

Electronic Supplementary Information

Saltwater as the energy source for low-cost, safe rechargeable batteries

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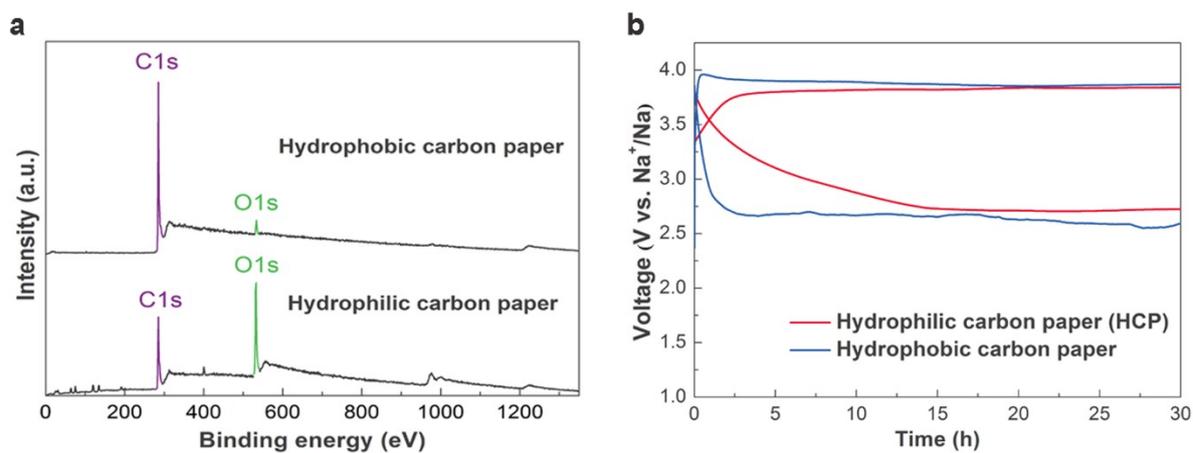


Fig. S1 Characterisation of carbon paper as the cathodic current collector in saltwater batteries. (a) XPS wide-scan spectra of hydrophobic and hydrophilic carbon papers, showing that the neutral hydrophilic carbon paper has more oxygen-containing functional groups on the surface. (b) Galvanostatic charge and discharge curves of saltwater batteries (Na| 1 M saltwater) with different carbon papers.

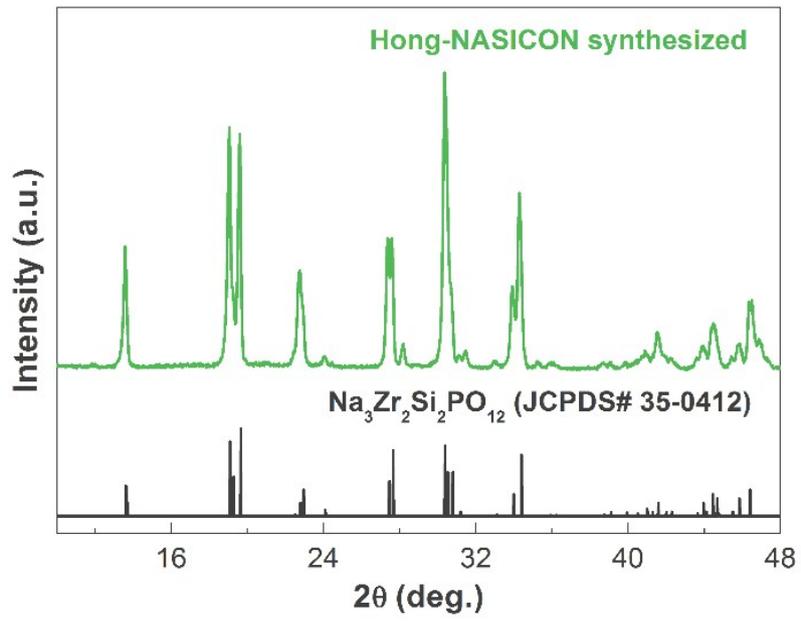


Fig. S2 XRD pattern of the synthesised NASICON solid electrolyte in saltwater batteries, and reference data of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$.

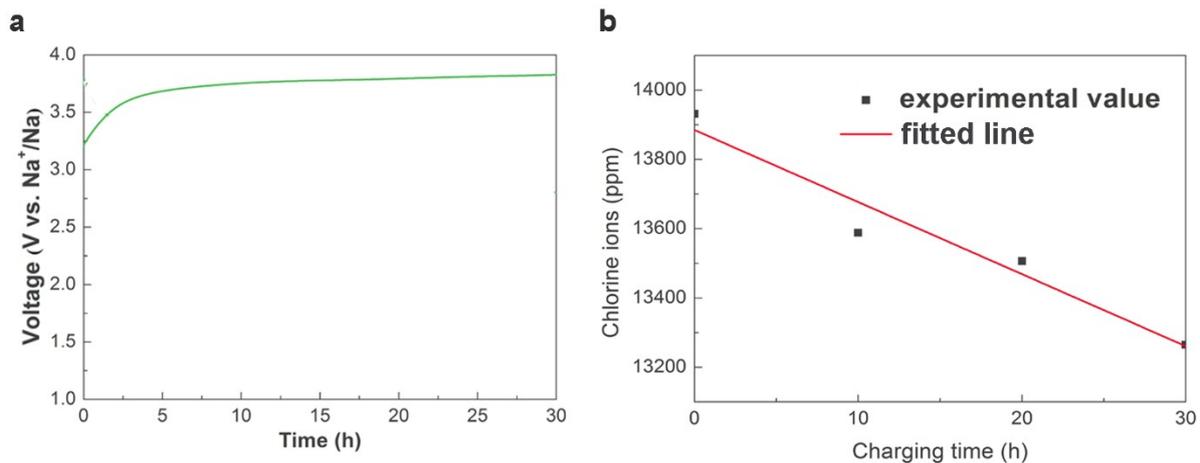


Fig. S3 (a) Charge curve of the saltwater battery (Na|0.4 M saltwater) at a current rate of 0.025 mA cm⁻² over 30 h. (b) Variation of the concentration of Cl⁻ ions in 0.4 M saltwater over 30 h of charging.

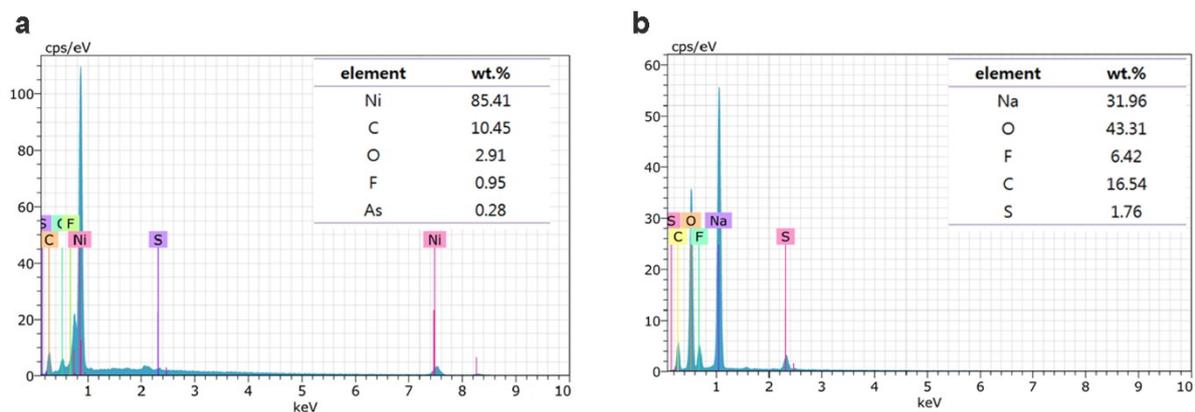


Fig. S4 EDS spectra for the anode side (a) before and (b) after charging over 200 h at a current rate of 0.1 mA cm^{-2} . The results demonstrate the extraction of Na from saltwater during charging.

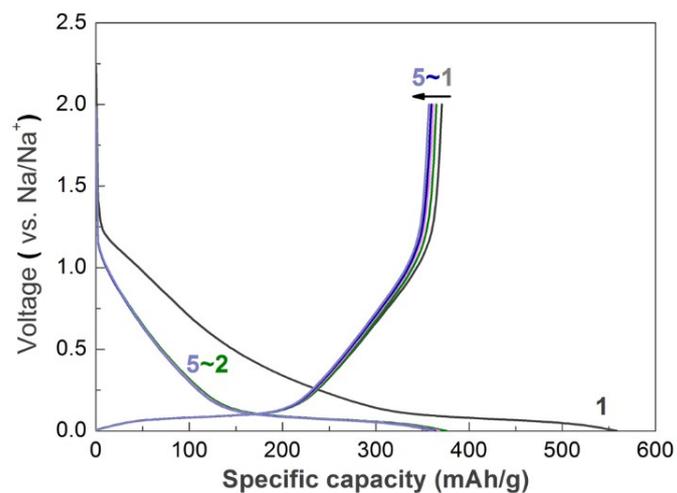


Fig. S5 Electrochemical performance of the 2032 coin-type half-cell (Na|hard carbon). The galvanostatic charge and discharge voltage profiles at a current rate of 0.025 mA cm^{-2} for 5 cycles show the reversible capacity of 350 mAh g^{-1} . The initial irreversible large capacity loss could be attributed to the formation of solid electrolyte interface (SEI) on the hard carbon ^{S1}.

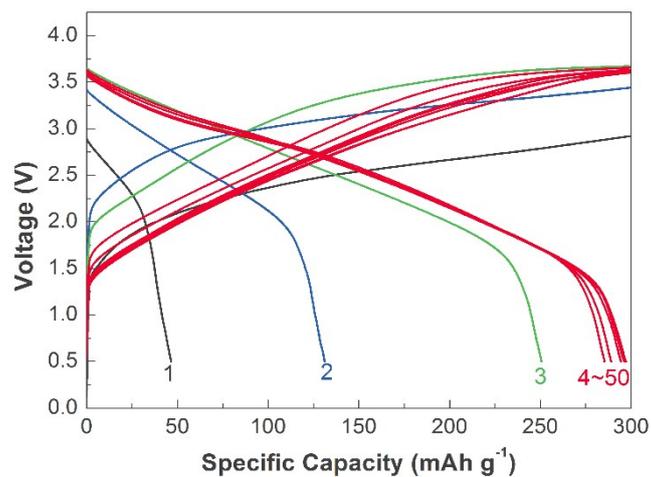


Fig. S6 Galvanostatic charge and discharge voltage curves of the full-cell (hard carbon|5 M saltwater) for 50 cycles at a current rate of 0.025 mA cm⁻². The average discharge voltage was 2.45 V and the saturated discharge capacity was 296 mAh g⁻¹.

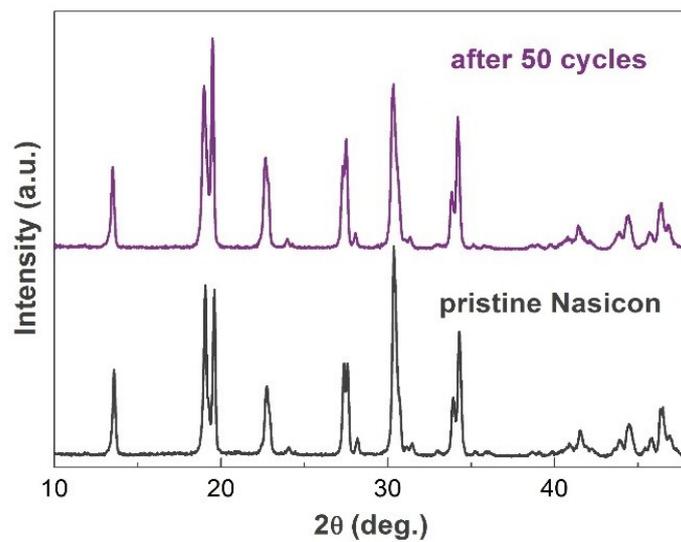


Fig. S7 XRD patterns of the pristine NASICON and after 50 cycles. Although the peak intensities changed slightly, no noticeable peak shift was observed between the two spectra, revealing the stability of NASICON in saltwater during cycling.

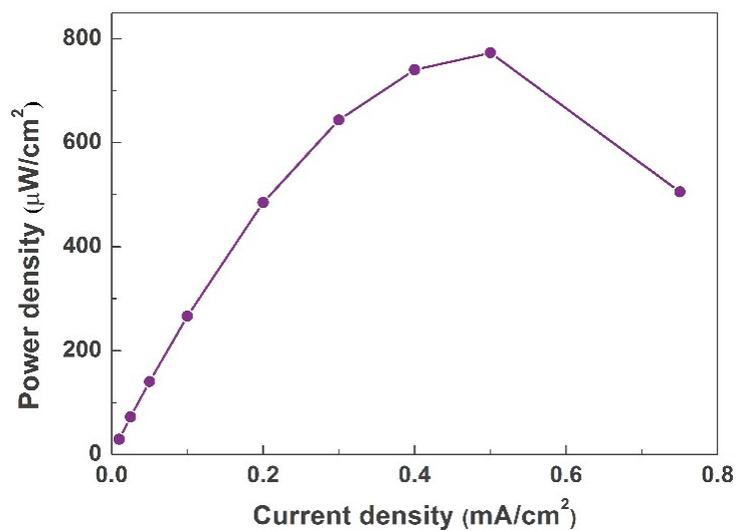


Fig. S8 Power density of the saltwater battery (Na|5 M saltwater) with respect to current density from 0.01 to 0.75 mA cm⁻². The maximum power density is 773 μW cm⁻² at 0.5 mA cm⁻².

Table S1 Cost of various types of batteries for ESS systems used for utility transmission and distribution grid support. The data are from DOE/EPRI 2013 electricity storage handbook ^{S2}, except for rechargeable saltwater batteries.

a

Batteries for ESS	Cost	
	\$/kW	\$/kWh
NaS	3152~3434	438~477
Na-NiCl	2907~5676	727~1135
Vanadium redox flow(VRB)	3335~3756	751~834
Fe-Cr	1473~1596	295~379
Zn-Br	1699~2957	361~1479
Zn-air	1858	310
Lead-Acid	2477~5876	502~2477
Li- ion(LIB)	1388~5265	996~2126
Saltwater(SWB)	1890	187

b

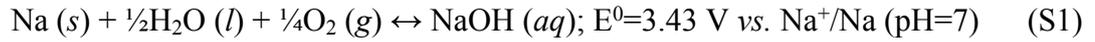
Battery	Redox flow	Zinc air	Saltwater
ES System			
ES Equipment	20,876,000	1,000,000	4,697,622
ES Installaion	4,870,000	7,500	1,095,871.67
Enclosures	722,000	24,810	162,468.04
Owner Interconnection			
Equipment	2,288,500	367,000	514,969.68
Installation	572,000	92,000	128,714.29
Enclosure			
Utility Interconnection			
Equipment	695,000	80,400	156,392.36
Installaion	695,000	80,400	156,392.36
Site BOP Installation(Civil Only)	40,000	1,267	9,001.00
Total Cost Equipment	24,581,500	1,472,210	5,531,451.64
Total cost Installation	6,177,000	181,167	1,389,979.33
General Contractor Facilities at 15% install	926,550	27,175	208,496.90
Engineering Fees @ 5% install	308,850	9,058	69,498.97
Project Contingency application @ 0-15% install	308,850	18,117	208,496.90
Process Contingency application @ 0-15% of battery	1,043,800	150,000	469,762.20
Total Plant Cost(TPC) (\$)	33,346,550	1,857,727	7,877,686
\$/kW	656	1,858	1,890.64
\$/kWh	670	310	187.60

Table S1a gives the cost range of existing battery types for large-scale ESS applications, using the maximum and minimum values listed in ref. S2 with the exception of the saltwater battery. Table S1b shows the costs breakdown based on vender quotes, such as OEM suppliers, power conditioning system (PCS) provider and system integrators, and financial assumptions. For example, process contingency assumption was applied with considering technology maturity and the level of development and commercialisation of each battery type. The cost of energy storage (ES) equipment in Table S1b, which indicates the material cost of the batteries and the total material cost composed of modules of 40000 kWh in serial-parallel system, is applied to the value of saltwater battery.

To convert from lab to commercial scale, the ES equipment cost of saltwater batteries was reduced by a factor of ten, which is the typical reduction ratio during commercialisation. Values other than ES equipment for rechargeable saltwater batteries are hard to calculate, since the batteries are in the stage of research and development. For this reason, values such as PCS cost for the saltwater battery were those of redox flow battery, which is the most similar system. Other values for the saltwater batteries in Table S1b were obtained by assuming the same cost ratio between the ES equipment and other values as that in redox flow battery, except the process contingency cost, which was estimated based on a zinc-air battery that is still in developmental stage.

Calculation of the theoretical energy density of saltwater battery

In the case of 5 M saltwater, the theoretical potential of the following redox reactions in the cathode side is calculated to be 3.43 V vs. Na⁺/Na according to the Nernst equation.



The theoretical gravimetric energy density was calculated using the following equation

$$\text{Theoretical energy density (mass)} = \frac{E_{rev} \cdot Q(5M \text{ NaCl})}{m_{anode} + m_{cathode}} = 368 \text{ Wh kg}^{-1} \quad (\text{S2})$$

The theoretical redox potential E_{rev} is 3.43 V and Q is the quantity of electrical charge for 5 mole electrons generated from 1 L NaCl aqueous solution at 5 M ($Q = 96485 \text{ C/mol} \times 5 \text{ mole/L} \times \frac{1 \text{ hr}}{3600 \text{ sec}}$). The mass of 1L saltwater is derived from its density ($\rho_{5M, \text{saltwater}} = 1.241 \text{ g mL}^{-1}$) (ref. S3). Oxygen is assumed to be completely dissolved in the saltwater, and its mass is regarded as $\frac{1}{4}$ of 5 mole according to reaction (S1) (ref. S4). Since Na can be fully provided from the saltwater during charging, the mass of the anode is not considered in this calculation. Therefore, the total mass of the anode and cathode is 1.241 kg, resulting in a theoretical energy density of 368 Wh kg⁻¹. Likewise, for a battery with 6 M saltwater, the theoretical energy density is calculated to be 423 Wh kg⁻¹, based on the theoretical redox potential (3.42 V vs. Na⁺/Na) and density ($\rho_{6M, \text{saltwater}} = 1.295 \text{ g mL}^{-1}$).

References

- S1. Ponrouch, A., Goñi, A. & Palacín, M. R. High capacity hard carbon anodes for sodium ion batteries in additive free electrolyte. *Electrochem. Comm.* **27**, 85–88 (2013).
- S2. Akhil, A. A. *et al.* *DOE/EPRI 2013 Electricity Storage Handbook In Collaboration With NRECA*. (Sandia National Laboratories Albuquerque, NM, USA, 2013).
- S3. *Water Density Calculator*, URL: <http://www.csgnetwork.com/h2odenscalc.html> (Updated September 24, 2011; accessed December 31, 2015).
- S4. Cramer, S. D. The solubility of oxygen in brines from 0 to 300 °C. *Ind. Eng. Chem. Proc. Des. Dev.* **19**, 300–305 (1980).