

Electronic Supplementary Information

Anomalous n-type conversion of thermoelectric polarity in ionic hydrogels using PEDOT:PSS electrodes

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§1. Chemicals used

Table S1. List of chemicals.

Chemical	Purity (%)	Supplier
1-Ethyl-3-methylimidazolium chloride (Emim:Cl)	98	FUJIFILM Wako Pure Chemical
1-Hexyl-3-methylimidazolium chloride (Hmim:Cl)	92	FUJIFILM Wako Pure Chemical
1-Decyl-3-methylimidazolium chloride (Dmim:Cl)	95	FUJIFILM Wako Pure Chemical
Poly(vinyl alcohol) (PVA)	–	FUJIFILM Wako Pure Chemical
Deionized water (Conductivity $\leq 0.1 \text{ mS m}^{-1}$)	–	AS ONE
Poly(3,3-ethylenedioxythiophene):poly(styrenesulfonyl) (PEDOT:PSS)	–	H.C.Starck. Product name: Clevios PH1000
Ethylene glycol	99.5	Wako Pure Chemical

§2. Thermoelectric evaluation of PEDOT:PSS film (electrode)

Thermoelectric measurement results of the free-standing PEDOT:PSS film are given here to verify the contribution of the electronic Seebeck effect from the PEDOT:PSS electrodes to the overall voltage generation from the supercapacitors.

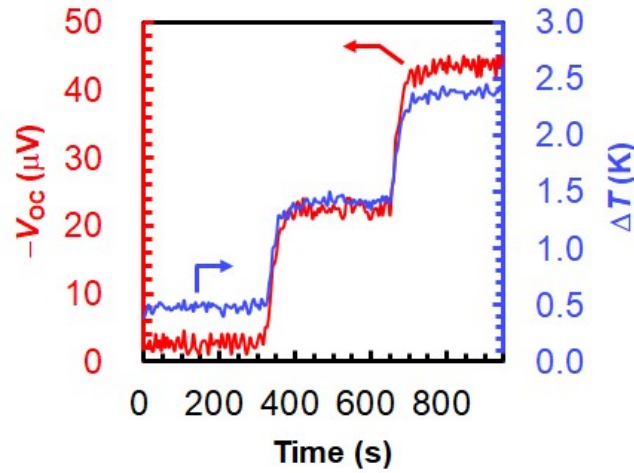


Figure S1. Representative voltage (ΔV_{OC}) response of the free-standing PEDOT:PSS films under a temperature difference (ΔT) for Seebeck coefficient determination. The tested specimens are the same as those used as electrodes for the voltage measurement of Rmim:Cl/PVA. The measurement was performed using a similar setup as that for testing the Rmim:Cl/PVA hydrogels.

PEDOT:PSS itself has attracted much attention as a p-type organic thermoelectric material. However, the Seebeck coefficient of PEDOT:PSS is usually small. Our specimens are no exception, as they exhibit Seebeck coefficients of approximately $+20 \mu V K^{-1}$. As shown in Figure S1, the absolute voltage value from the PEDOT:PSS film is in the order of tens of micro-volts and is much smaller than those from Rmim:Cl/PVA hydrogels (in the order of milli-volts). In the configuration of thermoelectric supercapacitors, shown in Figure 1b of the main article, the width of the PEDOT:PSS electrodes is at least 2 mm across the temperature gradient while that of the Rmim:Cl/PVA hydrogel is approximately 1 cm; and therefore, the supplied temperature difference to the PEDOT:PSS electrodes is rather small compared to that with the Rmim:Cl/PVA hydrogels. On the basis of these considerations, the contribution of the thermopower induced by the electronic Seebeck effect in PEDOT:PSS to the overall open-circuit voltage of the Rmim:Cl/PVA supercapacitor should be negligible.

§3. Open-circuit voltage temperature-difference plot for calculating the Seebeck coefficient

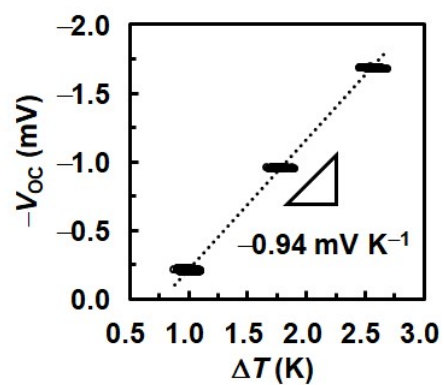


Figure S2. Open-circuit voltage ($-V_{oc}$)–temperature difference (ΔT) plot for calculating the Seebeck coefficient of Emim:Cl/PVA hydrogel measured using PEDOT:PSS electrodes. This plot was produced using the data shown in Figure 2a of the main article.

§4. Temperature difference-dependent voltage response of Emim:Cl/PVA hydrogel measured using PEDOT:PSS electrodes

In the main article, we discussed the anomalous open-circuit voltage ($-V_{OC}$) in response to the expansion of the temperature difference (ΔT) as shown in Figure 2c, by separating the device into the electrolyte bulk and the electrolyte/PEDOT:PSS interface. The initial movement of the voltage toward the p-type direction and the following dynamic n-type directed flow were attributed to the faster but transient Soret effect in the electrolyte bulk and the slower but larger interfacial polarization at the electrolyte/electrode interface, respectively. Here, we demonstrate that the initial $-V_{OC}$ movement toward p-type direction (induced by the Soret effect) depends on the ΔT , and the resulting positive Seebeck coefficient by this process is small. Figure S3a shows the ΔT -dependent voltage response from the Emim:Cl/PVA hydrogel measured using PEDOT:PSS (the same configuration as that shown in Figure 1b of the main article). The temperature differences (3.5, 12, and 25 K) indicated in panel a are the values after the temperature difference becomes constant. The dynamic n-type thermoelectric voltage takes a larger value when a larger temperature difference is applied. Figure S3b is the enlarged view of panel a in the time interval of 0.1–0.6 ks. Immediately after the expansion of ΔT , the voltage once moves toward the p-type direction, and then dynamically converts to the n-type polarity. Here, the peak-top voltage (turning point from the p- to n-type direction) becomes larger with the applied temperature difference, which confirms that the voltage induced by the Soret effect also correlates with the temperature difference. In Figure S3c, the peak top voltages shown in panel b are plotted against the applied temperature difference. The plot shows a good linearity, with which thermopower of $+0.10 \text{ mV K}^{-1}$ is derived. This value is quite small compared to the overall negative Seebeck coefficient (-1 mV K^{-1} , shown in the main article) or the positive one of the Emim:Cl/PVA hydrogel measured by Ag electrodes ($+10 \text{ mV K}^{-1}$, large contribution from the interfacial polarization at the electrolyte/electrode interface). On the other hand, it shows a good agreement with the Seebeck coefficient of the gel measured using Au electrodes ($+0.4 \text{ mV K}^{-1}$, negligible contribution from the interfacial polarization), which further supports our model that the initial voltage movement toward the p-type direction is caused by the intrinsic property of Emim:Cl/PVA hydrogel that is independent of the electrode material.

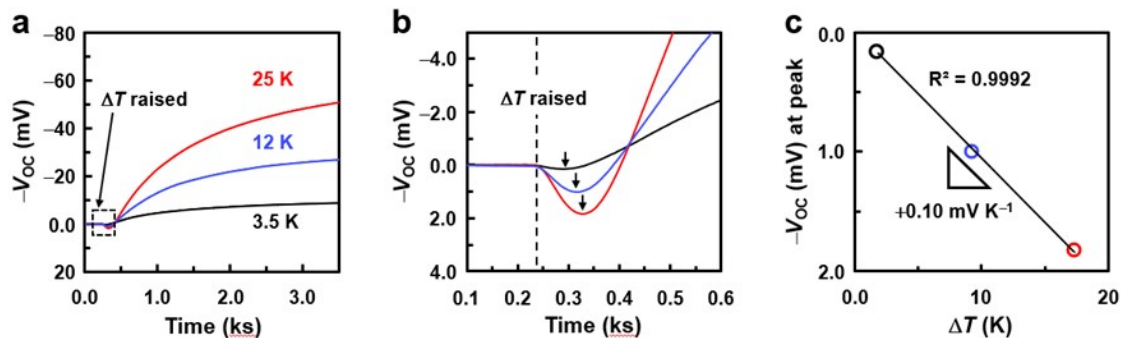


Figure S3. (a) Temperature difference (ΔT)-dependence of open-circuit voltage ($-V_{OC}$) response after the expansion of ΔT of the Emim:Cl/PVA hydrogel. The electrode at the lower temperature side is defined as earth. Note that $-V_{OC}$ at the time region before the ΔT expansion was set to zero to compare the voltage change in response to the ΔT change (raw data can be seen in Figure S4). (b) Enlarged view of panel a within the range of 0.1–0.6 ks. (c) The peak $-V_{OC}$ (indicated by arrows in panel b)– ΔT plot to examine the Seebeck coefficient which is a consequence of the Soret effect.

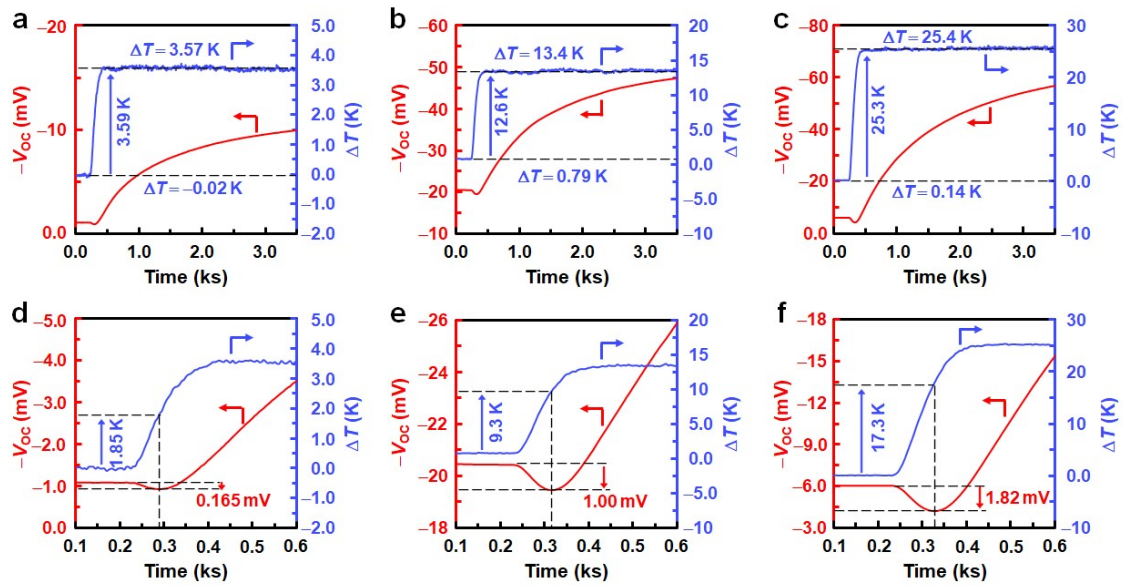


Figure S4. Raw data of open-circuit voltage ($-V_{OC}$) response according to temperature difference (ΔT) shown in Figure S3 when subjected to the ΔT of (a) 3.5, (b) 12, and (c) 25 K. In Figures S3a, b, $-V_{OC}$ before the expansion of ΔT of panels a–c was corrected as zero to easily compare the voltage change in response to the expansion of ΔT . (d–f) Enlarged views of panels a–c in the time region of 0.1–0.6 ks. To produce Figure S3c, the peak $-V_{OC}$ (0.165, 1.00, and 1.82 mV, the relative voltage value with respect to the base voltage before the expansion of ΔT) and the corresponding ΔT (1.85, 9.3, and 17.3 K) were used.

§5. X-ray photoelectron spectroscopy

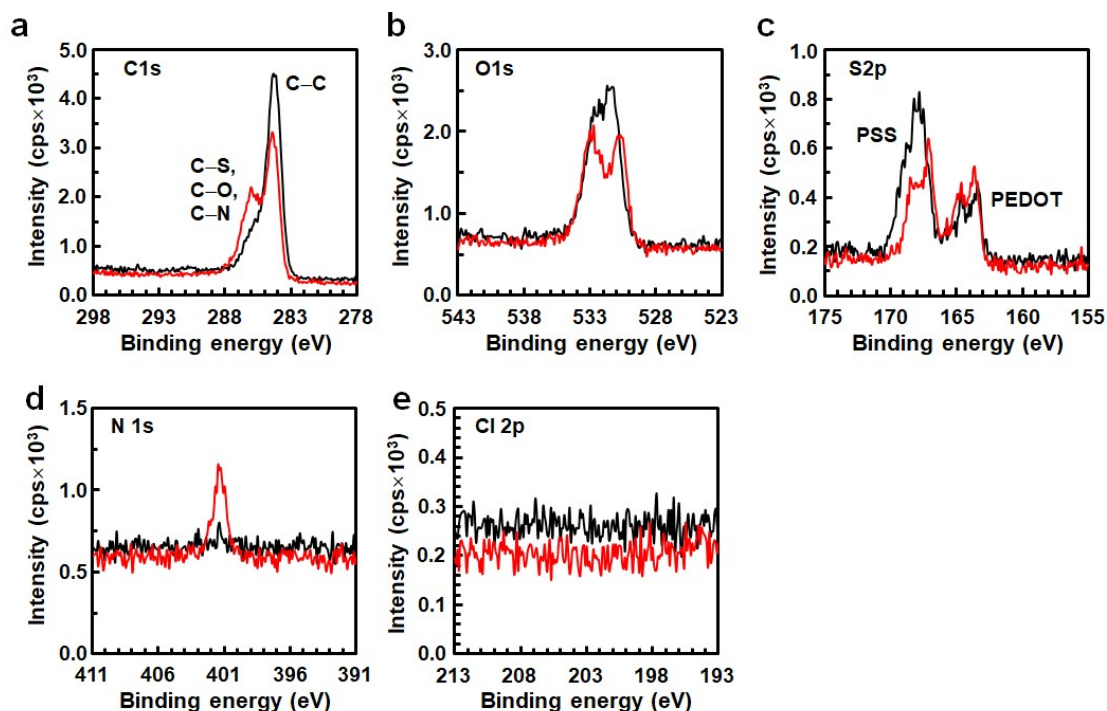


Figure S5. X-ray photoelectron spectroscopy (XPS) data of PEDOT:PSS films in the energy regions of (a) C1s, (b) O1s, (c) S2p, (d) N1s, and (e) Cl2p. Black and red colors indicate the data obtained from the raw (as-prepared) and Emim:Cl-treated PEDOT:PSS films, respectively. For the Emim:Cl-treated specimen, the PEDOT:PSS film was immersed into the Emim:Cl aqueous solution (0.1 g mL⁻¹) at 80 °C for 20 min, rinsed 3 times by immersing it into deionized water for 5 min, and then dried under vacuum for 15 min. Data statistics: $n = 2$. Panel a: Sharp feature of carbon/carbon bonds (both PEDOT and PSS chains) observed at the lower binding energy decreases after Emim:Cl treating while the one originating from the carbon/hetero atoms at the higher energy side increases. This is caused by the PSS elution from the film due to the addition of Emim:Cl and the rinsing process. The latter change would be due to the introduction of C–N bonds by the addition of the Emim cation. Panel b: O1s peak originates from PEDOT and PSS. The splitting of this peak is enhanced after the Emim:Cl treatment, possible due to the newly created ion interaction (Emim:PSS). Panel c: S2p peaks are initially split due to the presence of the S atoms with the differed bond type (sulfates of PEDOT and PSS). After the addition of Emim:Cl, the peak intensity contributed from PSS decreases relative to that from PEDOT. This change was also reported by Kee *et al.*, which was attributed to the elution of PSS chains from the film. Panels d and e: Both nitrogen and chlorine signals are not observed for the raw PEDOT:PSS film. While chlorine is also not detected from the Emim:Cl-treated PEDOT:PSS film, the nitrogen signal is clearly observed for the same specimen. The attachment of Emim cation (the origin of nitrogen atom) on the PEDOT:PSS film is relatively strong so that they can exist on the film while the chloride anion can be easily rinsed by water. This difference of ion (Emim cation or

chloride anion) affinity to the PEDOT:PSS supports the negative polarization at their interfaces under heating.

Reference

(S1) S. Kee, N. Kim, B. S. Kim, S. Park, Y. H. Jang, S. H. Lee, J. Kim, J. Kim, S. Kwon, and K. Lee, *Adv. Mater.*, 2016, **28**, 8625.