Intrinsically Stretchable Organic Electrochemical Transistors with Rigid-Device-Benchmarckable Performance

Dingyao Liu, Xinyu Tian, Jing Bai, Yan Wang, Yixun Cheng, Weijie Ning, Paddy K. L. Chan, Kai Wu, Junqi Sun, and Shiming Zhang*

Intrinsically stretchable organic electrochemical transistors (OECTs) are being pursued as the next-generation tissue-like bioelectronic technologies to improve the interfacing with the soft human body. However, the performance of current intrinsically stretchable OECTs is far inferior to their rigid counterparts. In this work, for the first time, the authors report intrinsically stretchable OECTs with overall performance benchmarkable to conventional rigid devices. In particular, oxygen level in the stretchable substrate is revealed to have a significant impact on the on/off ratio. By employing stretchable substrates with low oxygen permeabilities, the on/off ratio is elevated from \( \approx 10 \) to a record-high value of \( \approx 10^4 \), which is on par with a rigid OECT. The device remained functional after cyclic stretching tests. This work demonstrates that intrinsically stretchable OECTs have the potential to serve as a new building block for emerging soft bioelectronic applications such as electronic skin, soft implantables, and soft neuromorphic computing.

1. Introduction

Organic electrochemical transistors (OECTs) based on poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS)

D. Liu, X. Tian, J. Bai, Y. Wang, Y. Cheng, W. Ning, S. Zhang
Department of Electrical and Electronic Engineering
The University of Hong Kong
Hong Kong SAR, China
E-mail: szhang@eee.hku.hk

P. K. L. Chan
Department of Mechanical Engineering
The University of Hong Kong
Hong Kong SAR, China

K. Wu
State Key Laboratory of Polymer Materials Engineering
College of Polymer Science and Engineering
Sichuan University
Chengdu 610065, China

J. Sun
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry
Jilin University
Changchun 130012, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/advs.202203418
© 2022 The Authors. Advanced Science published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/advs.202203418
example, the on/off ratio of intrinsically stretchable PEDOT:PSS OECTs fabricated on stretchable substrates such as PDMS was two orders of magnitude lower than that of a rigid device. Besides, the charge carrier mobility of stretchable OECTs has yet to be investigated. The on/off ratio and mobility of stretchable OECTs are essential parameters for evaluating their frequency response and switching properties for emerging soft bioelectronic applications such as stretchable neuromorphic computing and stretchable display. Therefore, in the past years, intensive efforts have been dedicated to resolving these problems, including using a buffer layer between the substrate and channel and using different substrates. However, limited progress was made, and the underlying reasons remain unclear.

In this work, we report the first intrinsically stretchable PEDOT:PSS OECTs with overall performance benchmarkable to a rigid device. In particular, we reveal that the oxygen level of the stretchable substrates plays a decisive role in affecting the on/off ratio. By employing stretchable substrates with low oxygen permeability, the on/off ratio was elevated from ≈10 to a record-high value of ≈10⁴. The device remained functional after cyclic strain tests between 0% and 50%. Besides, those devices showed high mobilities of ≈1.1 cm² V⁻¹ s⁻¹, comparable to that of the rigid device. These results encourage further development of intrinsically stretchable OECTs for emerging soft bioelectronics applications.

2. Results and Discussion

Compared to a rigid device, PEDOT:PSS OECTs fabricated on stretchable elastomers have been suffering from low on/off ratios. Given that the on/off ratio of OECT is mainly dominated by the off-state current (i.e., the de-doping level of the PEDOT:PSS channel) (Figure 1a), we thus hypothesized that there

Figure 1. Performance of intrinsically stretchable OECTs on substrates with different oxygen permeabilities (P_{O_2}). a) Structure of OECTs based on conducting polymer PEDOT:PSS channel. b) The schematic of an intrinsically stretchable OECT. Stretchable elastomers tend to have a larger free volume, which increases the oxygen level and prevents PEDOT⁺ from de-doping at the substrate/channel interface. c) Transfer curves of intrinsically stretchable OECTs fabricated on PDMS substrates of different mixing ratios. d) The correlation between on/off ratios of the devices and oxygen permeabilities (P_{O_2}) of the substrates.
are hidden parameters in the stretchable substrate preventing the channel from de-doping. We further hypothesized oxygen permeability ($P_{O_2}$) is a dominant hidden parameter. As is known, oxygen molecules significantly affect the redox process.\cite{35-37} Different from the rigid substrates, stretchable elastomers are porous and have large free volumes, which can provide accessible pathways for oxygen molecules (Figure 1b). It’s worth noting that the oxygen level in some stretchable elastomers can be ten times higher than that in the electrolyte\cite{38,39} thus, it may considerably affect the on/off ratio.

To verify the above hypothesis, we prepared PDMS elastomers with different $P_{O_2}$ values by controlling the mixing ratios.\cite{40} Stretchable OECTs were subsequently fabricated on these substrates (Figure 1c, detailed in Experimental Section). The correlation between the on/off ratios and the $P_{O_2}$ values is shown in Figure 1d. In line with our hypothesis, reducing the $P_{O_2}$ value significantly reduces the off-state current (Figure 1c). For example, an off-state current of $10^{-1}$ mA was measured on substrates with $P_{O_2}$ of $\approx 1700$ Barrer, while the value dropped to $5\times 10^{-3}$ mA when the $P_{O_2}$ value decreased to $\approx 100$ Barrer (Figure 1c). As a result, the on/off ratio increased dramatically from 10 to 300 (Figure 1d) ($I_{ds}$ ($V_g = 0$ V)/$I_{ds}$ ($V_g = 0.8$ V)).

To further verify the above results, we subsequently fabricated devices on different types of common elastomers, including PDMS, styrene-butadiene rubber (SBR), ethylene propylene diene monomer rubber (EPDM), poly(styrene-ethylene butylene-styrene) (SEBS), ethylene-vinyl acrylate (EVA) and thermoplastic polyurethane (TPU) (Figure 2). The fabrication condition was controlled to let $P_{O_2}$ be the major variable parameter (See details in Experimental Section). The correlation between the on/off ratios and the $P_{O_2}$ values of those different substrates is shown in Figure 2b. In agreement with the above results, an inverse relationship was found between the $P_{O_2}$ values and the on/off ratios. That is, OECTs on substrates with lower $P_{O_2}$ values obtained higher on/off ratios. In particular, the device fabricated on the TPU substrate with an extremely low $P_{O_2}$ value of $\approx 1.0$ Barrer obtained a record-high on/off ratio of $\approx 10^4$, which is benchmarkable to the best value reported for a rigid device of the same dimension. These results were further verified by comparing on/off ratios of devices fabricated on TPU substrates with different $P_{O_2}$ values (Figure S1, Supporting Information).

The high on/off ratio obtained on stretchable substrates of low $P_{O_2}$ values (such as TPU) encourages us to compare its overall
After confirming the high performance, we investigated the stretchability of devices. To make the device fully stretchable, stretchable PEDOT:PSS thin film was used as the planar gate electrode (Figure 4a). A stretchable ionic gel was used as the solid-state electrolyte, and liquid metal (eutectic gallium–indium, EGaIn) was used as probing electrodes to facilitate the connection (detailed in the Experimental Section and Figure S5, Supporting Information). Before the strain test, the device was pre-stretched to 50% strain to stabilize the channel’s conductivity (Figure S6, Supporting Information). The transfer curves obtained during the strain test are shown in Figure 4b,c. Overall, these transfer curves showed minor changes at different strain values or increased strain cycles (Figure S7, Supporting Information). The same trend was recorded for the $g_m$ (Figure S8, Supporting Information), demonstrating the robustness of the device. The mobility maintained at a stable value of $\approx 1$ cm$^2$ V$^{-1}$ s$^{-1}$ before 15% strain. It slightly decreased to $0.85$ cm$^2$ V$^{-1}$ s$^{-1}$ at 50% strain (Figure S9, Supporting Information), attributable to the strain-induced separation of the conductive PEDOT$^+$ conjugated polymer chains, which prohibited the interchain hopping of the holes. The overall performance of the stretchable OECTs is summarized in Figure 4d and Table S1, Supporting Information. To conclude, the devices showed record-high on/off ratio ($\approx 10^4$), high mobility ($\approx 1$ cm$^2$ V$^{-1}$ s$^{-1}$), and intrinsically stretchability (>50%). This is the first time these merits can be harvested in one intrinsically stretchable OECT.
encouraging its immediate use for various soft bioelectronics applications.

Finally, we investigated the mechanism for the devices’ high intrinsic stretchability by comparing the optical microscopic images of PEDOT:PSS films at different strain values (Figure 4e). We noted that PEDOT:PSS films on TPU substrates showed little cracks and maintained a substantial current at 50% strain, while films on other substrates showed evident cracking and a considerable current loss at lower strain values (Figure S10, Supporting Information). It is worth mentioning that the high intrinsic stretchability of PEDOT:PSS films on TPU was obtained without the addition of any plasticizers which were needed for previously reported works. Moreover, the film’s high stretchability could be maintained after increasing the film’s thickness to 1 μm (Figure S11, Supporting Information) or adding the (3-glycidyloxypropyl) trimethoxy silane (GOPS) crosslinker (Figure S12, Supporting Information). Besides, these films showed minor current loss under cyclic strain tests (Figure S13, Supporting Information). The high intrinsic stretchability is attributed to the improved matching of Young’s modulus between the TPU substrates and the PEDOT:PSS films. This conclusion is supported by the finite element analysis (Figured S14 and S15, Supporting Information), which demonstrates that an improved modulus match of those two layers facilitates the dissipation of the stress and favors the formation of microcracks rather than the large transverse cracks, thus improving the intrinsic stretchability of the channel.

3. Conclusions

In summary, we have reported the first intrinsically stretchable PEDOT:PSS OECTs with overall performance benchmarkable to a rigid device. The device obtained a record-high on/off ratio of \( \approx 10^4 \), high mobility of \( \approx 1.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \), and maintained stable performance up to 50% strain. The high performance was realized by minimizing the \( P_{\text{O}_2} \) values of the stretchable substrates, which facilities the de-doping of the PEDOT:PSS channel. The presented high-performance intrinsically stretchable OECTs can be immediately used as a new device paradigm to impact the field of soft bioelectronics. We envision that this work will significantly promote the further development of tissue-like OECTs in those fast-rising research areas such as epidermal biosensing, soft neuromorphic computing, and soft human-machine interfaces.

4. Experimental Section

Materials: PEDOT:PSS aqueous suspension (Clevios PH1000) was purchased from Heraeus Electronic Material (USA). Glycerol, dodecylbenzene sulfonic acid (DBSA), sodium chloride, (3-glycidyloxypropyl)
trimethoxysilane (GOPS), cetyltrimethylammonium bromide (CTAB), ammonium persulfide (APS), acrylamide (AAm), N-Tetramethylethylenediamine (TEMED) and N,N'-methylenebisacrylamide (MBAA) were purchased from Sigma-Aldrich Co (USA). The liquid metal, eutectic gallium-indium (ECaIn), was supplied by Flystone Electronics Co. (Zhejiang, China). PDMS (Sylgard 184 silicone elastomer) was purchased from Dow Corning (USA). Styrene-butadiene rubber (SBR) was provided by Baling Petrochemical Co (China). Ethylene-vinyl acetate copolymer (EVASO, 50% vinyl acetate) was purchased from Yanshan Petrochemical Co. (China). Polyether-based TPU was provided by Covestro AG. (Desmopan 9385) and BASF Co. (Elastollan 1195 A). The semi-permeable TPU film was purchased from 3M Co. (The United States). Poly(styrene-ethylene-butylene-styrene) (SEBS) was provided by Sigma-Aldrich Co (The United States). N,N-dimethylformamide (DMF), tetrahydrofuran (THF), and toluene were obtained from Aladdin Co. (Shanghai, China). The silver paste was purchased from Voltera Co. (USA). The water-soluble tape (HD 5414) was provided by 3M Co. (USA).

Preparation of PEDOT:PSS Mixtures: PEDOT:PSS aqueous suspension was firstly stirred for 3 min and then mixed with glycerol (5 v/v%) and DBSA (0.1 v/v%) with a Vortex (MX-S). The addition of glycerol was to increase the film conductivity. DBSA was added to facilitate the wetting property of films on substrates. Then the mixed suspension was filtered with a polytetrafluoroethylene (PTFE) membrane (aperture size of 0.45 µm) to remove aggregates for further use.

Preparation of Stretchable Substrates: Elastic substrates were fabricated through a typical solution casting process. Under the heating temperature of 80 °C, TPU grains were dissolved in DMF, SEBS and SBR were dissolved in toluene. EVA grains were dissolved in THF at room temperature. For all these elastomer solutions, 10 w/w.% solutions were prepared by mixing 1 g elastomer with 9 g corresponding solvent. After being fully dissolved, the obtained solution was cast on a 2.5 cm × 7.5 cm glass slide, and the elastic substrates were obtained after drying overnight at room temperature in the fume hood. Before preparing PDMS substrates, CTAB solution (0.005 M) was prepared and then spun coated on a glass slide as an anti-adhesive layer to ease PDMS peeling-off at the end of the process. In the next, the base and curing agent of PDMS were mixed. To obtain PDMS with different oxygen permeability, the mixing ratio of the base and curing agent was controlled between 5:1 (low permeable) and 20:1 (highly permeable). When benchmarking the performance of PEDOT:PSS films under strain was studied with a Nikon optical microscope. The Young’s modulus of the elastomers was measured with an Instron E-3000 tensile tester under a slow tensile rate of 5 mm min⁻¹. The O₂ permeation analysis was conducted under constant volume/variable pressure conditions using a VAC-V2 film permeability testing machine (Labthink Instruments, Jinan, China).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

D.L. and X.T. contributed equally to this work. S.Z. acknowledges the startup fund, the Innovation Wing Two Research Fund, the Seed Funding for Strategic Interdisciplinary Research Scheme from the University of Hong Kong (HKU), and The Innovation and Technology Fund (Mainland-Hong Kong Joint Funding Scheme, MHP/053/21) and Shenzhen-Hong Kong-Macau Technology Research Programme (SGDX20210823103537034) for supporting this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

high performance, oxygen permeability, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate), stretchable organic electrochemical transistors, stretchable substrates

Received: June 12, 2022
Published online: July 29, 2022
