# **Electronic supplementary information (ESI)**

## The enhanced ionic thermal potential by polarized electrospun membrane

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## Note S1. Experimental Section

**Materials**. Poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) ( $M_W$ =400,000), N,N-dimethylformamide (DMF), 1-Ethyl-3-methylimidazolium ethyl sulfate (EMIM ES) and Hydroxyethyl cellulose (HEC) ( $M_W$ =250,000) were purchased from Sigma Aldrich.

**Electrolyte preparation**. Hydroxyethyl cellulose (HEC) (10 wt%) was added into 1-Ethyl-3methylimidazolium ethyl sulfate (EMIM ES) and stirred at 110°C until homogeneous viscous solution formed. The final solution was then used as the electrolyte.

**Polarized fibrous membrane preparation**. 15 (w/v%) of P(VDF-HFP) pellets was dissolved in a mixed solvent of DMF and acetone (3:2 v/v). The mixture was then stirred for 4 h at room temperature. The solution was poured into a syringe. A pump was used to deliver the solution to a needle with diameter of 0.8 mm. During the electrospinning, the flow rate was 5  $\mu$ l/min, the voltage was 15 kV and the needle-to-collector distance was fixed at 15 cm. The fibers were collected at a grounded aluminum collector. The as-spun membrane was considered as downpolarized fiber mats, and up-polarized devices was prepared by transferring them facing down to another Al electrode.

**Device preparation**. All the glass slides used in experiments were cleaned in the following procedure. The glass slides were ultrasonicated in soap water followed by deionized (DI) water. Then they were rinsed with DI water, acetone, isopropanol and dried by blowing N<sub>2</sub> then baked at 130°C in oven for 30 min. Al foil strips of 1mm width were used for bare Al electrode. Al foil collector with electrospun fiber were also cut into strips of 1 mm width to be directly used as electrodes for the polarized membrane side of the device. A thin layer of the prepared electrolyte was coated on the clean glass slide and then the electrodes were placed in a face-down manner. Different electrodes were used according to the different configuration of the devices. For sealed devices the electrolyte layer were encapsulated with polyimide tape.

**Characterization**. The thermoelectric measurements were performed in a home-built setup. The temperature was controlled by two Peltier elements via Labview program, and the temperature difference between two electrodes was monitored using a pair of thermocouples simultaneously. The open-circuit voltage generated by the devices was measured using a Keithley 2182A nanovoltmeter set to auto-range. The temperature cycles were applied through Labview program. Open-circuit voltage measurements throughout this work were done under cleanroom humidity of 38% to 40% (if not specified). The Fourier Transform Infrared Spectroscopy (FT-IR) for the electrospun fiber membranes and electrolyte were recorded with Bruker, Equinox 55.

The piezoelectric response from the devices was tested at room temperature and recorded with National Instrument (NI) systems. The applied force was controlled by tuning the amplitude of the shaker, and the frequency was maintained at 5 Hz. The distance between the probe and the sample surface was kept at 1 mm for all the tests. The effective contact area is 1.13 cm<sup>2</sup>. The logging system is NI CDAQ 9174 chassis with NI 9263 voltage output and NI 9239 DAC modules interfaced with a computer using LabVIEW software.

#### Note S2. Characterization of the polarized membrane

The polarized electrospun fibers were characterized with piezoelectric response. As shown in Fig. S1a, the piezoelectric output voltage of 2.4 V can be measured when applying a force of 24 N. The piezoelectric coefficient of the electrospun fiber mats is 14 pC/N, which is in agreement with the previous reported values.<sup>1,2</sup> In order to confirm the different polarization directions of the electrospun fibers, two different devices with double layer of fibermats were made. For the device with fiber mats that have dipoles in two different directions the piezoelectric response cancels out and shows very small value (Fig. S1b). Whereas, when the dipoles are layered in the same direction they add up and show higher piezoelectric output voltage (Fig. S1c).



**Fig. S1**. Piezoelectric response of the P(VDF-HFP) membranes with (a) one layer, (b) Opposite polarization direction and (c) same polarization direction.

#### Note S3. Conductivity characterization of electrolyte

The EMIM ES with 10% HEC electrolytes with and without P(VDF-HFP) fiber mat was characterized with impedance spectroscopy (frequency: 10<sup>7</sup> to 10<sup>-1</sup> Hz, amplitude:10 mV). The distance between the two electrode was 2 mm and the area was 1.18 mm<sup>2</sup>. The real part of impedance and phase angle are given in Fig. S2a and b, and the Nyquist plot is given in Fig. S2c. The plot shows similar pattern of Nyquist plot with previously reported ionic conductors.3,4 The ionic conductivity of the two electrolytes was calculated by using the first intercept of the high frequency semi-circle, where the response is fully resistive. The ionic conductivity is found to be 11.7 and 11.5 mS/cm, respectively. This result shows that the ionic

conductivity of the electrolyte does not change obviously whether there is P(VDF-HFP) fiber mat layer in the device.



**Fig. S2**. (a) Real part of impedance and (b) phase angle versus frequency plot and (c) Nyquist plot for electrolyte with and without P(VDF-HFP) fiber mat.

### Note S4. The characterization setup for the ionic thermoelectric measurement

The Seebeck coefficient of all the devices were measured with the setup in Fig. S3. Two peltier elements with a controlled separation were used to apply temperature difference. A thermocouple was connected to the surface of the Peltier element with electronic loop to control the heating and cooling.



**Fig. S3.** The photograph of the ionic thermoelectric measurement setup (sealed sample as the example).

The two electrodes of the measured device were mounted on the peltier elements, and another pair of thermocouples were placed on top of each electrode to record the temperature difference. The thermal voltage was measured between the two electrodes.

Electrolyte materials	Seebeck coefficient	sealing	Humidity	Reported
			dependency	year (Ref)
NaOH in PEG	7-15 mV/K	yes	no	2022 (5,6)
EMIM ES with HEC	4-5 mV/K	yes	no	2022 (7)
EMIM ES with HEC	5-15 mV/K	no	yes	2022 (7)
PEGDA/ 2-HEA-EIMIM TFSI	10-30 mV/K	yes	yes	2023 (8)
PVDF-HFP/EMIM TFSI	-4 mV	no	Not reported	2020 (9)
PVDF-HFP/EMIM DCA	10-26 mV/K	no	Not reported	2020 (10)
SiO2/EMIM DCA	8-15 mV	no	Not reported	2020 (11)
PANI:PAAMPSA:PA	2-8 mV/K	no	yes	2020 (12)
PEDOT:CuCl2	-16-10 mV/K	no	yes	2019 (13)
PEDOT:PSSH	10-16 mV/K	no	yes	2018 (14)
PSSNa/CNF	5-8 mV/K	no	yes	2018 (15)
PSSNa	1-4 mV/K	no	yes	2017 (16)
EMIM ES with HEC in	20 mV/K	no	yes	This work
polarized P(VDF-HFP)				
EMIM ES with HEC in	15 mV/K	yes	no	This work
polarized P(VDF-HFP)				

**Table S1.** The comparison of typical reported ionic Seebeck coefficients.



Fig. S4. The potential difference between different electrodes at room temperature.

# Note S5. FTIR characterization of the composite of P(VDF-HFP) fiber mats and EMIM ES-HEC electrolyte



**Fig. S5**. The FTIR spectroscopy of PVDF-HFP fiber mats alone and as a composite with EMIM ES (with 10% HEC). (a) The full range of the spectroscopy. (b) Characteristic range of the crystalline phase of PVDF for P(VDF-HFP) fiber mat only. (c) Zoomed in spectra to show the  $\beta$ -phase for both fibers.

The FTIR spectroscopy of the P(VDF-HFP) composite shows a combination of P(VDF-HFP) and the EMIM ES-HEC electrolyte (Fig. S5a). The characteristic range of the crystalline phase of PVDF for P(VDF-HFP) fiber mat only is shown in Fig. S5b. The peak at 840 cm<sup>-1</sup> can be for both  $\beta$ - and  $\gamma$ -phase. But the characteristics peak of  $\gamma$ -phase at 1234 cm<sup>-1</sup> is absent in the spectra. And only the  $\beta$ -phase characteristics peak 1280 cm<sup>-1</sup> is present. Thus, we conclude that the P(VDF-HFP) is fully polarized in  $\beta$ -phase. For the composite of P(VDF-HFP) fiber and electrolyte we can't see the 1275 cm<sup>-1</sup> peak because of the high intensity characteristics ionic liquid peaks. So, a zoomed in spectra to show the 840 cm<sup>-1</sup> is given in Fig. S5c. The intensity of the crystalline phase does not change obviously after adding EMIM ES into the fiber mats. It indicates that incorporation of electrolyte does not destroy the polar nature of the fiber mats.



**Fig. S6**. The FTIR spectroscopy of EMIM ES-HEC (EMIM ES in the figures) and the composite with P(VDF-HFP) fiber mats (a) the full range spectroscopy. (b) Characteristic range of the EMIM cation. (c) Characteristic range of the OH groups. (d) Characteristic range of the ES anion.

The FTIR spectroscopy of the EMIM ES ionic liquid and the composite with P(VDF-HFP) fiber mats are shown in Fig. S6. Up- down-polarization indicated the direction of the dipoles in PVDF that is facing the detection window of FTIR. The full range spectroscopies in Fig. S6a show that the position of most characteristic peaks are similar for the ionic liquid after incorporating into the fiber mats. However, the enlarged figures of different range reveal that the ions might experience slight changes in the interaction with surroundings. The characteristic peak for EMIM cation in Fig S6b shows a small blue shift after mixing with P(VDF-HFP), which means increasing strength of the C-H bond.<sup>17</sup> This typically indicates the weakened H-bond of the H with anions and added HEC, which could be due to the strong interaction between EMIM cation and PVDF-HFP mats. Meanwhile, the stretching peaks of O-H in Fig. S6c and S-O in Fig. S6d all shifts toward low wavenumber with increasing intensity, indicating the formation of stronger H-bond. The enhanced interaction between ES anion and O-H from HEC or absorbed water also supports that the P(VDF-HFP) fiber mats prefer to host cation. We also notice that the FTIR spectroscopies of the composite with

different polarization direction completely overlap with each other for the whole range. It is difficult to probe the dipole-ion interaction with the macro characterization method here.



**Figure S7**. The potential difference between Al covered by fiber mats with different polarization direction. (a) on the hot side. (b) on the cold side. Top panels show the temperature difference between the measurement side and the counter side.

#### Note S6. The performance of devices with open surface

The Seebeck coefficient of the same devices with open surface is shown in Fig. S8. Heating Al electrode in Al-dipole up device lead to the same Seebeck coefficient as the Al-Al symmetric device (11 mV/K as previously reported). This implies that the dipole up fiber mats on the cold side has little impact on the water concentration difference. The Seebeck coefficient of device with dipole-down fiber mats increased compared to the previous two, but still has a similar value as in the sealed device in Fig. 2a. This shows that dipole-down fiber mats on the cold side of the device decreased the water concentration difference. When heating fiber mats side, the one with dipole-up does not have any increase compared to the value from sealed device, which shows the suppressing of water concentration. Opposite for the device with dipole-down fiber mats, the Seebeck coefficient in the open device is the highest among all configurations. This indicates that the dipole-down fiber mats on the hot side of the electrodes could enhance the water concentration with water. The different effect on the water concentration gradient of the set of the water interaction with water.

that bond with water. The shape of the peak in Fig. S8b is less sharp than that in the sealed device (Fig. 2c). This could be related to the faster screening effect due to slower water evaporation (ion diffuse faster with increasing water content in the electrolyte). When heating fiber mats with dipole-down, the peak is still relatively sharp because the water evaporates faster to provide larger water concentration difference. Further study is required to fully understand such a process. Here we mostly focus the effect of ferroelectric fiber mats on the Seebeck coefficient in sealed devices. As shown in Fig. S8c, for dipole-up heating with Al on the cold side and Al heating with dipole-down on the cold side, the Seebeck coefficient after sealing almost does not decrease. This shows that adding electrospun fiber mats of P(VDF-HFP) could successfully maintain high Seebeck coefficient of the device up to 15 mV/K.



**Fig. S8**. The overall Seebeck coefficient of devices with different electrodes combination. (a) The Seebeck coefficient in open devices. (b) and (d) the evolution of thermal voltage under heating for open devices. (c) The ratio between the Seebeck coefficients in sealed device and open device. The error bars correspond to the standard deviation from five samples.

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