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

Supplementary Information

Dual-ions Electrochemical Deionization: A desalination generator

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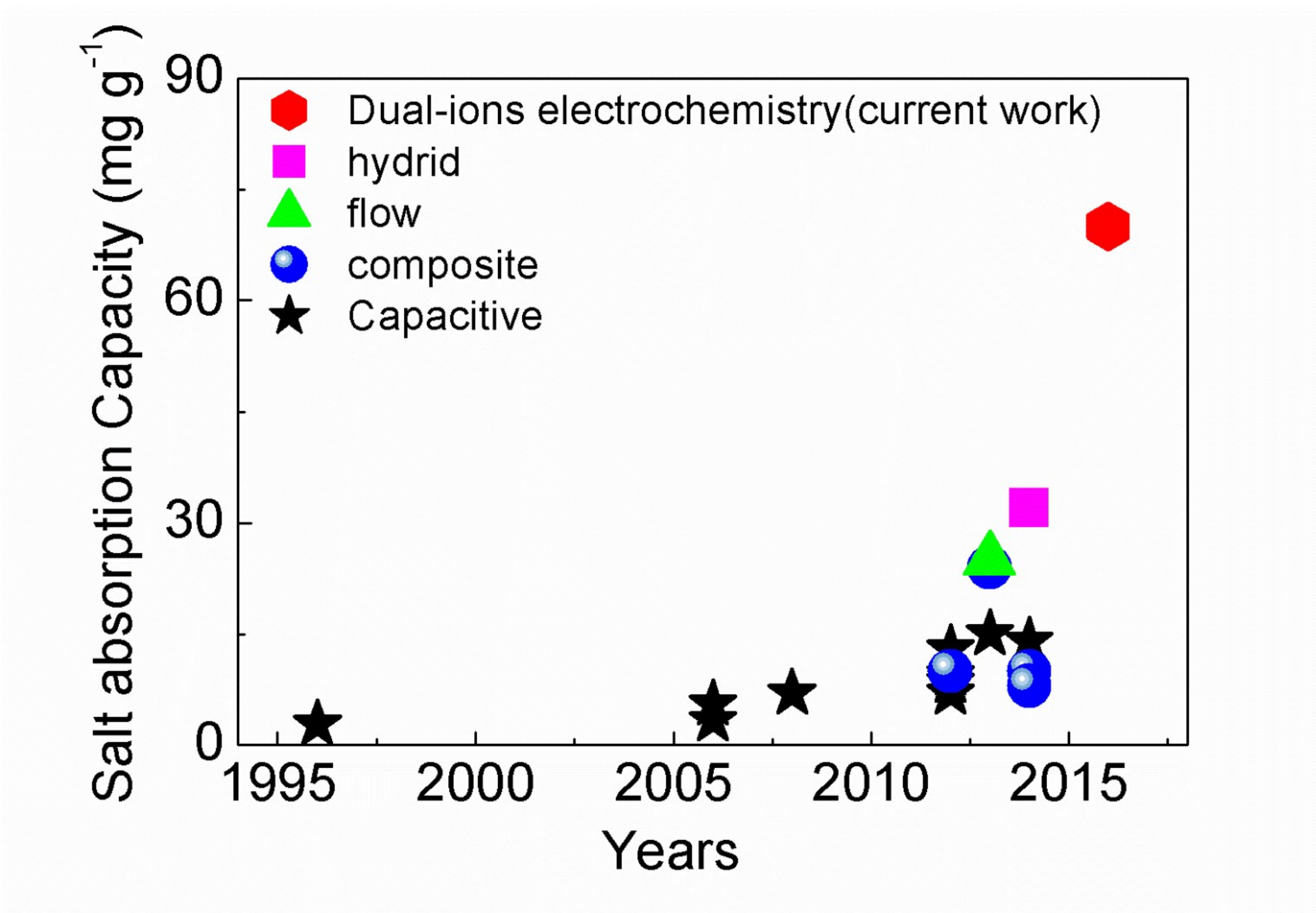
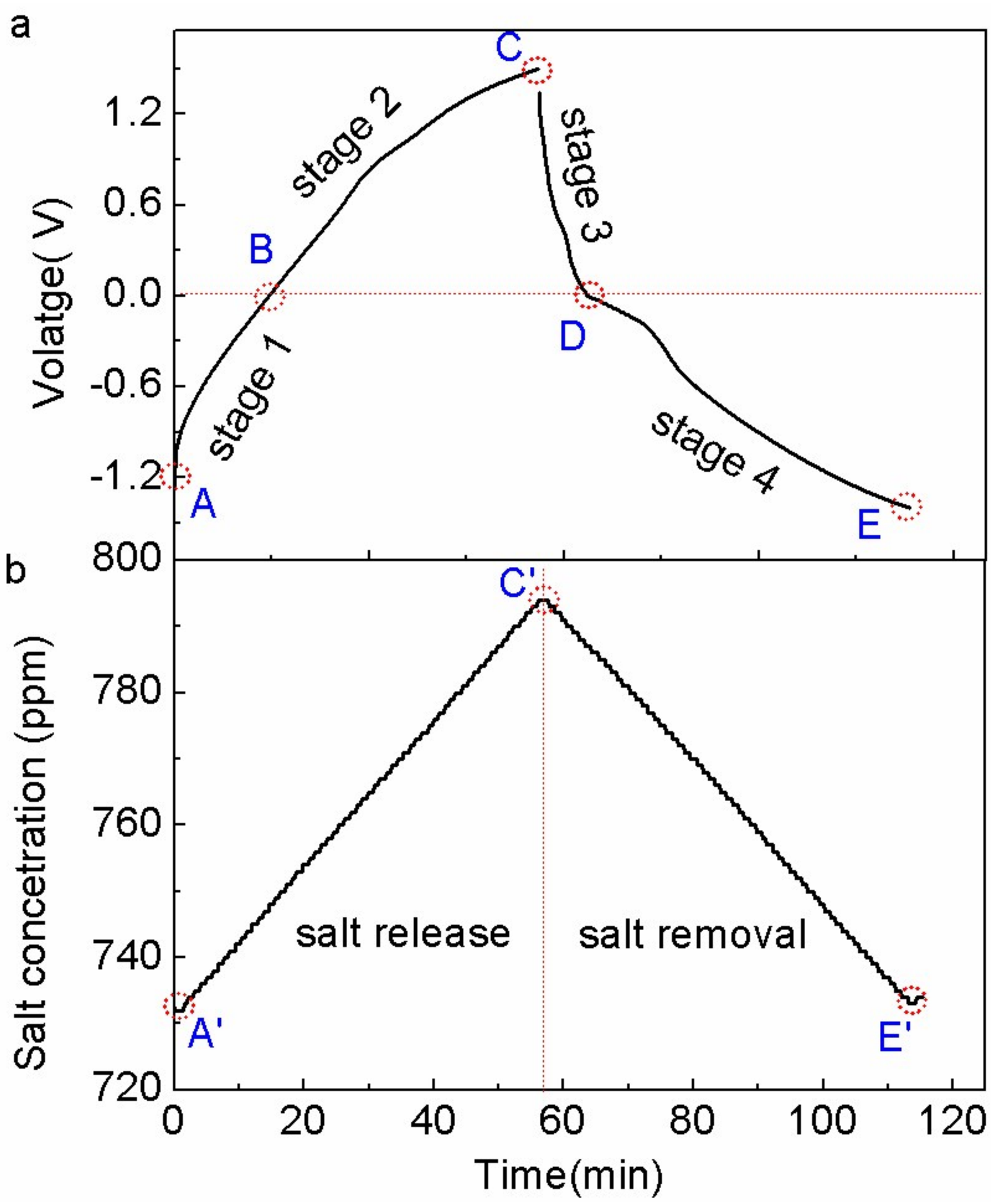
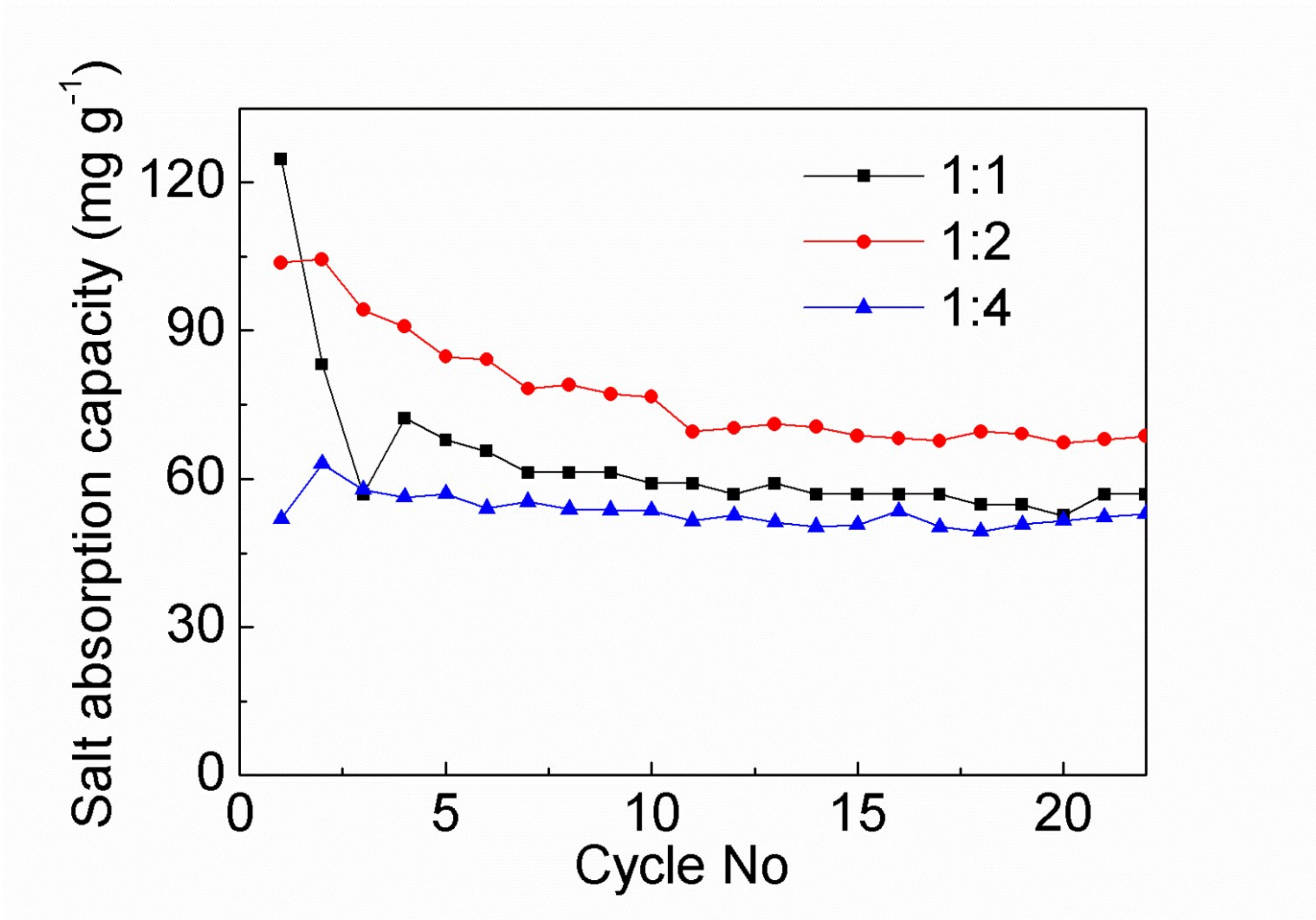
Supplementary Figures:



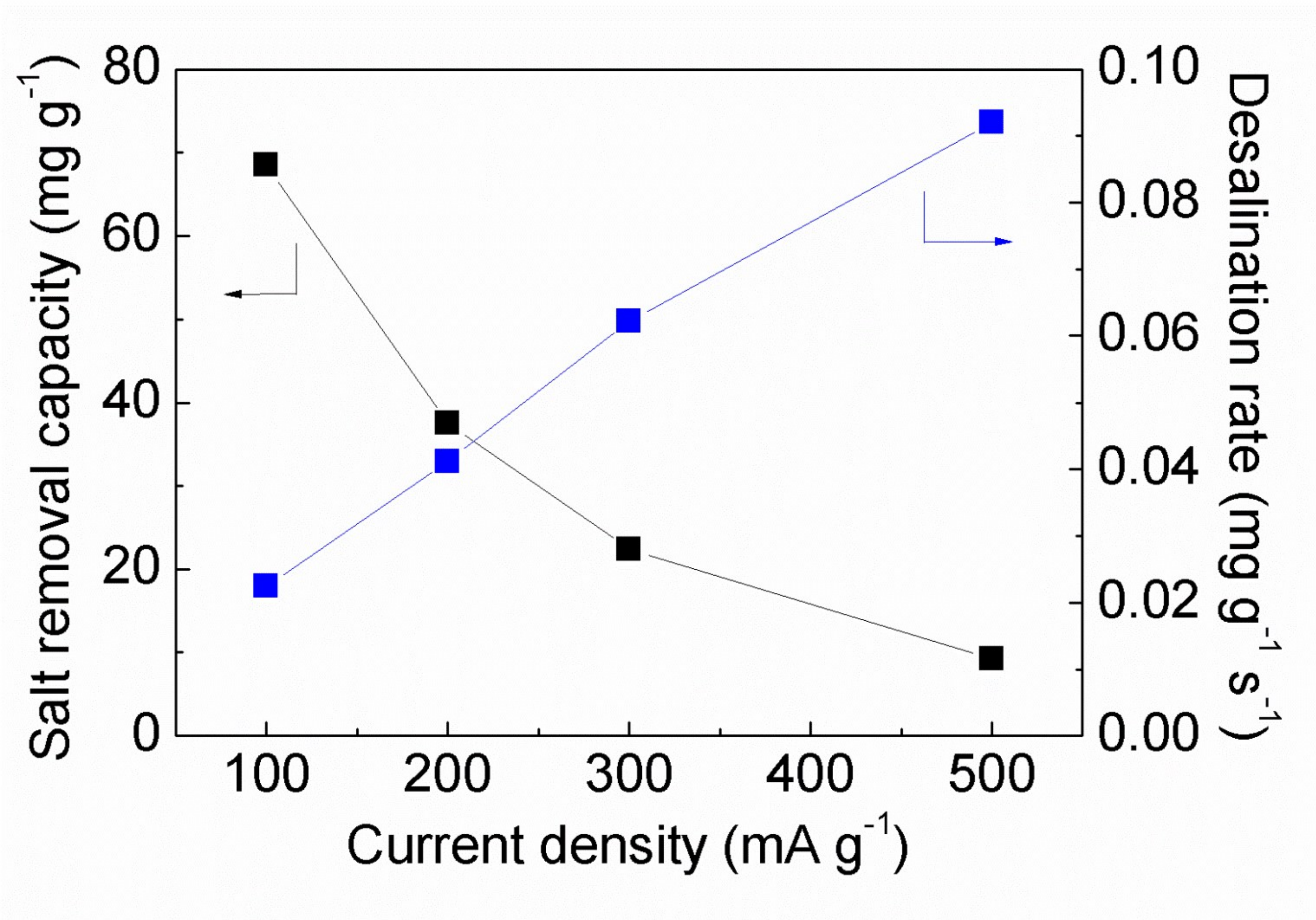
Supplementary Figure 1. Historical evolution of maximum salt adsorption capacity for capacitive, composite, hybrid, and flow CDI electrodes [1, 2], as well as dual-ions electrochemistry deionization (current work).



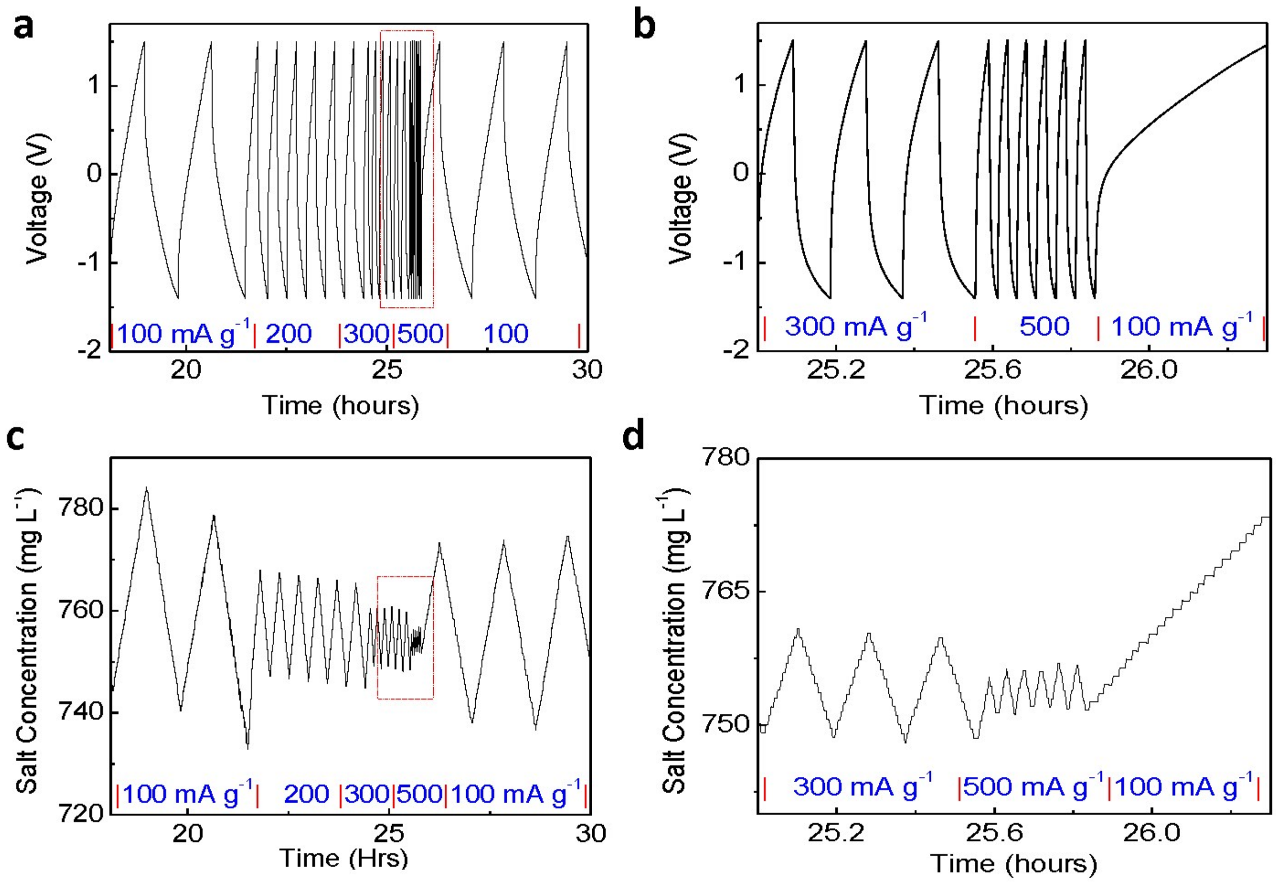
Supplementary Figure 2. Charge and discharge curve (a) and electrochemical salt removal behaviour (b) of the cycle 30 during cycling deionization process, Four stages of electrochemical desalination process, stage 1(A→B): reverse discharge, stage 2 (B→C): charge; stage 3(C→D):discharge; stage 4(D→E): reverse charge. The salt is release during stage 1 and 2 with the positive current applied, and the salt is removed during 3 and 4 with the negative current applied. The energy consumption (kWh/kg) is calculated as $(E_{BC}+E_{DE}-E_{AB}-E_{CD})/(V*(C_{C'}-C_{E'}))$, where E_{BC}, E_{DE}, E_{AB}, and E_{CD} are the energy consumption during the corresponding stage, V is the volume of NaCl solution (L) and $C_{C'}$ and $C_{E'}$ are NaCl concentrations (ppm) at C' and E'. The deionization rate is calculated by $(C_{C'}-C_{E'})*V/(Mt*T)$, where M_t is the total mass of the active electrodes (g), and T is the time during salt removal (s).



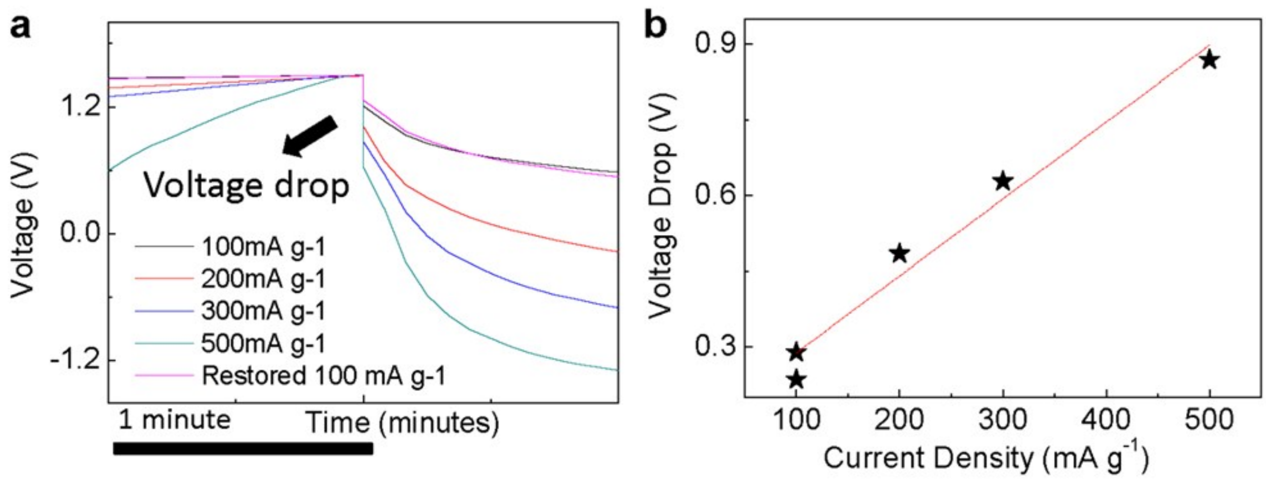
Supplementary Figure 3. the salt removal capacity for the weight ratio of 1:1, 1:2, and 1:4 of BiOCl: NMO



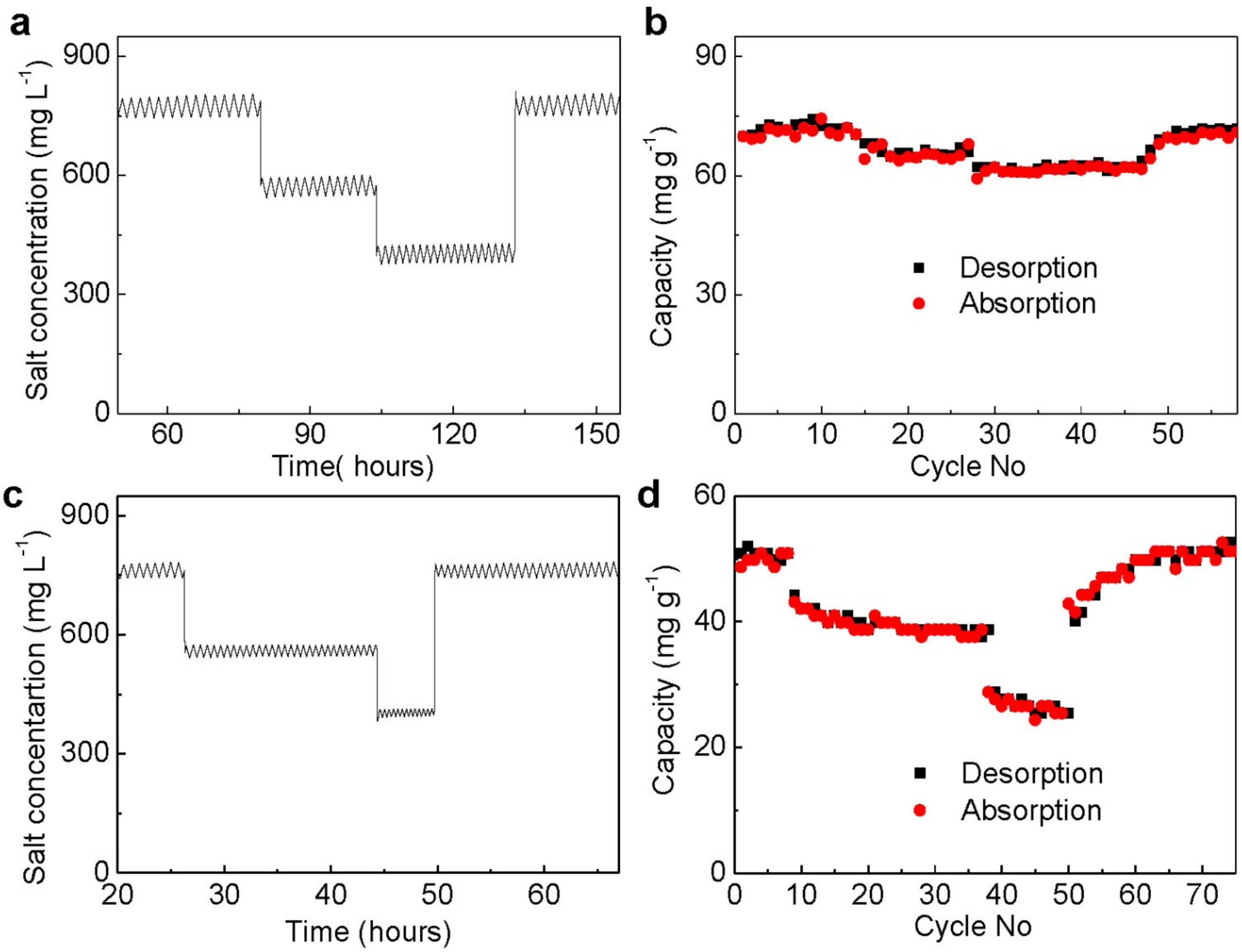
Supplementary Figure 4. The salt removal capacity and desalination rate at 100 mA g-1, 200 mA g-1, 300 mA g-1, and 500 mA g-1.



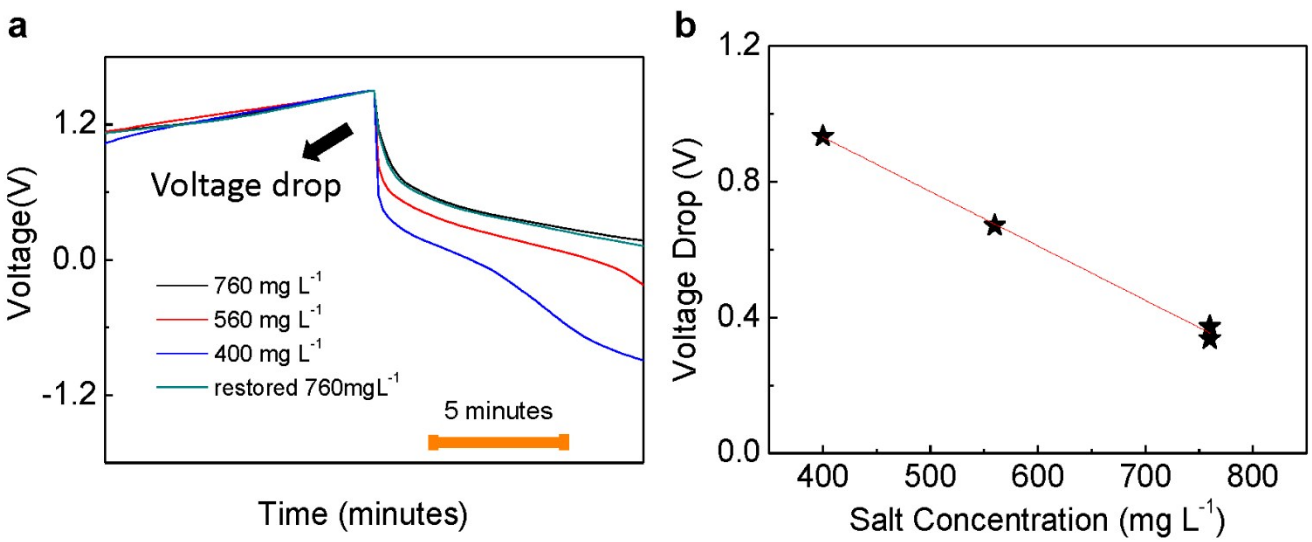
Supplementary Figure 5. (a) voltage vs. time curve at the various current density; (b) Zoom in area of (a) marked in red; (c) Salt concentration change during salt desorption/absorption process at the various current density; (d) Zoom in area of (c) marked in red.



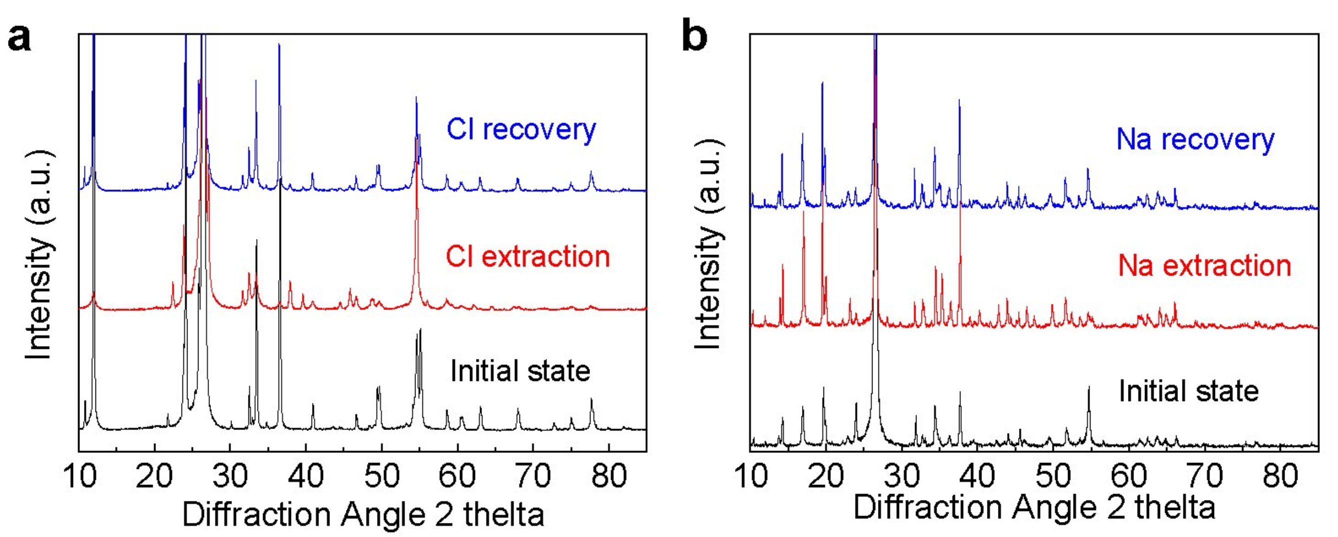
Supplementary Figure 6. the voltage drop at different current density, the representative curves were extracted from Figure 2f, black line: cycle 17; blue line: cycle 24; green line: 30; and red line: cycle 36



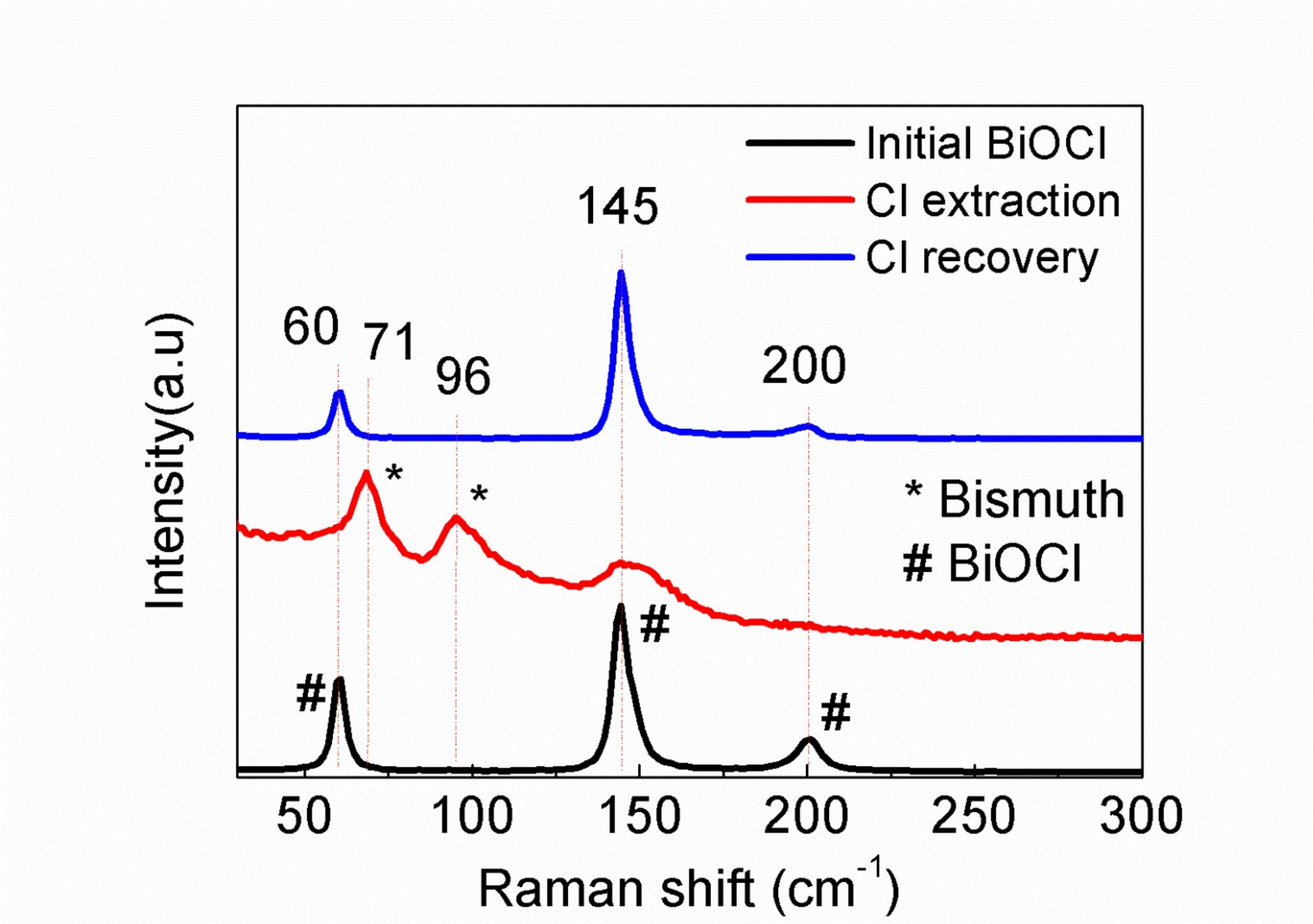
Supplementary Figure 7. the influence of feed concentration, (a) the feed concentration change vs. time during cycling and the corresponding salt absorption/desorption capacity(b) at the current density 100 mA g^{-1}; (c)the feed concentration change vs. time during cycling and the corresponding salt absorption/desorption capacity(d) at the current density 200 mA g^{-1};



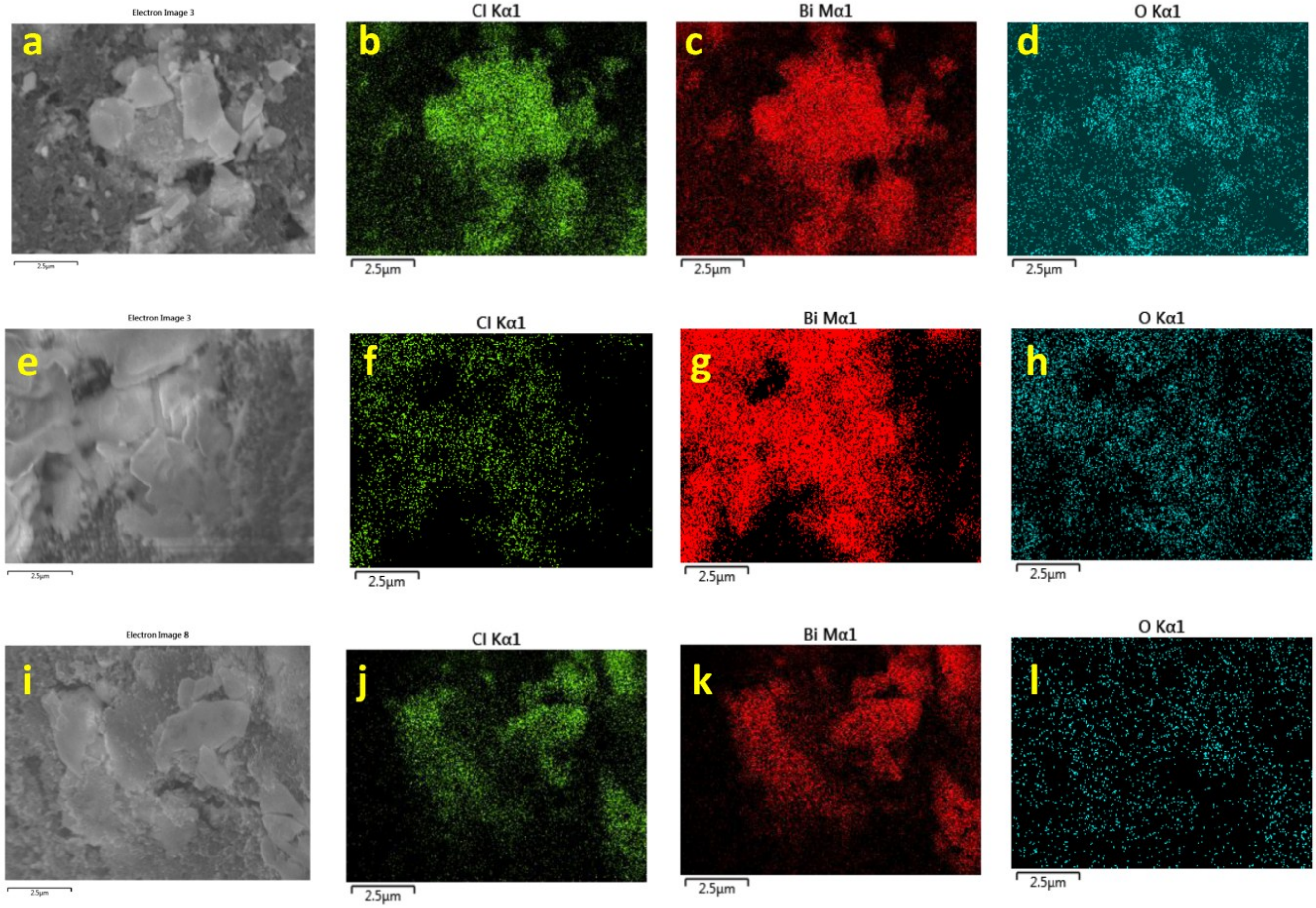
Supplementary Figure 8. (a) the voltage drop at different feed concentration, the representative curves were extracted from Figure S5 (d), black line: cycle 7; red line: cycle 32; blue line: 47; and dark cyan: cycle 69



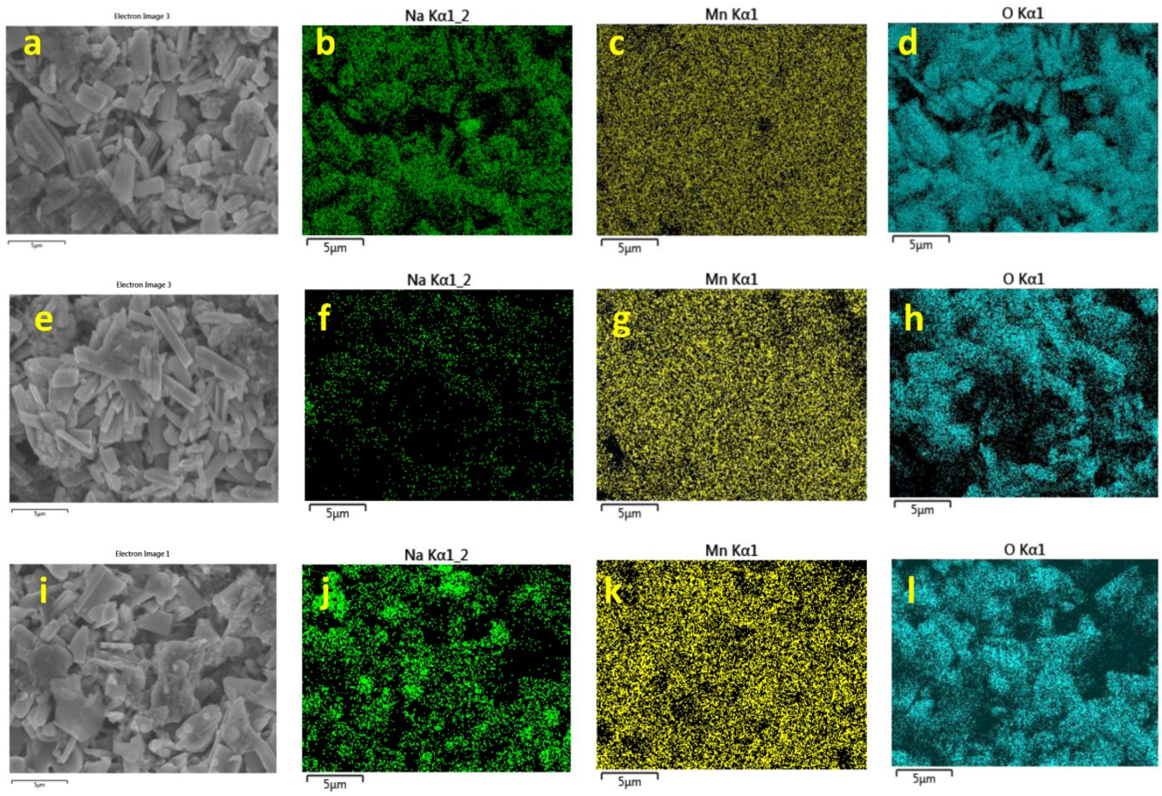
Supplementary Figure 9. (a) XRD patterns of the initial BiOCl, the state of chloride extraction, and the state of chloride recovery with wide diffraction angle. As-prepared BiOCl (black), chloride extraction state (red), chloride recovery state (blue) (b) XRD patterns of as-prepared NMO electrode, the state of sodium extraction, and the state of sodium recovery, As-prepared NMO (black), sodium extraction state (red), sodium recovery state (blue).The reflection peaks appearing at 2 theta = 26.2^{o}, 54.3^{o} are assigned to the graphite substrate.



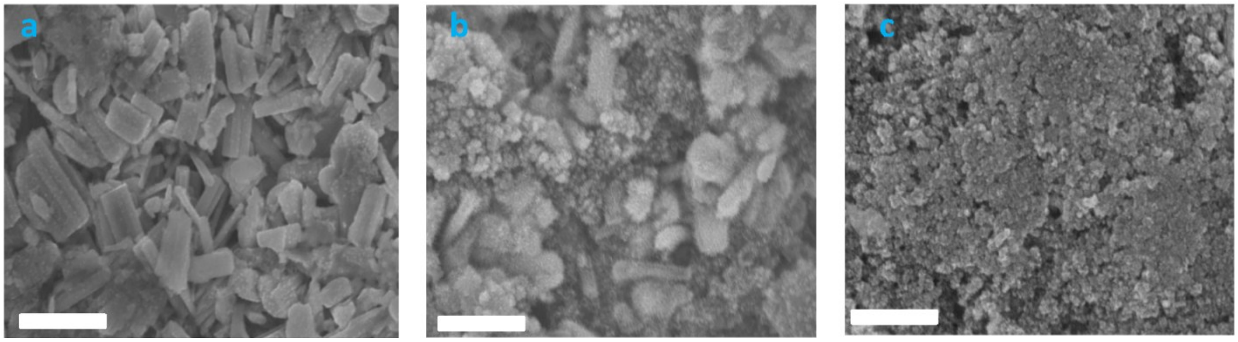
Supplementary Figure 10. Raman spectra of initial BiOCl, its state of chloride extraction, and the state of chloride recovery. No peaks were detected from Bi2O3 at the chloride extraction state, indicating its amorphous form.



Supplementary Figure 11. the SEM images of as-prepared BiOCl (a), the EDX mapping of chloride (b), bismuth (c), and oxygen (d); the SEM images of chloride extraction state of BiOCl (e), the EDX mapping of chloride (f), bismuth (g), and oxygen (h); the SEM images of chloride recovery state of BiOCl (i), the EDX mapping of chloride (j), bismuth (k), and oxygen (l)



Supplementary Figure 12. the SEM images of as-prepared NMO (a) and the corresponding EDX mapping of sodium (b), manganese(c), and oxide (d); the SEM images of sodium extraction state of NMO (e) and the corresponding EDX mapping of sodium (f), manganese(g), and oxide (h); the SEM images of sodium recovery state of NMO (i) and the corresponding EDX mapping of sodium (j), manganese(k), and oxide (l)



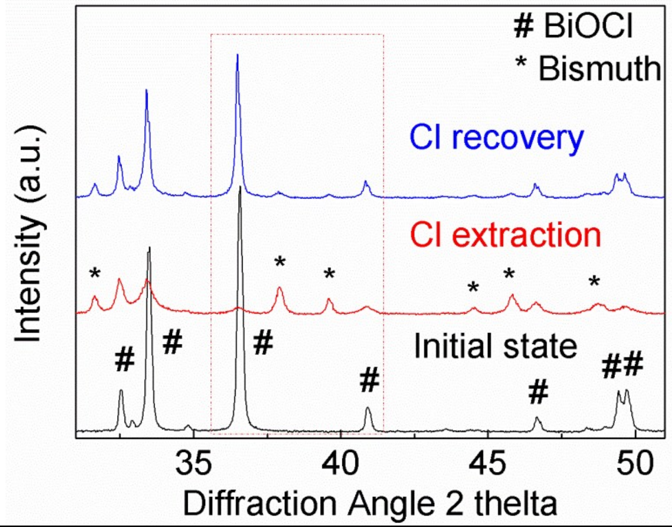
Supplementary Figure 13. Morphology change of NMO electrode at initial state (a) and after 20 cycles (b) and 50 cycles(c). Scale bar: 5um.

Supplementary Tables:

Supplementary Table 1. The ICP measured result during salt recovery and extraction process of the cycle 2 for synthetic mixed salt feed with the approximate ion ratio as real seawater (unit: ppm). The data was obtained by Shimadzu ICPE-9800 series.

State	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}
Starting state (-1.4V)	24	80	33	801
Salt recovery state (1.5V)	26	84	33	864
Salt extraction state (-1.4V)	24	79	33	800

Supplementary Table 2. the peak intensity ratio (bismuth at 39.5°/BiOCl at 40.8°) of initial state, the state of chloride extraction, and the state of chloride recovery of BiOCl electrode.

From Figure 5(a)	
	BiOCl anode electrode
i.e. circled in orange	Peak intensity ratio (* at 39.5°/# at 40.8° marked in red area)
Initial state	0.00
Chloride extraction	2.08
Chloride recovery	0.19

Supplementary Table 3. the element composition of Bi, O, and Cl in the as-prepared BiOCl, chloride extraction state and chloride recovery, and the calculated the atomic ratio of Cl:Bi

atomic %	Bi	Cl	O	Cl:Bi
Initial BiOCl	35.8	29.5	34.6	**0.824**
Chloride extraction	46.5	18.3	35.2	**0.393**
Chloride recovery	37.2	25.0	37.8	**0.672**

Supplementary Table 4. the element composition of Na, Mn, and O in the as-prepared NMO, sodium extraction state and sodium recovery state, and the calculated the atomic ratio of Na:Mn

atomic %	Na	Mn	O	Na:Mn
Initial NMO	15.5	37.4	47.1	**0.42**
Sodium extraction	7.7	43.5	48.8	**0.18**
Sodium recovery	13.6	38.7	47.6	**0.35**

Supplementary Video

Supplementary Video 1 desalination generator, salt removal during the discharge process. Three paralleled LED bulbs are lighted on while the conductivity decreases.

Reference:

1. M. E. Suss, S. Porada, X. Sun, P. M. Biesheuvel, J. Yoon and V. Presser, *Energy & Environmental Science*, 2015, 8, 2296-2319.
2. S. Porada, P. M. Biesheuvel and V. Presser, *Advanced Functional Materials*, 2015, 25, 179-181.