Supporting Information (SI)

Power Generation at Room Temperature

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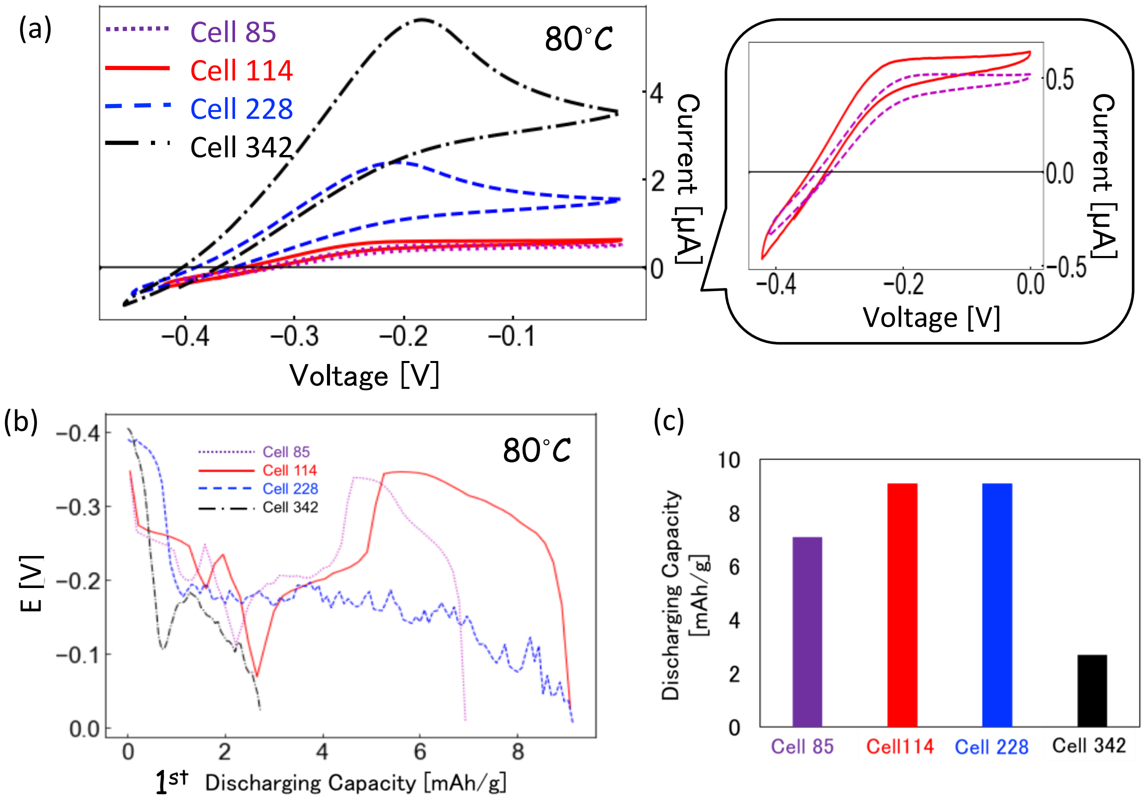


Supporting information 1. Battery characteristics of the 1st discharge at 80 °C. (a) Cyclic voltammetry (CV, scan rate = 10 mV/s), (b) time dependence of the voltage during the 1st 200 nA discharge and (c) the dischare capacity of the 1st discharge of Cell-85 (purple dotted line), Cell-114 (red solid line), Cell-228 (blue dashed line) and Cell-342 (black dash-dotted line).

Here, in Cell 85 and 114, the voltage gradually reduced; after this, it fluctuated and almost attained the initial open circuit voltage (V_{OC}).

The number of reactive ions reduced owing to the chemical reactions at the electrode/electrolyte interface. Therefore, the voltage (E) dropped according to Nernst equation (Eq. S1):

$$E = E^{o} + \frac{nF}{RT}\log\left(\frac{a_{ox}}{a_{red}}\right), \qquad \text{Eq. (S1)}$$

where E^{o} is the standard potential, n is the number of reactive electrons, F is Faraday's constant, R is the gas constant, T is the temperature, a_{ox} is the activity of the oxidized species and a_{red} is the activity of the reduced specie.

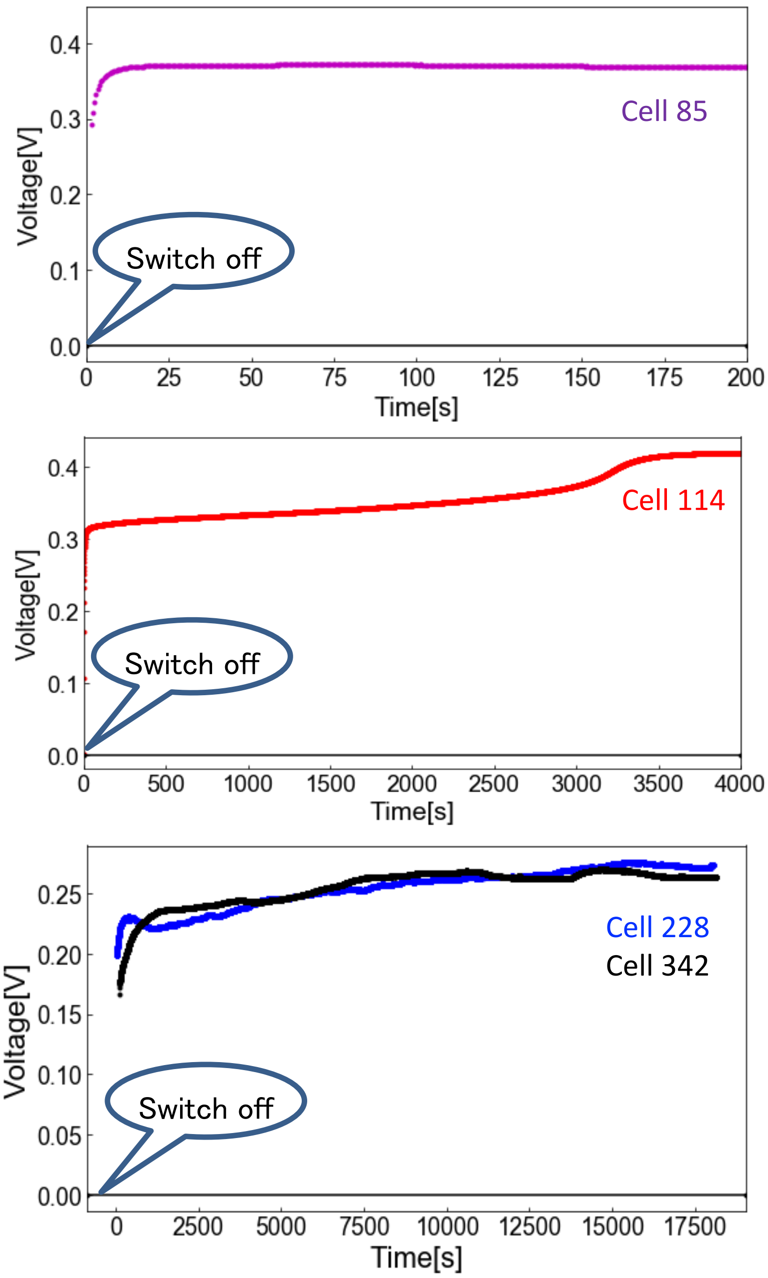
Thus, the resupply of the reactive ions to the interface should increase E. The diffusion of the reactive ions from other electrodes were enhanced in Cell 85 and 114; this caused the voltage recovery and subsequent voltage fluctuations. The electrolyte ions flowed between the electrodes through the diffusion layers (discussed in SI 4); and the convection of the oxidized and reduced species between the electrodes were enhanced in Cell 85 and 114.

In Cell 228 and 342, the voltage oscillated (with an amplitude of several tens of mV), while the average value gradually dropped to zero. The decrease in the averaged voltage during the discharge indicated that the reaction consumed the reactive ions at the interface until none were available, as observed in the primary battery.

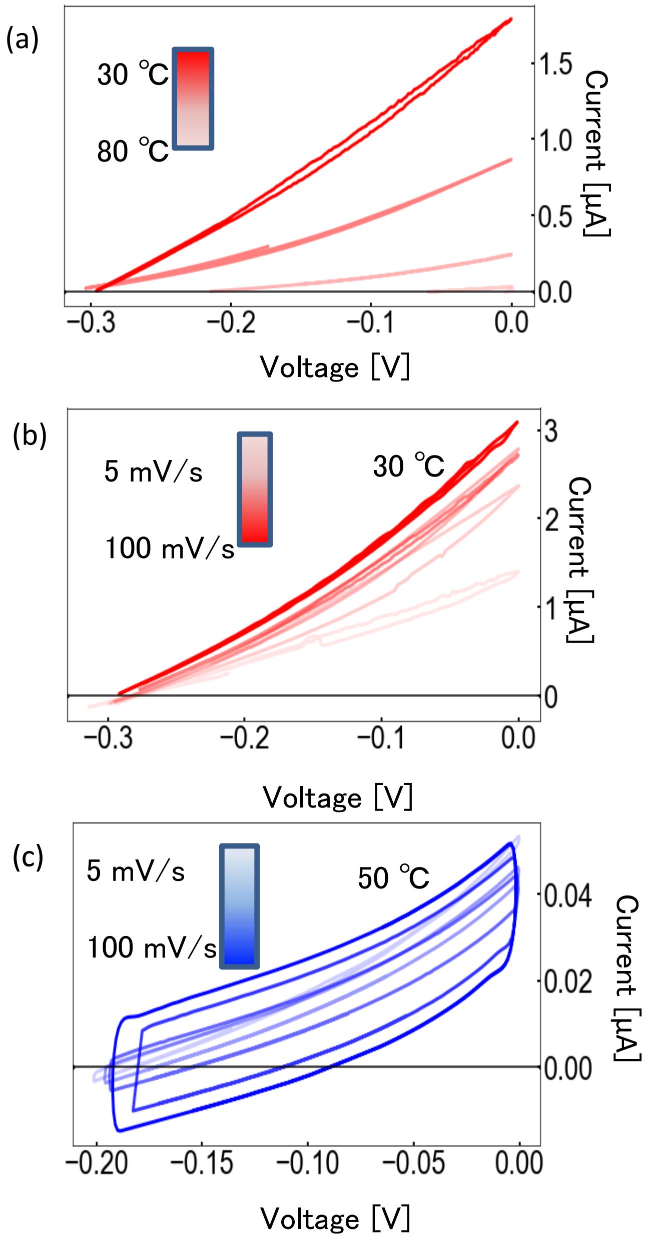
Since the oxidized and reduced species in this work are Cu^{2+} and Cu^{+}, respectively, the voltage-oscillation behaviour of Cell 228 and 342 might be generated via the following reactions:

$Cu^{+} \leftrightarrow Cu^{2+} + e$ (Eq. S2)
$Cu^{2+} + 2e \leftrightarrow Cu$ (Eq. S3)
$Cu^{+} + e \leftrightarrow Cu$ (Eq. S4)

Eq. S2 mainly occurred at the electrode/electrolyte interface. Furthermore, the redox level of this reaction determined V_{OC}. Contrarily, Eq. S3 and S4 could occur in the bulk electrolyte owing to the electric field that was generated during the discharge, as sometimes observed in Li-ion batteries. These reactions may be responsible for the fluctuations of the concentrations of Cu^{+} and Cu^{2+}, which caused the oscillation of the reaction potential in Eq. S2.



Supporting Information 2. Restart characteristics of Cell 85 (purple), 114 (red), 228 (blue) and 342 (black) after the 1st discharge at 80 ºC. The time required to stabilize the voltage increased as the interelectrode distance increased.



Supporting Information 3. (a) Temperature-dependent CV of Cell-2 (a). Scan rate dependence at (b) 30 °C and (c) 50 °C.

The open-circuit voltage (V_{OC}) was almost unchanged at different temperatures, confirming the fact that the V_{OC} of sensitized thermal cell (STC) is the difference between the Fermi and redox levels of the working electrode and electrolyte ion, respectively.

Conversely, within the range of the measurement temperature, the short-circuit current was changed with temperature. When the scan rate was changed at 30 °C, the short-circuit current increased as the scan rate increased. At 50 °C; the width of the box-shaped curves was increased, i.e., capacity was increased. This result indicates that the electrochemical behaviour of STC can be a battery or a capacitor-like depending on the temperature.

Supporting information 4. Determination of the diffusion length

To investigate the convection of ions in the electrolyte, electrochemical impedance spectroscopy (EIS) measurements were conducted during the discharge of each cell. Since the diffusion of reactive ions and the bulk resistance of the electrolyte influence the longevity power generation, the total circuit resistance, charge-transfer resistance at the Ge/electrolyte interface, and ion diffusion characteristics, which were represented by a Warburg element, W, were analyzed by galvanostat EIS (GEIS) and potentiostat EIS (PEIS).

The equivalent circuit was determined with two dummy cells: the FTO/electrolyte/FTO (FTO dummy cell) and Ge/electrolyte/Ge (Ge dummy cell). To investigate the frequency part of each component, the PEIS measurements were conducted while the cell was inserted in a temperature bath of 80 °C. The Cole–Cole plots of the Ge and FTO dummy cells are shown in Figs. S4-1a and S4-1b. The electric double layers, which corresponded to the electrode/electrolyte interfaces, were confirmed in both cells. Based on the frequency of the semicircle peak of each Cole–Cole plot, the frequencies of the FTO/electrolyte and Ge/electrolyte interfaces were in the orders of 10^3 and 10^1 Hz, respectively. The smaller semicircle, which corresponded to a high frequency in the Ge dummy cell, indicated that the conductor was in contact with the electrode. Furthermore, when the Warburg impedance element (Ws or Wo), a component that influences ion diffusion, was added, the frequency of the ion diffusion dropped to below 100 Hz.

Consequently, the equivalent circuit was determined, as shown in Fig. S4-1c, where R1 is the solution resistance, R2 is the contact resistance between the electrode and the conductors, CPE1 is the electric double layer at the electrode/conductor interface, R3 is the charge-transfer resistance at the FTO/electrolyte interface, CPE2 is the electric double layer at the FTO/electrolyte interface, R4 is the charge-transfer resistance at the Ge/electrolyte interface, CPE3 is the electric double layer at the Ge/electrolyte interface and Ws1 is the finite Warburg element.

An open Warburg element, Wo, was utilized to analyze Cell 85 and 114, instead of Ws, because their diffusive behaviours were different from those of Cell 228 and 342 (Fig. S4-2a). Comparing the plot models of the diffusion obtained by EIS (Fig. S4-2b), the diffusions of Cell 228 and 342 could be classified as infinite, while those of Cell-85 and -114 could be classified as semi-finite.

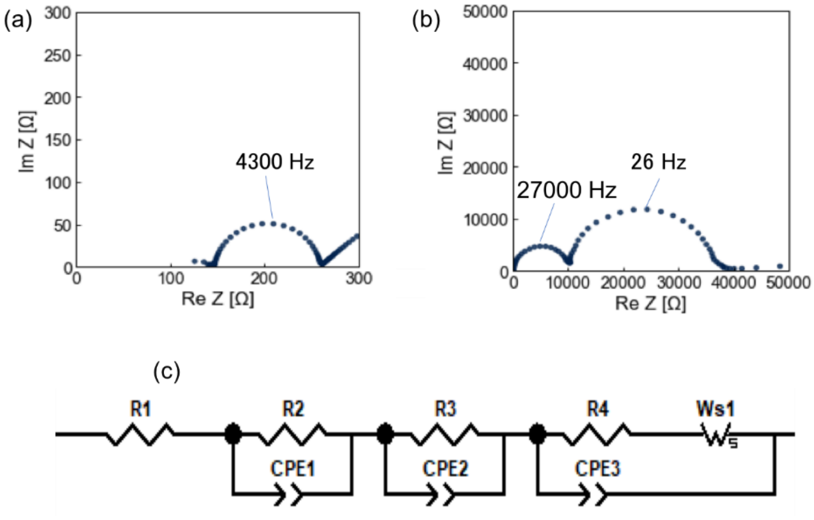


Fig. S4-1 Cole–Cole plots of PEIS of the (a) FTO symmetric cell, (b) Ge symmetric cell. (c) Equivalent circuit.

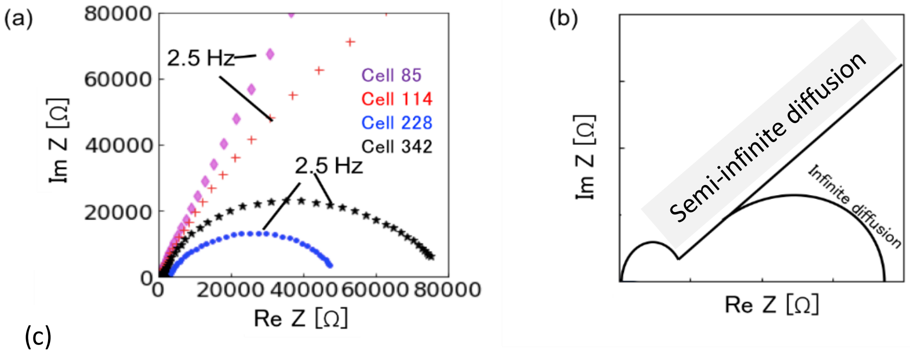


Fig. S4-2 (a) Cole–Cole plots of GEIS in the first discharge for Cell-85 (purple diamonds), Cell-114 (red crosses), Cell-228 (blue circles), and cell 342 (black stars) (b) the identical behaviour[1] and (c) the analysis results.

(c)

	R1 [Ω]	R4 [Ω]	W_R [$\times 10^5 \Omega$]	$W_T (= L^2/D)$	W_P	L [μm]
Cell 85	74.98	12000	10.0	26.23	0.5	71.4
Cell 114	79.18	25000	9	12.23	0.5	48.6
Cell 228	220.5	38000	0.105	0.808	0.5	12.5
Cell 342	203.2	60000	0.105	0.508	0.5	9.9

(SI 4. Determination of the diffusion length)

The ion diffusion length was analyzed to investigate the influence of the ion convection between the two electrodes. Eq. S5 and S6 were employed for the Warburg impedance analysis.

Finite Length Warburg (Ws) $\mathrm{Z} = \mathrm{W_R}\tanh((i\mathrm{W_T}\omega)^{0.5}))/(i\mathrm{W_T}\omega)^{0.5}$ Eq. (S5)

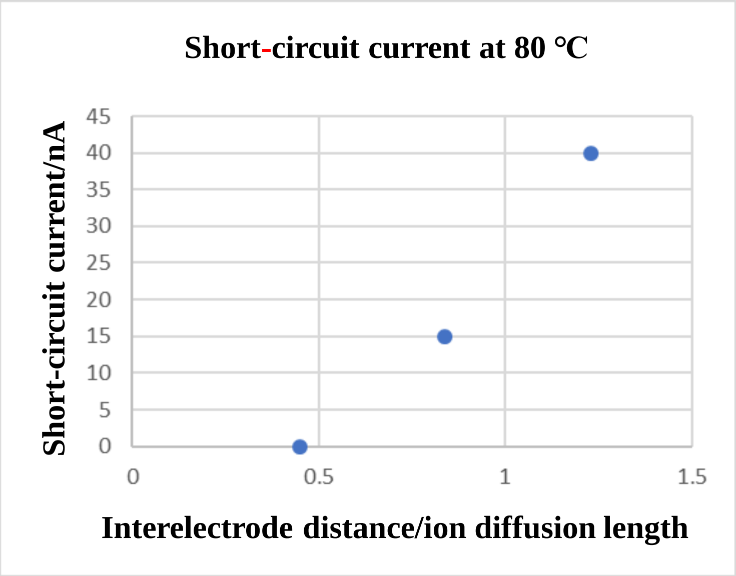
Open Warburg Impedance (Wo) $\mathrm{Z} = \mathrm{W_R}\mathrm{ctnh}((i\mathrm{W_T}\omega)^{0.5}))/(i\mathrm{W_T}\omega)^{0.5}$ Eq. (S6)

$\mathrm{W_R}$: diffusion resistance, $\mathrm{W_T}$: diffusion interpretation

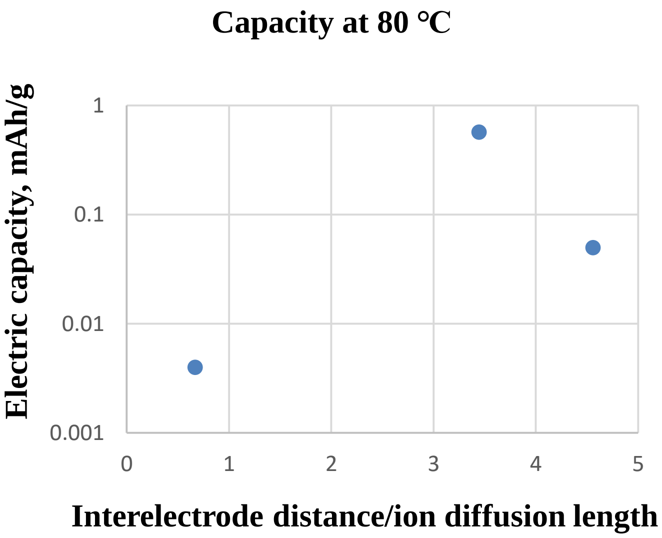
The fitting of these equations was performed by manually changing the values of $\mathrm{W_R}$ and $\mathrm{W_T}$. Afterwards, the diffusion length, $L = (D/\mathrm{W_T})^{1/2}$, was calculated. Figure S4-2c shows the analysis results during the discharge of 200 nA.

Supporting Information 5.

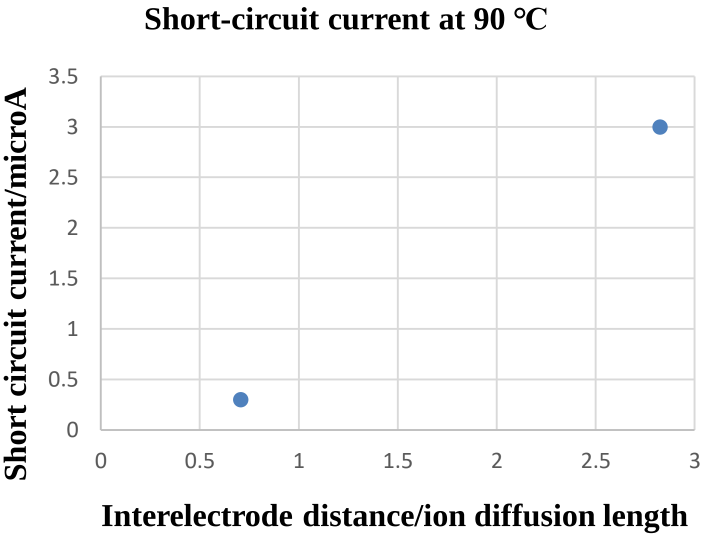
Working Electrode: n-Si/Ge
Electrolyte: 0.5 M NaI + 0.05 M I_2 in EC
Counter Electrode: FTO
Temperature: 80 °C



Working Electrode: n-Si/Ge
Electrolyte NaI + I_2 in DMSO (0.25M NaI + 0.025 M I_2, 0.5 M NaI + 0.05 M I_2, 1.0 M NaI + 1.0 M I_2)
Counter Electrode: FTO
Temperature: 80 °C



Working Electrode: TiO_2/ Ag_2S
Electrolyte: Cp (arene)
Counter Electrode:FTO
Temperature: 90 °C



Supporting Information 6. Bluetooth communication devices on asphalt worked by STCs. (Movie)

Tokyo Tech

Bluetooth communication devices
on asphalt worked by STCs

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Supporting Information 7. What do you think of the theoretical maximum output of STC?

The initial V_{OC} of STC was determined by the Fermi level of the working electrode and the redox level of the electrolyte ions, and it is not expected to differ significantly with temperature. Conversely, the short-circuit current of STC was determined by the number of thermally excited charges and the number of electrolyte ions that reached the electrode interface. Here, the number of thermally excited charges in the semiconductors is a fixed number that is determined by the material and temperature (it should be said that ‘the temperature of the semiconductor is the temperature when the said number of excited charges is present’). Therefore, when considering the short-circuit current value theoretically, it is preferable to consider the number of electrolyte ions that reached the interface of the electrodes.

The maximum number of electrolyte ions that can reach the electrode interface in one second is given by the following:
(saturation solubility of the electrolyte) × (ion mobility in the electrolyte) × (magnitude of the electric field that was applied to the ions)

The experimental saturation concentrations of the copper ions in PEG were ~0.8 mmol/g at room temperature and ~1.5 mmol/g at 60 °C. The ion mobilities in PEG were studied previously[1] and assumed to be 0.00000001 $cm^2/(Vsec)$ at 30 °C and constant (~0.00000001 $cm^2/(Vsec)$) at above 60 °C. Assuming 5 µm distance between the electrodes, the V_{OC} is ~350 mV and the magnitude of the electric field on the ions would be 700 V/cm. Thus, the output power would be 0.2 mW/cm^2 at room temperature and 40 mW/cm^2 at 60 °C.

[1] D. Fragiadakis, S. Dou, R. H. Colby, J. Runt, Macromolecules 2008, 41, 5723-5728.