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A general strategy to achieve high-fidelity electron-ion transduction

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In a recent work published in *Matter*, Yao et al. proposed a general strategy to resolve the intrinsic conflict among capacitance, conductivity, and mechanical properties in conventional electrode design, by rationally designing the porous structure of conducting polymer hydrogel at micro- and nanoscales. Distinct from the inert metal electrodes, the designed conducting polymer hydrogel electrode renders high-fidelity of ionic-electronic transduction and interfacial stability, paving the way for developing next-generation ionotronics devices.

Electron-ion transduction is prevalent and widely occurs at the interface of human-machine interaction for electrophysiological collection of the brain, heart, and muscle, as well as in energy storage devices such as batteries, supercapacitors, and fuel cells [1]. To achieve

high-fidelity electron-ion transduction, a promising technology termed ionotronics was proposed to make electron and ionic signals mutually transduced in both directions.[2] The key of ionotronics lies in the rational design of electrode materials by decorating the commonly-used inert metal electrodes with conductive porous materials such as conducting polymer hydrogels.[3] Ideal electrode materials for ionotronics devices necessitate several key features simultaneously: high electric-double-layered capacitance in a wide-ranging frequency, large electrical conductivity, excellent mechanical-compliant properties, and good biocompatibility.[4] Despite remarkable progress, exploiting optimal electrodes for electron-ion transduction is still limited by some formidable challenges. First, the large capacitance of electrodes is typically achieved by improving porosity,[5] which inevitably impairs the electrical conductance pathway and structural integrity, leading to inferior electrical conductivity and mechanical properties. Thus, an inherent conflict exists between capacitance, conductivity, and mechanical properties, posing severe difficulty in the design of electrode materials.[6] Second, the commonly-used inert metal electrodes are generally plagued with direct contact with ionic electrolytes, causing an undesirable faradic electrochemical reaction, generating high and unstable impedance crossing the electrode/electrolyte interface. Moreover, the undesirable interfacial impedance caused a significant loss and distortion of signal, standing in striking contrast to many applications in such frequency signals, especially low-frequency signals (<100 Hz). Third, owing to the intrinsic rigid feature, the inert metal electrodes as the current collectors have been found to induce adverse immune responses, especially in the scenario of implantation sites, due to the mechanical mismatch between the electronic materials and the organism. The above-mentioned vital issues are faced by nearly all ionotronics and need

more attention to solve.

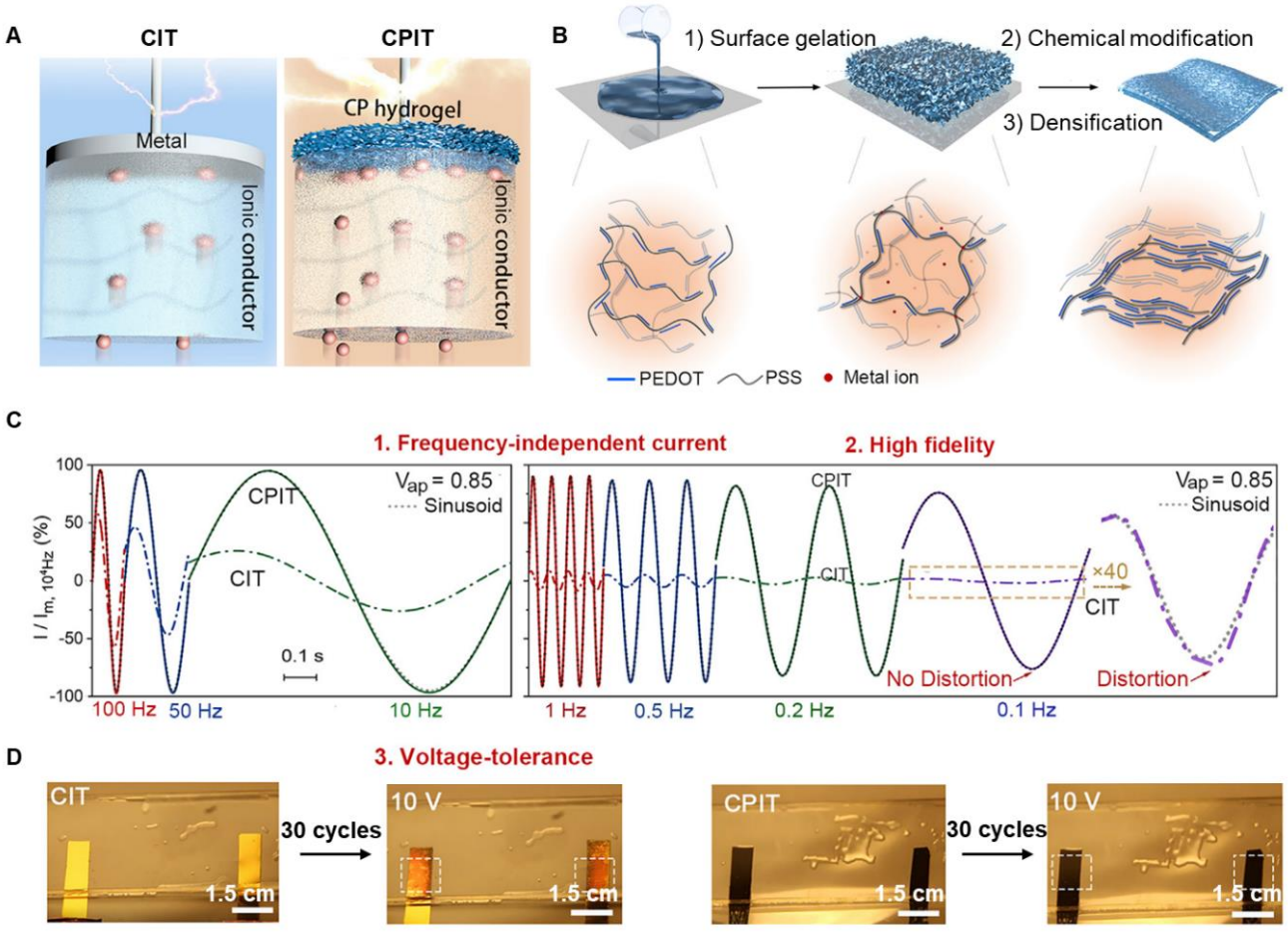

Figure 1. Synthesis process and the performance of a common ionotronics (CIT) and a conducting polymer-assisted ionotronics (CPIT). A. Illustrative schematics of common ionotronics (CIT) with the inert metal electrode and conducting polymer-assisted ionotronics (CPIT) with the PEDOT:PSS hydrogel-based electrode. B. Preparation procedures for CP hydrogels with the corresponding structural change of CP chains. C. Normalized current vs. time curves of CITs (dashed line) and CPITs (solid line) upon sinusoidal AC voltage. D. Digital photographs of CIT and CPIT before and after 30 cycles of sinusoidal AC voltage were applied (amplitude 10 V, frequency 1 Hz).

The present study by Yao et al.[4] in *Matter* introduced a general strategy to resolve those issues encountered in the electron-ion transduction of conventional metal electrodes,

by developing an ultrastrong, highly capacitive, and conductive PEDOT: PSS-based conductive polymer (CP) hydrogel electrode to replace the conventional metal counterparts via a three-step fabrication method (Figure 1A). As shown in Figure 1B, the commercially available PEDOT:PSS suspension was first spontaneously cross-liked on a polydimethylsiloxane (PDMS) substrate coated with a thin layer of carbonyl Fe microparticles (Fe_{mp}). The underlying mechanism originates from the strong electrostatic interaction between PSS chains and the in-situ formed Fe^{2+} through the corrosion of Fe_{mp} within the highly-acid PEDOT:PSS suspension. To improve the conductivity of the PEDOT:PSS hydrogel, H_2SO_4 was employed to chemically induce phase separation and configurational transformation, accompanied by partially removal of Fe^{2+}. Finally, the PEDOT: PSS hydrogel was infiltrated with a diluted H_2SO_4 aqueous solution, followed by drying and dialyzing, all of which are very crucial to tune the micro- and nanoscales pore structure of hydrogels for achieving optimal capacitance, mechanical strength, and conductivity.

The synthesized PEDOT:PSS-based CP hydrogel containing numerous nanopores possesses a high surface area and exhibits a nearly ideal electric double-layer capacitance, which is the cornerstone for guaranteeing efficient electron-ion transduction. Different from the previously reported conductive porous materials[7,8], sacrificing mechanical strength and conductivity to pursue a maximum charge storage ability, the PEDOT:PSS-based CP hydrogel delivers high volumetric capacitance, improved mechanical strength, and high conductivity, owing to the phase separation and configurational transformation that induce numerous and more substantial π-π interactions and the interconnected conductive PEDOT-rich domains. Particularly, by optimizing the chemical treatment process and densification

degrees, the PEDOT: PSS-based CP hydrogel showed an ultrahigh conductivity of 1254 $S \cdot cm^{-1}$ and high tensile strength of 30 MPa, much higher than those of conductive hydrogels reported previously. To demonstrate the advantage of electron-ion transduction, the PEDOT: PSS-based CP hydrogel was applied as conducting polymer-assisted ionotronics (CPIT), replacing the Pt electrodes in the common ionotronics (CIT). Contrary to CIT, CPIT was hardly interfered by the electrochemical redox reactions at the electrolyte/electronic interface, reflected by the stable impedance and phase angle upon decreasing the frequency from 10^5 to 1 Hz in the EIS plots. Owing to the negligible occurrence of interfacial redox reactions, CPIT outputted a frequency-independent current under a low amplitude (Vap,0.85V) with the frequency decreased from 10^5 to 0.1Hz, showing the excellent advantages as an ionotronic device to perfectly transmit electrical signals with high fidelity. Moreover, the CPIT exhibited a high voltage tolerance of up to 10 V because of the low interfacial voltage across the CP-electrode/electrolyte interface. Such high voltage tolerance can be sustained for at least 10,000 cycles without a noticeable change in electrode appearance or the occurrence of gas evolution, indicating excellent stability in high voltage tolerance (Figures 1C and D).

The improved signal fidelity and voltage tolerance of highly capacitive PEDOT:PSS-based CP hydrogel electrode offer extensive opportunities to explore many promising applications in soft ionic-conductor-based devices such as bioelectronics. First, PEDOT:PSS-based CP hydrogel electrode can be harnessed for electrical stimulations in neuromodulation applications. By manipulating the spatial position of the PEDOT:PSS-based CP hydrogel pattern to regulate the spatial distribution of current density, multipoint selective electrical stimulation can be obtained in a simple device configuration. Taking the electrical stimulation

of fibroblast cells as a typical example, the PEDOT:PSS-based CP hydrogel significantly facilitated fibroblast cell proliferation over the control group, exhibiting decent therapeutic ability in wound healing. In addition to electrical stimulations, the PEDOT: PSS-based CP hydrogel was also fabricated as an epicardial electrode to pace a euthanized porcine heart. The PEDOT:PSS-based CP hydrogel stimulated the heart response at a much lower voltage of 0.4 V, much lower than both Au (1.6 V) and Pt/C (1.0 V) electrodes. Such a significant reduction in stimulation power makes the PEDOT: PSS-based CP electrodes promising as a pacemaker in ultralow energy consumption and safer manner.

This work of Yao et al. is an example of how to achieve high-fidelity electron-ion transduction by designing a porous structure of conducting polymer hydrogel at multiple length scales, taking a step forward for ionotronics to better bridge rigid electronics with soft biological organisms. Moving forward, the interface between PEDOT:PSS-based CP hydrogel electrode and the electron-conducting lead of the external circuit could be further investigated. In the present work, the authors leveraged PEDOT:PSS-based CP hydrogel electrode to satisfactorily resolve the issues of electron-ion transduction in the interface of electrolyte, yet they ignore the interface of the external circuit that faces the same challenge. More effort should be spared to explore electrode materials for fully addressing the interfacial issues of electron-ion transduction. Furthermore, the PEDOT:PSS-based CP hydrogel electrode demands many additional functions, such as interface bio-adhesion and dynamical mechanical compliance, to better interact with soft biological organisms. It will also be important to consider how to scale up and integrate the PEDOT:PSS-based CP hydrogel electrodes into other functional devices to achieve better performance, such as excellent

rectifying performance of ionic-based transistors, high output performance of triboelectric generators, and large signal-to-noise ratio of neural probes. From a broad perspective, this work of Yao et al. is an important contribution toward the development of next-generation ionotronics devices and beyond.

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Reference

1. Rapid Electron TunnelingThrough Oligophenylenevinylene Bridges.
2. Yang, C., and Suo, Z. (2018). Hydrogel ionotronics. Nature Reviews Materials *3*, 125-142. 10.1038/s41578-018-0018-7.
3. Yao, B., Wu, S., Wang, R., Yan, Y., Cardenas, A., Wu, D., Alsaid, Y., Wu, W., Zhu, X., and He, X. (2021). Hydrogel Ionotronics with Ultra‐Low Impedance and High Signal Fidelity across Broad Frequency and Temperature Ranges. Advanced Functional Materials *32*. 10.1002/adfm.202109506.
4. Yao, B., Yan, Y., Cui, Q., Duan, S., Wang, C., Du, Y., Zhao, Y., Wu, D., Wu, S., Zhu, X., et al. (2022). Ultrastrong, highly conductive and capacitive hydrogel electrode for electron-ion transduction. Matter. 10.1016/j.matt.2022.09.004.
5. Fang, Y., Prominski, A., Rotenberg, M.Y., Meng, L., Acaron Ledesma, H., Lv, Y., Yue, J., Schaumann, E., Jeong, J., Yamamoto, N., et al. (2021). Micelle-enabled self-assembly of porous and monolithic carbon membranes for bioelectronic interfaces. Nat Nanotechnol *16*, 206-213. 10.1038/s41565-020-00805-z.
6. Jia, K., Li, X., and Wang, Y. (2021). Electrochemical breakdown in hydrogel ionotronic devices. Soft Matter *17*, 834-839. 10.1039/d0sm01789b.
7. Li, Z., Gadipelli, S., Li, H., Howard, C.A., Brett, D.J.L., Shearing, P.R., Guo, Z., Parkin, I.P., and Li, F. (2020). Tuning the interlayer spacing of graphene laminate films for efficient pore utilization towards compact capacitive energy storage. Nature Energy *5*, 160-168. 10.1038/s41560-020-0560-6.
8. Yang, X., Cheng, C., Wang, Y., Qiu, L., and Li, D. (2013). Liquid-mediated dense integration of graphene materials for compact capacitive energy storage. Science *341*, 534-537. 10.1126/science.1239089.