Supporting information

1 Negative Space Charge Modulated Ion Transport through
2 PEDOT: PSS Hydrogel Integrating Nanofluidic Channels for
3 High-Efficient Osmotic Energy Harvesting

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Supporting information

Experimental Methods

To further verify the effect of the thickness and composition (PEDOT: PSS) of the hydrogel membrane on the acquisition of osmotic energy, different single-factor experiments were executed separately. Firstly, hydrogel membranes of 100 µm, 200 µm, 300 µm, 400 µm, 500 µm, and 600 µm sizes were prepared and assembled into the osmotic energy acquisition device to verify the effect of membrane thickness on osmotic energy performance with the concentration gradient of artificial seawater and river water, respectively. Then, the thickness of the membrane was fixed at 236 µm, and the effect of PEDOT: PSS addition on the output power was verified by controlling the amount of PEDOT: PSS added (1%, 3%, 5%, 7%, 10%, 15%, 20%, and 25%) with the concentration gradient of artificial seawater and river water.
Fig. S1 Schematic of synthesis of conventional permeable membrane. The preparation of permeable membranes by composite/modified polymers with 2D materials was previously considered a viable option, but the complicated process and lower stability posed significant challenges to its advancement.
Supporting information

Fig. S2 (a)-(c) C1s XPS spectra and (d)-(f) S2p XPS spectra of PEDOT: PSS hydrogel.

As depicted in Fig. 1(b), the shift of the $C\alpha=C\beta$ bond in PEDOT to lower wavelengths, the slight shift of the C-S-C bond ($579 \text{ cm}^{-1}$) to shorter wavelengths, coupled with its significant enhancement upon $\text{H}_2\text{SO}_4$ doping, which these indicate the increase of quinone structure in the main chain of PEDOT. As shown in Fig. S2(a)-(c), the peak at 284 eV corresponds to the C-C/C=C bond in PSS, while the peak at 286 eV corresponds to the C-O/C-S bond in PEDOT. Obviously, the increased ratio of C-C/C=C to C-O/C-S indicates that more sulfonates in the PSS chain segments form hydrogen bonds with PVA or PA. Meanwhile, in the S(2p) XPS spectra (Fig. S2(d)-(f)), the peaks at 166-172 eV and 161-166 eV were attributed to the sulfur atoms in PSS and PEDOT, respectively. The proportion of sulfur elements in PSS and PEDOT gradually increases with further doping cross-linking, which was attributed to the substitution of partial PSS by PA during the cross-linking process and the doping of $\text{H}_2\text{SO}_4$. 
**Fig. S3** Bending strain analysis model.
Fig. S4 Conductivity test results of PEDOT: PSS hydrogels adding different amounts of (a) GA, (b) PA and (c) H$_2$SO$_4$, respectively.
Fig. S5 Comparison of conductivity with the reported composite conductive hydrogels.\textsuperscript{1-20}
Fig. S6 Nano-channel computational modeling.
MEASUREMENT OF OSMOTIC ENERGY CONVERSION

As shown in Fig. 4(f), the whole circuit diagram consists of three parts: the electrode, membrane, and external circuit. Among them, the membrane includes membrane resistance $r_{int}$ and transmembrane diffusion potential. $r_{int}$ denotes the ion transport resistance in the ion-selective membrane. $E_{diff}$ is generated by the concentration gradient on both sides of the membrane, which can be calculated by the following equation:

$$E_{diff} = (2t + 1) \frac{RT}{zF} \ln \left( \frac{\gamma_H C_H}{\gamma_L C_L} \right)$$

where $R$ is the universal gas constant, $T$ is the Kelvin temperature, $Z$ is the ion valence state, and $F$ is the Faraday constant. $C_H$ and $C_L$ are the ion concentrations at high concentrations and low concentrations, respectively. $\gamma_H$ and $\gamma_L$ are the ion activity coefficients of the high-concentration solution and low-concentration solution, respectively.

The measured $V_{oc}$ is the sum of $E_{diff}$ and $E_{redox}$ as in the following formula:

$$V_{oc} = E_{diff} + E_{redox}$$

The electrodes can be abstracted as the redox potential $E_{redox}$, which is derived from the electrode potential drop when the two electrodes enter solutions of different concentrations. The $E_{redox}$ can be calculated by the following equation:

$$E_{redox} = \frac{RT}{zF} \ln \left( \frac{\gamma_H C_H}{\gamma_L C_L} \right)$$

The external circuit consists of an external load $r_L$ and an ammeter used to measure the current in the circuit.
Supporting information
Fig. S7 The device stability of power generation.
Fig. S8 The influence of the hydrogel membrane thickness in osmotic energy performance.
Supporting information

**Fig. S9** The influence of PEDOT: PSS addition in osmotic energy performance.
Supporting information

**Fig. S10** Schematic representation of the ICEG setup.

**Table S1** Electrochemical parameters of a single unit of the ICEG.

<table>
<thead>
<tr>
<th>Configuration (I)</th>
<th>$V_0$ (mV)</th>
<th>$V_{theo}$ (mV)</th>
<th>Permselectivity (%)</th>
<th>Conversion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>396</td>
<td>414</td>
<td>95.6</td>
<td>45.8</td>
</tr>
</tbody>
</table>

The parameters of a single unit of the PEDOT: PSS membrane pair were measured in an ICEG device (Fig. S10). Ag/AgCl was used as the cathode and anode. The high concentration (HC) and low concentration (LC) of the salt solutions were 3.0 M and 0.3 µM, respectively. The membrane permselectivity ($\alpha$) could be calculated as the ratio between the measured membrane potential ($V_{meas}$) and the theoretical membrane potential ($V_{theo}$): \(^{21,22}\)

$$\alpha(\%) = \frac{V_{meas}}{V_{theo}} \times 100$$

$$V_{theo} = \frac{NRT}{zF} \ln \left( \frac{a_H}{a_L} \right)$$

where $N$ is the number of membranes, $\alpha$ is the average membrane permselectivity of an anion and a cation exchange membrane, $R$ is the universal gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)), $T$ is the absolute temperature (K), $z$ is the electrochemical valence, $F$ is the
Supporting information

Faraday constant (96485 C·mol\(^{-1}\)), \(a_H\) is the activity of the concentrated solution (mol·L\(^{-1}\)), and \(a_L\) is the activity of the diluted solution (mol·L\(^{-1}\)). For seawater (3.0 M KCl) and river water (0.3 µM KCl) the theoretical voltage difference over each membrane for 100% selective membranes is 414 mV.

The electrochemical conversion efficiency (\(\eta\)) can be calculated by the following formula:

\[
\eta_{\text{max}} = \frac{\alpha^2}{2}
\]
**Supporting information**

**Table S2** Comparison of osmotic energy conversion performance.

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Testing area (mm²)</th>
<th>Energy conversion performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET membrane</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>0.86 W/m²</td>
<td>[54]</td>
</tr>
<tr>
<td>PAM hydrogel membrane</td>
<td>Artificial seawater and river water</td>
<td>28</td>
<td>0.37 W/m²</td>
<td>[55]</td>
</tr>
<tr>
<td>SPEEK membranes</td>
<td>Artificial seawater and river water</td>
<td>28</td>
<td>5.8 W/m²</td>
<td>[56]</td>
</tr>
<tr>
<td>HEMAP hydrogel membrane</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>5.38 W/m²</td>
<td>[57]</td>
</tr>
<tr>
<td>Loofah sponge membranes</td>
<td>Artificial seawater and river water</td>
<td>60</td>
<td>0.0183 W/m²</td>
<td>[58]</td>
</tr>
<tr>
<td>MMT membranes</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>2.1 W/m²</td>
<td>[59]</td>
</tr>
<tr>
<td>KANF membranes</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>4.8 W/m²</td>
<td>[60]</td>
</tr>
<tr>
<td>GOMs membrane</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>4.94 W/m²</td>
<td>[61]</td>
</tr>
<tr>
<td>PPC membrane</td>
<td>Artificial seawater and river water</td>
<td>0.075</td>
<td>2.2 W/m²</td>
<td>[62]</td>
</tr>
</tbody>
</table>
## Supporting information

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Solution Type</th>
<th>Transmittance</th>
<th>W/m²</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOF membrane</td>
<td>0.5M/1mM NaCl solution</td>
<td>0.02</td>
<td>5.7</td>
<td>[63]</td>
</tr>
<tr>
<td>Glass membrane</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>4.16</td>
<td>[64]</td>
</tr>
<tr>
<td>MMT membranes</td>
<td>Artificial seawater and river water</td>
<td>0.03</td>
<td>4.13</td>
<td>[65]</td>
</tr>
<tr>
<td>PEDOT: PSS</td>
<td>Artificial seawater and river water</td>
<td>38.5</td>
<td>6.26</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: Composition of simulated seawater (NaCl: 0.454M; MgSO₄: 0.028M; MgCl₂: 0.0257M; CaCl₂: 0.0103M; KCl: 0.00972M; NaHCO₃: 0.00241M) and river water (NaCl: 0.01M).
**Supporting information**

**Fig. S11** Electrochemical cell series device.
Fig. S12 River water pre-treatment unit. In practical application, flowing river water flows into the series-connected ICEG devices through serpentine microchannels and settling tanks, which can effectively buffer the current impact and reduce impurities.
Fig. S13 Schematic diagram of ICEG devices.
Supporting information

Fig. S14 (a) Schematic diagram of the electrical double layer mechanism (EDL) next to a negatively charged wall. (b) Diffusion-osmotic current induced by salt concentration difference. (c) Sketch of the nanofluidic osmotic energy conversion model. (d) Electrical distribution from charged wall to bulk solution.

We built a two-dimensional model to illustrate the osmotic energy conversion process, as shown in Fig. S14c. The model consists of a high concentration of seawater, a low concentration of river water and a hydrogel nanochannel membrane. In the negatively charged nano-channels, the electrostatic force repels ions with the same charge (co-ions, negatively charged Cl\(^{-}\) ions in our work) near the channel surface and attracts ions with the opposite charge (counter-ions, positively charge K\(^{+}\) ions in our work) to compensate the fixed charges (in our study negatively charges introduced by sulphuric or phosphoric acid groups) on the surface, thus leading to a charge redistribution. However, only a fraction of counter-ions ends up at the charged wall. A graded electric double-layer (abbreviated as EDL) is created between the nano-channel wall and the electrolyte solution, with an increased concentration of counter-ions and a decreased concentration of co-ions (Fig. S14a). The EDL refers to the Stern and diffusion layers.
The Stern layer is comprised entirely of counter-ions due to contact interactions. The diffusion layer is the region from the Stern layer to the bulk solution, where the distribution of free ions is still governed by the Coulomb force, electrically screened by the Stern layer. As depicted in Fig. S14b, the interaction between counterions in the nano-channel and the charge of its inner wall is usually simplified by an exponentially decaying potential. Through this interaction, by which way the channel is filled with a close to unipolar solution of counter-ions, and ion selectivity of transport can be observed. Based on the ion-selectivity mechanism, a streaming current is generated when the ionic solution is propelled by an external mechanical driving force (a transmembrane concentration difference) through charged nanofluidic channels (Fig. S14d). In this way, the net charge (counter-ions, K$^+$ in our work) within the diffused double layer moves at a certain velocity under the effect of a concentration gradient. At this point, counter-ions (K$^+$ ions in this work) spontaneously and preferentially diffuse along the diffused double layer within the nano-channels. Ideally, the transport of counter-ions is proportional to the charge density on the surface of the nano-channel. Conductance measurements reveal the charge-control ion transportation within the PEDOT: PSS hydrogel membrane, as shown in Fig. 3(c), where the measured ionic conductance exhibited two distinct characteristic behaviors. Specifically, above the 0.5M concentration point, the ionic conductance of the membrane follows the bulk rule of linearly increasing with concentration. However, the conductance deviates from the bulk value and gradually approached smoothing at concentrations less than 0.5M. In the low concentration region, the selective transport of ions tends to be controlled by the double electric layer within the nano-channel, as depicted in Fig. S14d. Because of the negatively charged surface in the channel (the intrinsic negative charge of the nano-channel inner wall is introduced by sulfate or phosphate groups during the synthesis of the hydrogel), K$^+$
Supporting information

ions with opposite charges will be separated from identically charged Cl\(^-\) ions in the channel, creating a unipolar environment.
Table S3 Price Comparison of Permeable Membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Component</th>
<th>Functional Group</th>
<th>Size for single sheet</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMI-7001S anion exchange membrane a</td>
<td>Gel polystyrene cross linked with divinylbenzene</td>
<td>Quaternary Ammonium</td>
<td>1.2 m × 1.0 m × 0.45 mm</td>
<td>$350 per sheet</td>
</tr>
<tr>
<td>CMI-7000S cation exchange membrane a</td>
<td>Gel polystyrene cross linked with divinylbenzene</td>
<td>Sulphonic Acid</td>
<td>1.2 m × 1.0 m × 0.45 mm</td>
<td>$350 per sheet</td>
</tr>
<tr>
<td>PEDOT: PSS membrane</td>
<td>PEDOT: PSS hydrogel</td>
<td>Phytic Acid PSS</td>
<td>1.2 m × 1.0 m × 1.0 mm</td>
<td>$10 per sheet</td>
</tr>
</tbody>
</table>

a The commercial ion exchange membranes were provided by Membrane International Inc.
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