Electronic Supplementary Material (ESI) for Energy & Environmental Science.

(Supplementary Information)

Anode-less seawater batteries with Na-ion conducting solid-polymer electrolyte for power to metal and metal to power energy storage

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Temperature (°C)	Conductivity (mS cm^{-1})	Temperature (°C)	Conductivity (mS cm^{-1})
80	6.32	20	1.43
70	5.47	10	0.88
60	4.68	0	0.50
50	3.69	-10	0.25
40	2.89	-20	0.11
30	2.11		

Table S1. Ionic conductivity of the Na-SPE as a function of the temperature.

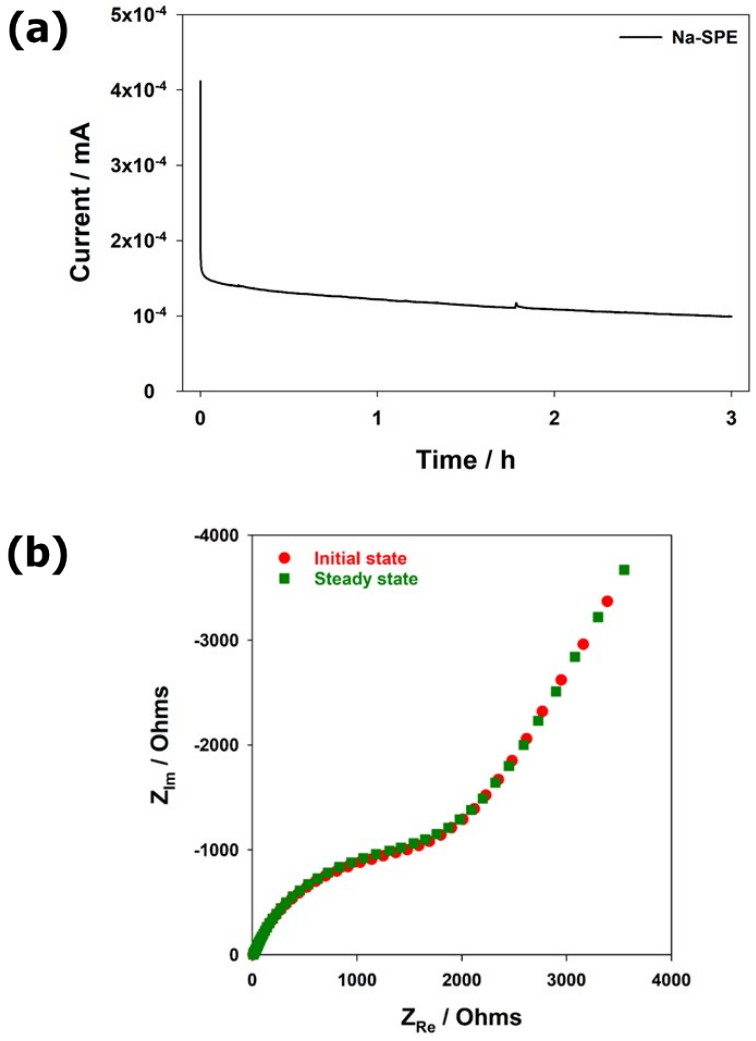


Figure S1. (a) Chronoamperometry and (b) impedance spectra for the Na-SPE. T= 20 ℃.

The Na-ion transference number (t_{Na^+}) was measured using the D.C. polarization method suggested by Bruce and Vincent.1 The symmetric Na | Na-SPE | Na cell was constructed and subjected to chronoamperometry test with an applied voltage of 10 mV for 3 hours. Impedance spectra were taken before and after the chronoamperometry.

Reference:

1. Bruce, P. G., and Vincent, C. A. (1987). Steady state current flow in solid binary electrolyte cells. J Electroanal Chem Interfacial Electrochem, *225*(1-2), 1-17.

ΔV [mV]	R_0 [Ω]	R_{ss} [Ω]	I_0 [mA]	I_{ss} [mA]	t_{Na^+}
10	2778	2855	0.0004	0.0001	0.22

Table S2. Na-ion transference number (t_{Na^+}) for the Na-SPE and measured data from Figure S1. T= 20 ℃.

R_0 and R_{SS}: The initial and steady state interfacial resistances

I_0 and I_{ss}: The initial and steady state currents

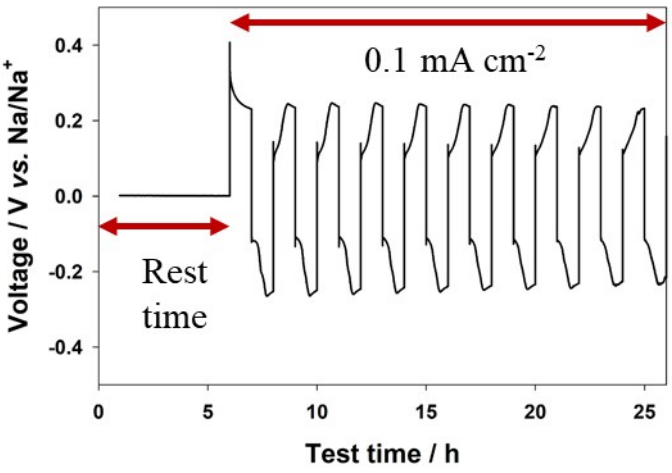
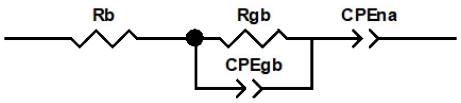


Figure S2. Galvanostatic Na plating and stripping performed in a symmetric Na | Na-SPE | Na cell at a current density of 0.1 mA cm^{-2}. Each plating or stripping step lasted for 1 hour. T = 20 °C.

(a)

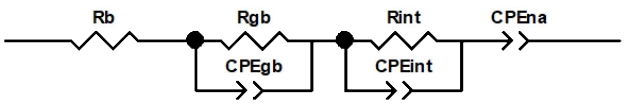


R_b: Bulk resistance of NASICON solid electrolyte

R_{gb} & CPE_{gb}: Grain boundary resistance and capacitance of NASICON solid electrolyte

CPE_{na}: Capacitance of NASICON solid electrolyte

(b)



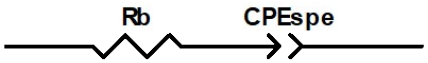
R_b: Bulk resistance of NASICON solid electrolyte and resistance of Na-SPE

R_{gb} & CPE_{gb}: Grain boundary resistance and capacitance of NASICON solid electrolyte

R_{int} & CPE_{int}: Interface resistance and capacitance of NASICON | Na-SPE

CPE_{na}: Capacitance of NASICON solid electrolyte and Na-SPE

(c)



R_b: Resistance of Na-SPE

CPE_{spe}: Capacitance of Na-SPE

Figure S3. Equivalent circuit model notation for electrochemical impedance spectra at OCV state; (a) NASICON, (b) NASICON | Na-SPE, and (c) Na-SPE.

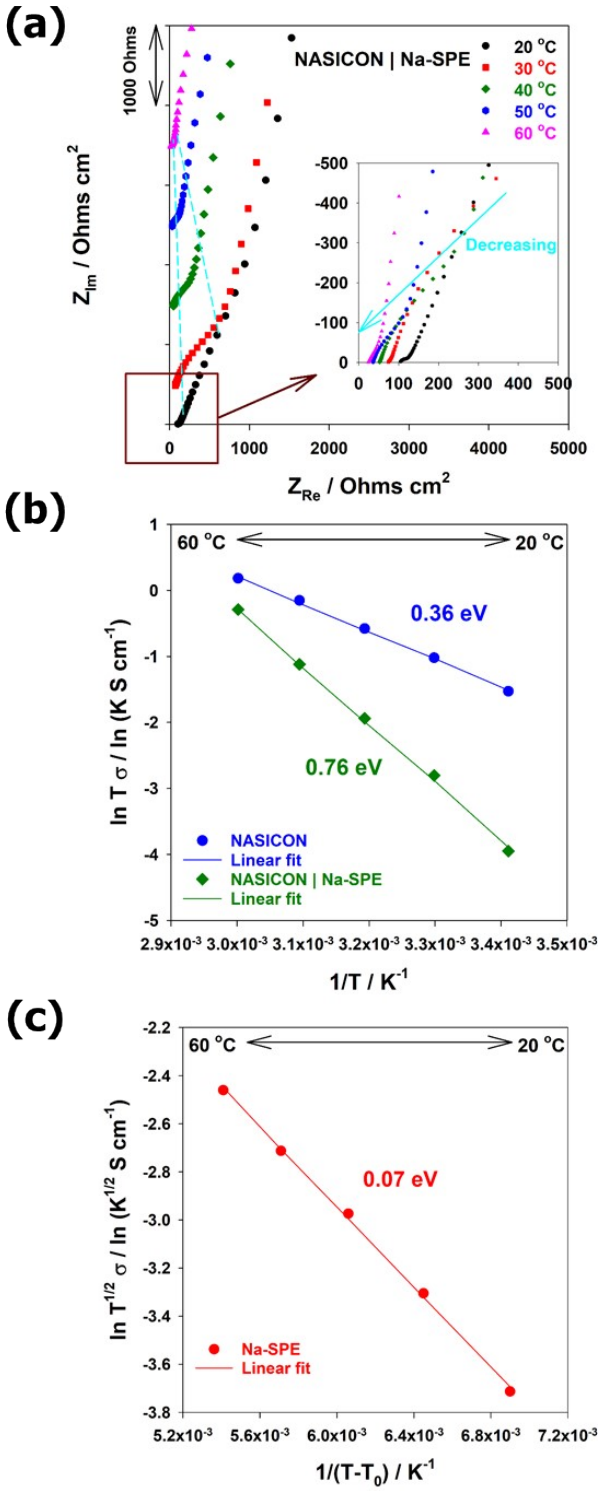
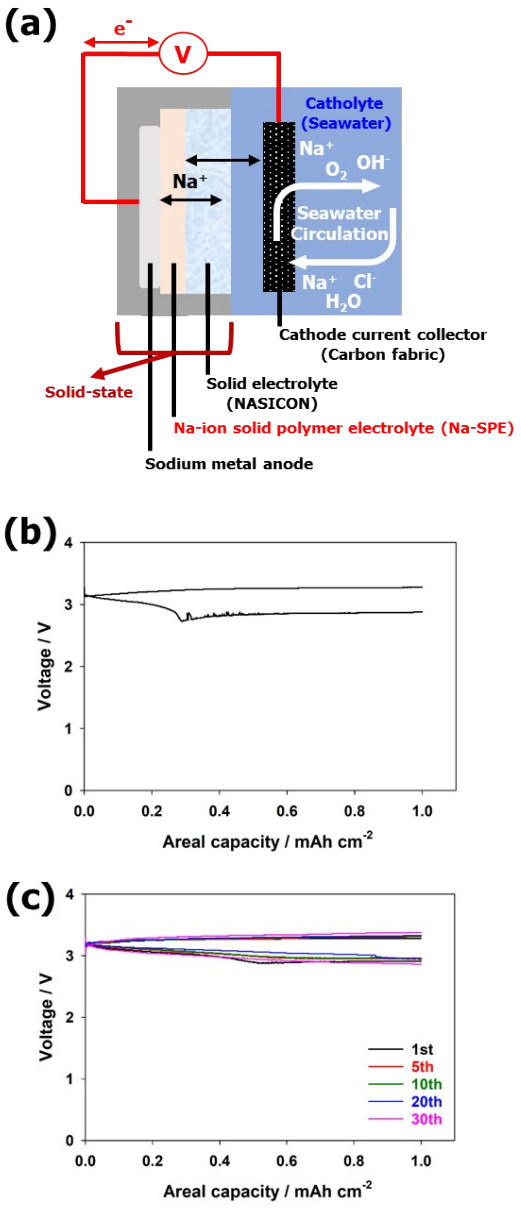


Figure S4. (a) Nyquist plots between NASICON | Na-SPE. T = 20 ~ 60 °C. (b, c) Arrhenius plots of 3 types of electrolytes (NASICON, Na-SPE, and NASICON | Na-SPE) to measure activation energies: (b) Na-SPE and (c) NASICON and NASICON | Na-SPE.



Figures S5. (a) Schematic illustration of the cell setup for a Na-Seawater battery (Na-SWB) employing the Na-SPE. The cell compartments are physically separated by a NASICON solid electrolyte layer. Sodium metal and carbon fabric serve for the negative electrode material and the positive current collector, respectively. (b) Pre-cycle voltage profile applying a current density of 0.1 mA cm^{-2} (up to charge/dis- capacity of 1.0 mAh cm^{-2}). (c) Charge/dis- profiles of galvanostatic cycle, applying a current density of 0.1 mA cm^{-2} (up to charge/dis- capacity of 1.0 mAh cm^{-2}). T = 20 ±3 °C.

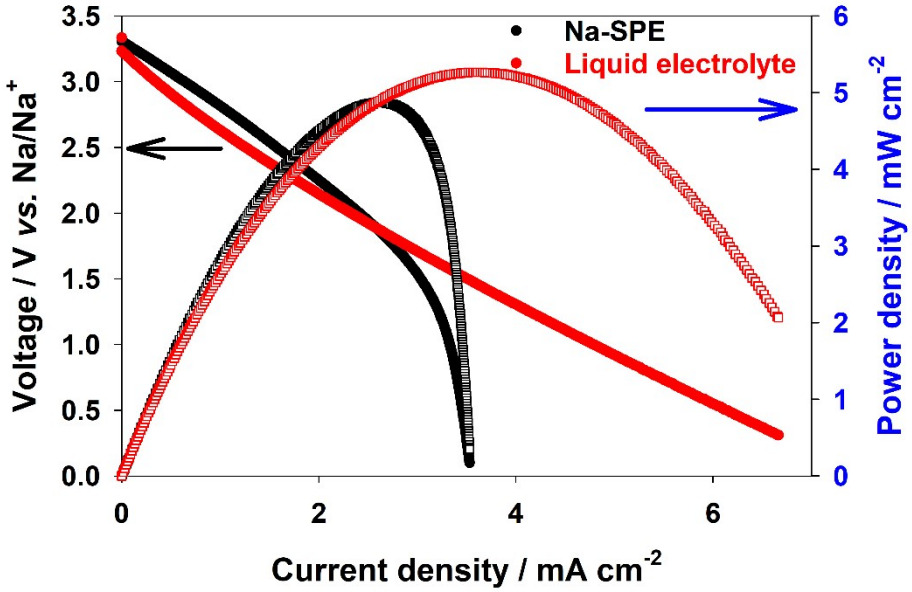
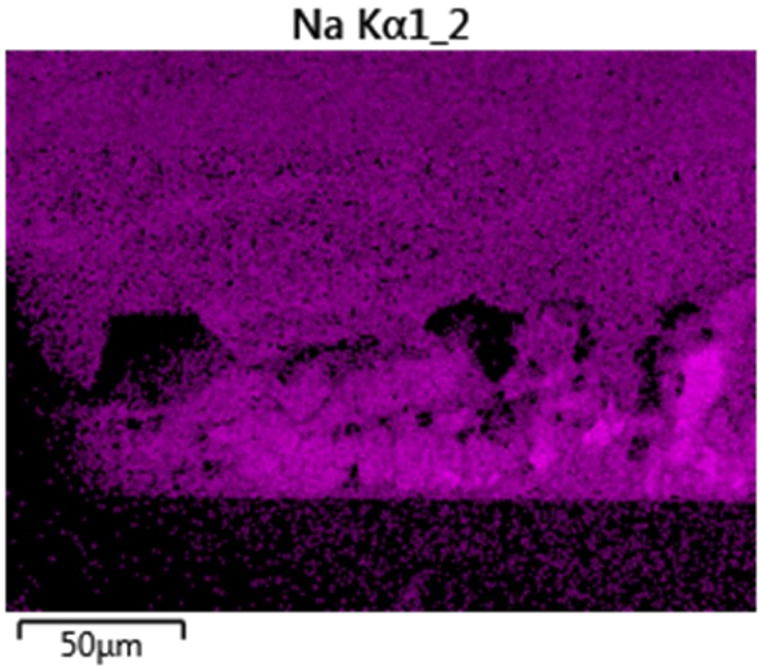


Figure S6. Polarization and power density curves measured at a scan rate of 0.05 mA s^{-1}. Cell configuration: Cu | Na | Na-SPE or Liquid electrolyte | NASICON | Seawater | Carbon.

Figure S6 shows the polarization curve and power density characteristics at a scan rate of 0.05 mA s^{-1}. The Na-SPE generates a maximum output power of ~4.9 mW cm^{-2}, which is lower than that of the liquid electrolyte (~5.3 mW cm^{-2}). Although the liquid electrolyte cell shows higher power density and operates at higher current densities, the Na-SPE shows improved performance at current density below 2.2 mA cm^{-2} thanks to the smaller polarization.



Figures S7. EDX mapping image of Na element (cross-sectional image cut by a FIB) for the Na metal harvested anode (composed of the Na-SPE, Na metal, and Al foil current collector).