Supporting Information

A Thermo-Electrochemical Converter using High Temperature Polybenzimidazole (PBI) Membranes for Harvesting Heat Energy

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Proton Conductivity Measurement

The through-plane proton conductivities were measured by an AC Zahner IM6e electrochemical work station using four-probe impedance spectroscopy method over the frequency range from 1 Hz to 100 kHz with an amplitude of 5mV. A rectangular piece of membrane ($3.5 \text{ cm} \times 7.0 \text{ cm}$) was cut from the bulk membrane and placed between two Kapton support layers. Four platinum wire acting as four probes were set in a custom designed glass cell. The membrane ohmic resistance was determined by the model fitting according to the Nyquist plot based on a three-component equivalent circuit.¹⁻²



Figure S1. (a) Schematic four-probe proton conductivity testing setup, (b) Equivalent circuit model, and (c) A typical Nyquist plot used for membrane resistance fitting.

Effect of the Membranes on the JTEC Performance

Membrane	Monomer Charge (wt%)	IV (dL/g)	Polymer Content (wt%)	PA content (wt%)	PA/PBI r.u. (molar ratio)
DiOH-PBI	3	/	6.6	56.9	27.3
para-PBI	2	3.3	5.6	57.3	32.3
m/p-PBI	10	1.8	16.8	57.6	10.8

Table S1. PBI membrane composition



Figure S2. Proton conductivities of DiOH-PBI, para-PBI, and m/p-PBI membranes as a function of temperature.

Table S2. Creep compliance test results of DiOH-PBI, para-PBI, and m/p-PBI membranes.

	DiOH-PBI	para-PBI	m/p-PBI
$J_{s}^{0} (10^{-6} Pa^{-1})$	2.5	10.3	1.9
creep rate $(10^{-12} Pa^{-1} s^{-1})$	18.9	21.8	4.1



Figure S3. Creep compliance of the DiOH-PBI, para-PBI, and m/p-PBI copolymer membranes. Membranes were preconditioned at 180°C for 24h and compressed at 0.1MPa at 180°C for 20h.

References

(1) Bard, A. J.; Faulkner, L. R. Fundamentals and applications. *Electrochemical Methods* 2001, 2, 482.

(2) Xie, Z.; Song, C.; Andreaus, B.; Navessin, T.; Shi, Z.; Zhang, J.; Holdcroft, S. Discrepancies in the measurement of ionic conductivity of PEMs using two-and four-probe AC impedance spectroscopy. *J. Electrochem. Soc.* **2006**, *153*, E173-E178.