measure the pressure effect for UV-vis absorption, flexible ITO on plastic polyethylene glycol terephthalate were used as gate electrode and the side to apply pressure. A Keysight precision source/measure unit (B2912A) was chosen to apply biasing between gate electrode and ITO glass. The absorption spectra were recorded using a UV-vis-NIR spectrophotometer (SHIMADZU, UV-3600) over the wavelength range from 300-1500 nm as sample was biased.

[00133] **Statements of the Disclosure**

[00134] The disclosure relates to an all solid-state OECT for tactile sensing. The OECT may be used for tactile sensing in robotic devices, human-machine interactions and health monitoring devices.

[00135] A solid-state organic electrochemical transistor for tactile sensing, comprising:

- an active channel comprising a conjugated polymer and/or a small conjugated molecule with the ability of ionic and electronic transport;
- a source electrode separated from a drain electrode, which are connected via the active channel;
- a solid polymer electrolyte for providing ions source to the active channel;
- a gate electrode provided on the solid polymer electrolyte;
- wherein the solid polymer electrolyte comprises an ionic liquid and an ionic conductive polymer, preferably with a weight ratio of ionic liquid to ionic conductive polymer of from 1:0.1 to 1:30;

- the solid-state organic electrochemical transistor may be formed on a rigid (e.g. silicon oxide, glass, quartz) or a flexible (e.g. plastic, PDMS, metal foil) substrate;
- optionally wherein the solid polymer electrolyte comprises microstructures for higher sensitivity (e.g. micro-pyramids, micro-domes, micro-pillars, micro-porous, fiber-shape, conical shape, rough interface, air-gap);
- optionally the gate electrode may be top-gate or side-gate construction;
- optionally the electrodes for source, drain, gate may be metals including gold, silver, nickel, titanium, platinum, or conducting polymers including poly(3,4-ethylenedioxythiophene), poly(thiophene)s, polyaniline, polypyrrole, or other material with high electrical conductivity including carbon, ITO, FTO, AZO;
- optionally the conjugated polymer may be doped with a dopant; and
- optionally the active channel may further comprise a second ionic liquid or additives (e.g. ethylene glycol, DMSO, sorbitol, and/or glycerol) to increase the ionic conductivity.

[00136] The ionic conductive polymer may comprise a material formed from vinylene-based, vinylidene fluoride-based, methacrylate-based, polyethylene oxide-based, vinyl alcohol-based, ethylene carbonate-based, vinyl pyrrolidone-based monomers. Examples are PVDF, PVDF-HFP, PVDF-TrFE, PEO, PVA, PEC, PVP.

[00137] The cation of the ionic liquid may comprise 1-ethyl-3-methylimidazolium [EMIM]⁺ or [BMIM]⁺ or metal cations including Mg²⁺, Ca²⁺, Zn²⁺, Ni²⁺, Cu²⁺, Pb²⁺, Ba²⁺. The anion of the ionic liquid may comprise bis(fluorosulfonyl)imide ([FSI]⁻), bis(trifluoromethylsulfonyl)amide [TFSI]⁻, dicyanamide [DCA]⁻, hexafluorophosphate [PF₆]⁻, tetrafluoroborate [BF₄]⁻, perchlorate [ClO₄]⁻, chloride [Cl]⁻.

[00138] The conjugated polymer may comprise n-type or p-type organic conjugated polymers. The small conjugated molecule with the ability of ionic and electronic transport may comprise fullerene or fullerene derivatives, for example, fullerene derivatives with glycolated side chains.

[00139] The solid-state organic electrochemical transistor (OECT) may work in both depletion and accumulation mode.

[00140] Where the solid-state OECT works in depletion mode, p-type semiconducting material may be used in the active channel. Examples of p-type semiconducting materials

include p-type conjugated polymer, including poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT may be doped by a dopant poly(styrenesulfonate) (PSS).

[00141] Where the solid-state OECT works in accumulation mode, p-type or n-type semiconducting materials may be used in the active channel. Examples of p-type semiconducting materials include p-type conjugated polymers including P3HT and PCDTFBT and example of n-type semiconducting materials includes PC₇₀BM.

[00142] The microstructures may be micro-pyramids, micro-pillars, micro-domes, micro-porous, fiber-shape, conical shape, rough interface, air-gap or hierarchical microstructures of mixture thereof.

[00143] Any substrate may be used. Examples include silicon and glass substrates. Where it is necessary to have a flexible solid-state OECT, flexible substrates may also be used. Example of flexible substrates include polyimide, polyethylene terephthalate, parylene-C, PDMS, polyethylene naphthalate, paper, cellulose, polyacrylonitrile.

[00144] The solid-state electrochemical transistor may be further encapsulated to protect the transistor for long-term stability. For example, a layer of 2 μm parylene-C may be deposited to encapsulate the fabricated devices.

[00145] There is no limitation to the width (W), thickness (d) and length (L) of the active channel. For good transconductance (g_m), a larger channel geometry (Wd/L) such as 200-800 nm is preferred. Hence, possible thickness (d) of the active channel may range from 10-200 nm, possible width (W) may range from 500-2000 μm , and possible length (L) may range 10-500 μm .

[00146] As for the solid polymer electrolyte, the thickness may be fabricated to less than 10 μm . Nonetheless, if the solid polymer electrolyte comprises microstructures, a thicker solid polymer electrolyte may be necessary. For example, the solid polymer electrolyte comprising microstructures may have a thickness of about 50 μm . Generally, a thin electrolyte layer allows for flexibility and softness.

[00147] A method of forming solid polymer electrolyte, comprising:

- dissolving an ionic conductive polymer in a solvent, the solvent may have a low boiling point of less than 120 °C;
- mixing an ionic liquid with the solution of ionic conductive polymer to form a second solution, a weight ratio of the ionic liquid to ionic conductive polymer may be of from 1:0.1 to 1:30; and
- depositing the second solution on a surface to form the solid polymer electrolyte.

[00148] The second solution may be left standing prior to depositing on a surface to remove bubbles in the second solution.

[00149] Examples of depositing the second solution include dip-coating, drop-casting, spin-coating, screen printing, inkjet printing or spray printing. For example, spin-coating may be carried out at 1500 rpm for 60 s.

[00150] The solvent to dissolve ionic conductive polymer may be acetone, chloroform, ethanol, tetrahydrofuran, toluene, water. The amount of ionic conductive polymer and solvent required may vary depending on the ionic conductive polymer and the solvent used. As an example, a mass ratio of ionic conductive polymer to solvent may range from 1:4 to 1:20, such as 1:7, e.g., when PVDF:HFP is used as the ionic conductive polymer and acetone was used as the solvent.

[00151] The surface may be a surface of a mold or a surface of a substrate, depending on the desired structure for the solid polymer electrolyte. For example, the solid polymer electrolyte may be casted on the lotus leaf or another microtemplate to acquire an irregular surface.

[00152] Suitable ionic conductive polymer, cation of the ionic liquid and anion of the ionic liquid are listed above.

[00153] While the disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.