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Contact modulated ionic transfer doping in all-solid-state organic electrochemical transistor for ultra-high sensitive tactile perception at low operating voltage

*Shuai Chen, Abhijith Surendran, Xihu Wu, and Wei Lin Leong**

Dr. S. Chen, A. Surendran, X. Wu, Prof. W. L. Leong
School of Electrical Electronic Engineering
Nanyang Technological University
50 Nanyang Avenue, Singapore 639798, Singapore
E-mail: wlleong@ntu.edu.sg

Abstract

Ionic-electronic coupling across the entire volume of conjugated polymer films endows organic electrochemical transistors (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. Here we show that a solid polymer electrolyte, can 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. Our findings 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.

Keywords: Organic electrochemical transistor, Ultrasensitive pressure sensor, Solid electrolyte, Conjugated polymer, Flexible organic electronics

1. Introduction

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^[1, 2], capacitive^[3, 4] and piezoelectric^[5, 6]. Although they allow for good pressure sensitivity ($0.7\text{--}100\text{ kPa}^{-1}$)^[7-9], 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.^[10-12] 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) limits their integration and portability.

A class of devices that demonstrate good electrical performance at low operational voltages ($< 1\text{ V}$) is the organic electrochemical transistor (OECT).^[13] In an OECT, the conjugated polymer channel is in direct contact with an electrolyte which is the source of ions. Reversible ionic insertion/extraction from the active polymer channel is modulated through applied gate voltage. OECTs have strong signal amplification since the ionic doping occurs over the entire volume of the polymer channel, and thus significant modulations in the current can be achieved under low gate voltages. OECTs have therefore attracted increasing attention in various applications ranging from neuromorphic computing,^[14, 15] biological sensing,^[16, 17] cell monitoring^[18, 19] and neural interfacing^[20, 21]. However, OECTs utilize liquid electrolytes which restrict their scalability, integration and miniaturization^[22, 23]. Long-term operation necessitates careful encapsulation.^[23-25] Independent gating is also not possible since the ions in the liquid electrolyte are shared between all the fabricated transistors. The use of a liquid electrolyte also precludes it from a wide variety of sensing applications including tactile input. The demonstration of a high performance flexible OECT utilising a solid state polymer electrolyte could be therefore significant for a wide variety of applications. However, solid electrolytes have not been successfully implemented in OECTs as they typically present lower ionic conductivity than liquid electrolytes and thus results in inefficient ion transport and slow switching response.^[26-28] Present strategies for solid-state electrolytes include hydrogels, ion-gels which incorporate aqueous electrolytes, ionic liquids within an organic matrix.^[29-31] However, hydrogels-based ionic conductive materials are susceptible to moisture or weight loss, a side effect of dehydration at higher temperature^[31, 32], leading to a short operational life. The poor miscibility of the ionic liquids within polymers at concentrations required for realizing high ionic conductivity result in viscous, thick gel electrolytes with plastic deformation during mechanical stimuli^[33] that are not appropriate for use in flexible and conformal epidermal applications.

Herein, we demonstrate high performance OECTs (thickness-normalized transconductance of $386.0 - 711.5\text{ S/cm}$) employing a solid polymer electrolyte that facilitates good electrochemical response in four different ion-permeable conjugated polymers and molecules. We also demonstrate, for the first time, pressure sensing through OECTs fabricated using the prototypical

poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as well as poly(3-hexylthiophene-2,5-diyl) (P3HT) at dramatically low voltages ($<1\text{V}$) and ultralow power consumption ($<5\text{ }\mu\text{W}$). The pressure sensing is modulated through the ionic doping process from the solid electrolyte to the conjugated polymer channel. 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,^[34-36] about 10^2 times higher than resistive sensors,^[37, 38] and about 10 times better than OFET-type sensors.^[39, 40]

2. Results and Discussion

Figure 1. Ionic-electronic interaction in all-solid-state organic electrochemical transistor. (a) All-solid-state OECT device architecture, which comprising of a conjugated polymer as the channel, with the source and drain metal electrodes and the solid polymer electrolyte on top of the channel layer. (b) Schematic of the PVDF-HFP solid electrolyte, [EMIM][TFSI] ionic liquid, polymer structures of PEDOT:PSS, P3HT. (c-d) The output, transfer, thickness (d) -normalized transconductance and switching response performance for PEDOT:PSS and P3HT based OECTs. (width/length/thickness (W/L/d) = $1000\text{ }\mu\text{m}/200\text{ }\mu\text{m}/68.9\text{ nm}$ for PEDOT:PSS and $1000\text{ }\mu\text{m}/200\text{ }\mu\text{m}/81.0\text{ nm}$ for P3HT) (e) Schematic illustration of in-situ spectro-electrochemistry measurements of (f), PEDOT:PSS or P3HT films interfaced with solid electrolyte under

different gate voltages, showing optical switching behaviour.

Figure 1a shows the device architecture of the OECT with a solid electrolyte consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) ionic conductive polymer and ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSI]) (**Figure 1b**). The high chain dipole moment of the PVDF-co-HFP copolymer interacts with the ionic liquid to form an elastomeric ionic gel^[41-43] that allows for facile ion migration under applied electric field.^[44] Transfer and output characteristics of the all-solid-state PEDOT:PSS OECT (**Figure 1c**) 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 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 ~ 3.5 mS ($W/L/d=1000$ $\mu\text{m}/200$ $\mu\text{m}/68.9$ nm) at $V_G=0.1$ 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 (**Figure S1**, Supporting Information). The g_m of OECTs increases proportionally with respect to both the channel thickness (d) and geometry (Wd/L) (**Figure S2**, Supporting Information). From the transfer curves of five samples with different thickness, we also quantify the thickness-normalized g_m (at $V_D=-0.5$ V) to 386.0 S/cm, which is much higher than that obtained with other PEDOT:PSS OECTs using liquid electrolyte^[45, 46]. Devices utilizing pristine PVDF-co-HFP (without [EMIM][TFSI], **Figure S3**, Supporting Information), 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) (**Figure 1c**). 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 (**Figure S4**, Supporting Information). The all-solid-state OECTs had a rise time of 3.87 ms (**Figure S5**, Supporting Information), 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),^[22] 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 ($\sim 91.8\%$) liquid-state PEDOT:PSS OECTs (**Figure S6**, Supporting Information). We also show that the solid 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 (**Figure S7**, Supporting Information). This also correlates well with recent report which show temperature-resilient behavior in solid-state OECTs.^[47] Furthermore, the devices operate well after multiple lamination and delamination processes, which therefore allow reuse (**Figure S8**, Supporting Information).

To further assess the suitability of the solid electrolyte, we extend our studies to P3HT, which is a widely used enhancement mode OECT material, as well as typical

OFET materials such as p-type 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) and n-type [6,6]-phenyl-C71-butyric acid methyl ester [PC₇₀BM] (**Figure 1d** and **Figures S9-10**, Supporting Information). The results demonstrated that the solid 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 ~ 4.7 mS ($W/L/d = 1000 \mu\text{m}/200 \mu\text{m}/81.0 \text{ nm}$) at $V_G = -1$ V and $V_D = -0.5$ V (**Figure 1d**) and good device stability after multiple lamination and delamination processes and 1 week storage in the air (**Figure S8b**, Supporting Information). The thickness-normalized g_m is up to 711.5 S/cm (at $V_D = -0.5$ V), and a rise time of ~ 0.95 s is obtained for anion doping in P3HT, which is considerably faster than previous reports.^[48, 49]

We investigated the spectrochemical response of the films to confirm the doping and de-doping processes of the conjugated systems. **Figure 1e** and **Figure S11** show the change in optical absorption of the conjugated polymer films interfaced with the solid 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 is observed, attributable to the π - π^* transition of neutral PEDOT, while the intensity of the polaronic and bipolaronic optical transitions at near IR region decreases correspondingly. At higher positive gate voltages, the intensity of the new absorption feature increases while the intensity of initial polaron-induced transition decreases, consistent with the depletion mode in PEDOT:PSS based OEECT.^[50, 51] For P3HT, its neutral state exhibits an absorption band from ~ 350 nm to ~ 700 nm, corresponding to π - π^* transitions. With increasing negative bias, the first oxidation state appears 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 [TFSI]⁻ anion doping effect.

With the demonstration of a high performance solid state OEECT, we next explore the pressure sensing capability of such a device (**Figure 2a**). For this, the polymer electrolyte is patterned as micro-pyramid arrays using a silicon mold, following by the peel-off and lamination process to assemble an OEECT-based pressure sensor. We note that unlike most of the ion-gels which are viscous and thick, this solid electrolyte is easy to pattern to form micro-pyramid arrays on the surface, acting as active pressure-sensing layer. Each of these pyramids has a square base of $10.5 \mu\text{m}$ side, and tapers to a tip with a height of $8.0 \mu\text{m}$ (SEM images, **Figure S12**, Supporting Information). As shown in the transfer characteristics (**Figure 2b**), the source-drain current changes significantly in response to different pressures, indicating successful detection of pressure stimuli. We also observe that at a constant gate voltage, the leakage current (I_{GS}) increases with increasing applied pressure (**Figure 2c**), which implies the increase in ion migration events to the channel. We therefore hypothesize

that our pressure sensor exploits a new 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.

Figure 2. (a) Device schematic of pressure sensor based on all-solid-state OECT with pyramid structures on polymer electrolyte layer. (b) Transfer and output performance of the pressure sensor under different pressure. (c) The leakage current (I_{GS}) under different pressure stimuli at $V_G = 0.5$ V. Note that error bars represent the s.d. from three different devices. (d) Schematic illustration of the contact modulated ionic doping mechanism for pressure sensor. (e) Pulse measurements (V_G vary from -0.6 V to 0.6 V, pulse length = 0.5 s, $V_D = -0.5$ V) with over 1000 cycles of continuous operation for the all-solid-state OECT under a constant pressure (15 kPa). Inset is the transient response of drain current to gate pulse after 1000 cycles. (f) The sensitivity to pressure of the PEDOT:PSS-based OECT. Error bars represent the sample variation (N=4 devices with same W/L/d= 1000 μm/ 200 μm/ 68.9 nm) and measurement uncertainty. (g) The limit of detection with a flower and a grain of rice. The limit of detection of the OECT-based pressure sensor was performed at $V_D = -0.5$ V and $V_G = 0.6$ V.

According to Bernards and Malliaras model^[52], 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) (**Figure 2a**). Under no applied pressure, there is negligible ion penetration from the solid electrolyte to the polymer channel since the contact area (A) between the electrolyte pyramids and polymer is minimal. 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, resulting in negligible change in I_{DS} . Hence, the charging is limited by C_G (i.e. $C_{CH} > C_G$). Under applied

pressure, the contact area (A) and the compressed thickness (d_c) of pyramid structure increases, ensuing an increase in C_G (i.e. $C_{CH} < C_G$), causing more EMIM⁺ ions to be penetrated 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 **Figure 2d**). The deformed pyramidal structure of electrolyte under pressure can also reduce the resistance of electrolyte (R_E)^[53] due to the compression effect which induces a higher ionic concentration in the channel.^[54-56] The decreased electrolyte resistance thus leads to a higher effective gate potential to modulate the source-drain current. This also corroborates well with **Figure S13** 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 (**Figure 2e**, **Figure S14**, Supporting Information).

The sensitivity of the all-solid-state OECT-based pressure sensor is shown in **Figure 2f**. By deriving the slope in linear sensing regions, we obtain the sensitivity up to ~71.9 kPa⁻¹ in high pressure region (5-15 kPa), which is much higher than previously reported values using capacitive-type (0.55 kPa⁻¹)^[57], piezoresistive-type (27.9 kPa⁻¹)^[8] or micro-structured PDMS dielectric transistor-type (8.2 kPa⁻¹)^[58], **Table S1**. The device also exhibits a response to very low pressure (< 100 Pa) with a sensitivity of ~ 1.74 kPa⁻¹ (see **Figure S15**, Supporting Information). As shown in **Figure 2g**, a flower (~ 11 mg; 1.1 Pa) and a grain of rice (~ 20 mg; 2.0 Pa) were placed on the sensor to test the signal response. The results exhibit the limit of pressure can be obtained as low as 1.1 Pa and the sensing to very low pressure presents good repeatability.

We note that the microstructured solid electrolyte greatly enhances the pressure sensitivity of the sensor relative to that of an unstructured film which does not present obvious response to pressure stimuli (see **Figure S16**, Supporting Information). The different sensitivity at the various pressure regimes can represent different deformation stages of micro-pyramids with pressure. At low pressures (< 4 kPa), the sensing mechanism can be 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 dramatically increases 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 tends to a flat plane due to almost complete compression, and the contact area reached its maximum limit (**Figure S17**, Supporting Information). The transient response (**Figure S18**, Supporting Information) of the current to high (> 5 kPa)/low (<1 kPa) pressure regions show stable stepped and cyclic response supporting the high pressure-sensitive resolution and reproducibility of the pressure sensor.

Figure 3. (a) Transfer performance under different pressure. (b) Sensitivity to pressure of the P3HT device at different pressure region. Error bars represent the sample variation (N=4 devices with same W/L/d= 1000 μm / 200 μm / 81.0 nm) and measurement uncertainty. (c) Color-coded contour plots of absorption spectra of polarized ultraviolet-visible spectroscopy from P3HT films with the solid electrolyte before and after applying pressure. (d) Volumetric capacitance of P3HT film as a function of the applied pressures. (e) Comparison of sensitivity to pressure and operating voltage for different types of pressure sensors. Detailed information and respective references were indicated in **Table S1** in supporting information.

Significantly, we observe an unprecedentedly higher sensitivity at both high and low pressure regimes when the OECT operates in the enhancement mode. Here, we demonstrate a P3HT based OECT where the transfer and output characteristics exhibited a dramatic increasing of I_{DS} with the increase of applied pressure from 0 to 15 kPa (**Figure 3a** and **Figure S19**, Supporting Information). 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 our knowledge, the highest ever reported sensitivity. The electrochemical doping process with applied pressure was also monitored through in-situ spectro-electrochemistry. As shown in **Figure 3c** and **Figure S20**, there is 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 induce electrochemical doping effect in P3HT (**Figure S21**, Supporting Information). At high pressures (>15kPa), when the contact area between the electrolyte and P3HT is maximised, the volumetric capacitance (C_p^*) approaches the volumetric capacitance of P3HT film using a planar solid electrolyte (without microstructures) (**Figure 3d**, **Figure S22**, Supporting Information), indicating efficient contact area induced doping.

The performance of our all-solid-state OECT-based pressure sensors hold the highest reported sensitivity (**Figure 3e**), while operating only at low voltages ($V_D = -0.5$ V and $V_G = -1.3$ 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 is as low as <1 μ W - 1 mW from 15 kPa pressure to no-pressure loading state ($I_D < 2$ μ A - 1.8 mA; $V_D = -0.5$ V, $V_G = 0.6$ V) for depletion mode PEDOT:PSS device. For enhancement mode P3HT device, the ultralow power consumption of < 28 nW at no-pressure loading can be achieved ($I_D < 56$ nA; $V_D = -0.5$ V), while the power consumption at 15 kPa pressure can be varied from <5 μ W - 1.1 mW with $V_G = -0.3$ - 1.3 V ($I_D < 9.6$ μ A - 2.2 mA; $V_D = -0.5$ V). The few μ W in power consumption is several dozen times lower than that of reported transistor-type pressure sensors (< 1 mW; $I_D = 10$ μ A, $V_G = -100$ V)^[58, 59] and piezoresistive-type pressure sensors (< 0.5 mW)^[38, 60].

Figure 4. (a) The tunability of sensitivity by gate voltage. (b) The enlarged view of electrical signals induced by radial artery pulse. (c) The device stability over time. (d) The stability test of sensor over 300 cycles at 1 kPa. (e-f) The schematic diagram and circuit schematic of the 6×6 pressure sensor array. (g) Photograph of flexible sensor array. (h) Static test for the pressure sensor array to demonstrate the ability to mapping the pressure stimuli distribution. The color of each pixel corresponds to the relative signal change caused by applied pressure on the sensing array. Legible N, T, U-shaped patterns can be observed from the mapping results, demonstrating the feasibility to precisely detect and recognize external pressure stimuli with patterned distribution in a static method.

The OECT-based sensors are able to show large tunable sensitivity range through the modulation of gate bias (Figure 4a, Figure S23, Supporting Information). 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 0.55V to 0.5V and to 0.4V respectively. Similarly, the electrical signal response to same pressure level can be tuned with applied gate bias (**Figure S24**, Supporting Information). 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 (**Figure 4b and S25**, Supporting Information) 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 **Figure S26**, 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 $V_G = 0.4 \text{ V}$.

The source-drain current shows no obvious degradation under different pressure over almost 70 days, confirming a high operational stability of the solid-state OECTs (**Figure 4c**). 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% (**Figure 4d**). 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 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 (**Figure 4e-f**). **Figure 4g** shows the highly flexible device array on polyimide substrate while **Figure 4h** 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 (**Figure S27**, Supporting Information).

3. Conclusion

In summary, we have developed high performance all solid-state OECTs based on polymer electrolytes with high ionic conductivity which facilitate excellent electrochemical response in a variety of ion-permeable conjugated polymers. Our all solid-state OECTs also reveal a new strategy for ultrasensitive tactile sensors based on a novel contact modulated 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 enhancement mode), excellent stability over time (more than 2 months), a low limit of detection of 1.1 Pa, a low operating voltage ($\sim \pm 1 \text{ V}$) and ultra-low power consumption ($< 5 \text{ } \mu\text{W}$). The contact modulated 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. We believe 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. We anticipate that our ultrasensitive pressure sensors can be a suitable alternative for monitoring the blood pressure in premature babies and neonates whose skin is extremely sensitive to external pressure.^[61, 62] Hence, the ultrahigh sensitivity at low pressure range (below 1 kPa) enable our soft, lightweight and flexible pressure sensor be attached to the under-developed neonate skin, guaranteeing a high spatial fidelity and ensuring the chances of registering systolic and diastolic pressure events. Furthermore, our pressure sensors are especially suitable for monitoring pressure statically or low frequency movement such as human finger touch, artificial prosthetics as well as many robotic applications, where the physical motions of the robots are not particularly fast. 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.

4. Experimental Section

Materials: Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios PH1000) were purchased from Heraeus. Poly(3-hexyothiophene-2,5-diyl) (P3HT), [6,6]-phenyl-C71-butyric acid methyl ester [PC₇₀BM] molecule, Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP, Mw= 400,000 g/mol), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([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, chlorform and toluene were purchased from Sigma-Aldrich and used as received. Regio-regular 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) was purchased from 1-material inc., Canada.

Fabrication of solid 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 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 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 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. We introduce ionic liquid additive in PEDOT:PSS system to achieve better electronic and ionic transport properties in OECTs as reported in our previous work^[51, 63]. 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 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 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 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 electrolyte with micro-pyramids was transferred as sensitive layer from the mold and used for the lamination on the gate electrode, in which the side without pyramids shapes is contacting with 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 is 5 mV/s 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 $\sim 1 \times 1 \text{ cm}^2$ was attached on the pressing tip of force gauge to provide a buffer force and used to calculate the applied pressure. 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 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.

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 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 (PET) 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.

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