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Supplementary Information

Continuous Desalination with Metal-free Redox-mediator

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Materials

The chemicals TEMPO (purity 97%) and NaCl (purity 99.5%) were ordered from Sigma-Aldrich and used without any further purification. Salt feed water was prepared by dissolving desired quality of NaCl into 100ml of deionized water. During the test, 25 ml of NaCl solution was drawn as the feed. The electrolyte solution was prepared by adding 4 mmol TEMPO in 50 ml NaCl solution at room temperature. To remove the oxygen dissolved in the solutions, high purity argon (99.99%) was used to purge the electrolyte solution prior to the tests.

Desalination Devices

As shown in Figure S1 (device configuration 1), the desalinization device consists of a graphite paper with carbon foam as the negative current collector, a negative chamber, a cation exchange membrane (CEM), salt feed, an anion exchange membrane (AEM), a positive chamber, and a graphite paper with carbon foam as the positive current collector. The standard grade AEM and CEM are ordered from ASTOM Japan.

The active area was 3cm X 3cm in our experiments. The membranes AEM and CEM allow only chloride ions and sodium ions in salt water to transport through respectively. Note that the organic molecule TEMPO and water cannot go through the ion exchange membrane. The carbon foams were applied to increase the effective reaction surface areas. The salt feed flows through the device between AEM and CEM, then back the reservoir to maintain the cycling. The TEMPO active electrolyte flows in the positive chamber to extract anions by an oxidation process, followed by the negative chamber to extract cations by a reduction process, and then circle back to the container. The two flowing channels are driven by peristaltic pumps and continue working at room temperature during desalination. The ion conductivity in salt feed is recorded online by the conductivity meter(eDAQ, EPU357 Conductivity isoPod™ with USB).

For the test of different current intensities, 0.06mA/cm^2, 0.11mA/cm^2, 0.22mA/cm^2, 0.44mA/cm^2 and 0.89mA/cm^2, the initial concentration of salt was prepared at 3000 ppm, and the flow rate of pump was controlled at 28.8 ml/min. In the tests, NaCl concentration in electrolyte is the same as the initial concentration in salt feed during each test. The addition of salt can enhance the conductivity of electrolyte stream. Without salt addition in TEMPO stream, it still could work. However, the resistance should be quite high, and high voltage should be applied due to the high resistance. TEMPO redox couple still could work in other salts. The device was desalinated (or charged) for 2 hours at 0.06mA/cm^2 and then for an hour at every subsequent electrical current. The impact of various salt concentrations was conducted at the initial 3000 ppm, 4500 ppm, 6000 ppm and 8000 ppm feed, respectively. The cell was kept running for 24 hours with the charging current of 0.06mA/cm^2 and flow rate of 25 rpm/min. Five cycling of charge-discharge was carried out at 0.06mA/cm^2, and each cycle lasts for 6 hours.

To enable the full cycling including the catalytic electrolyte and salt feed water, device configuration 2 is adopted as shown in Figure 4, where two AEMs and one CEM are used to separate salt water inlet and outlet chambers, and the current density of 0.44mA/cm^2 is applied. The CV measurement was conducted by Solartron 1470E electrochemical system. A constant current was applied on the device cell by battery charge/discharge analyzer (Brand: Neware, Shenzhen, China) in the electrocircuit.

The calculation of salt removal rate, energy consumption and charge efficiency

Salt removal rate, Γ (ng per centimeter square per second): The salt removal rate of redox-mediator deionization is calculated as:

$$\Gamma = 10^6 * V * \text{Slope}/(60*9)$$

where V is the volume of salt feed (L) , Slope is the rate of simulated line(Δmg/(L.min)), The active area of electrode is 3cm*3cm square.

The energy consumption (kJ/mol) is calculated as (E)/(V*(ΔC)/(58.5*1000)), where E is energy consumption, which can be directly obtained from the battery analyzer. V is the volume of salt feed (L) and ΔC is the change of concentrations. 58.5 is the molar mass of

NaCl. Charge efficiency (Λ) is the ratio of the ionic removal salt to the supplied electrical charge, The equation can be presented as : $\Lambda = V*(\Delta C)*F/(58.5*Capacity*3600*1000)$, where capacity has the unit of Ah, recording from the battery tester; F is Faraday constant (C/mol).

Supplementary Figures:

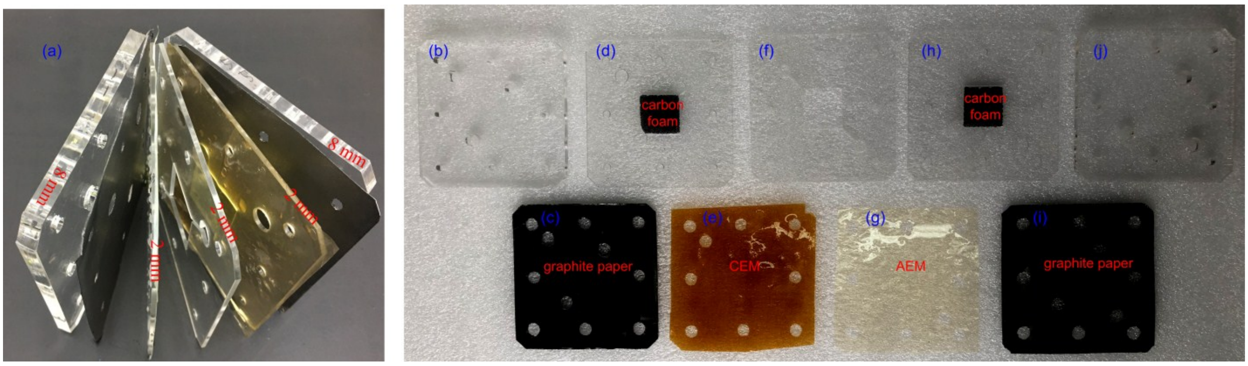

Figure S1. the part photograph of continuous redox-mediator desalination, (a) the assembled structure of deionization device (a), and the separated parts (b-j). The device (a) can be obtained by assembling (b-j) in sequence.

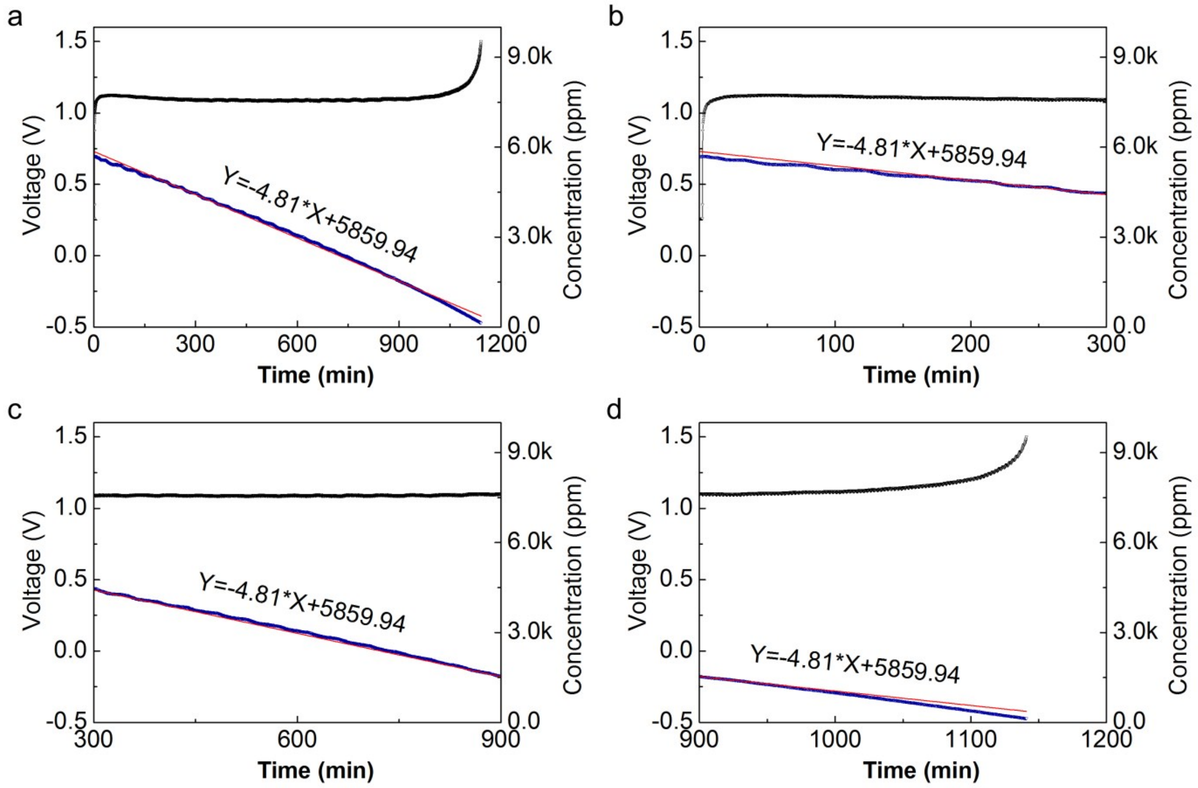

Figure S2, (a) the continuous desalination performance of redox-mediator process at the 0.44mA/cm^2 current density, (b-d) the zoom-in the area at the different time.

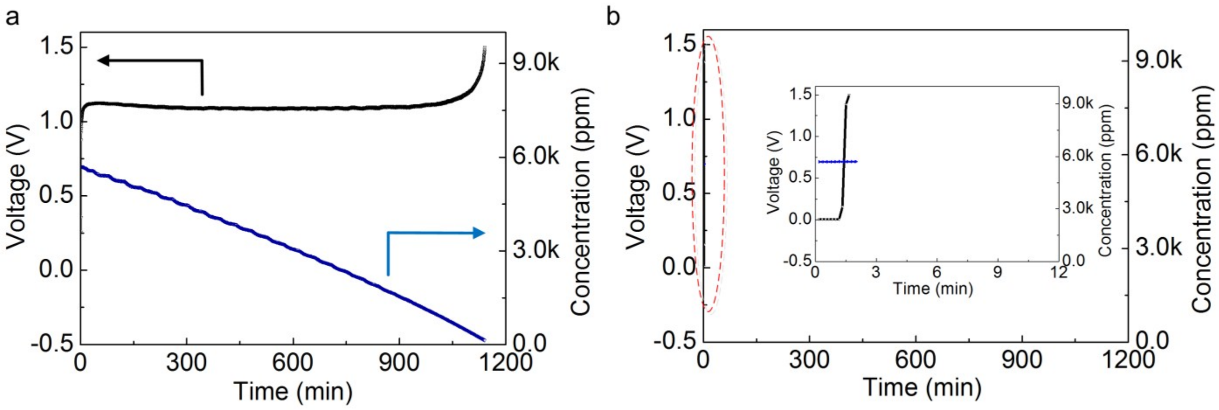

Figure S3, (a) The voltage and concentration curve during the continuous desalination with TEMPO in electrodes stream; (b) The voltage and concentration curves without TEMPO. The inserted figure is the magnified area in the red circled part. The current density is controlled at the same 0.44 mA/cm^2, and the active area is 3cm*3cm.

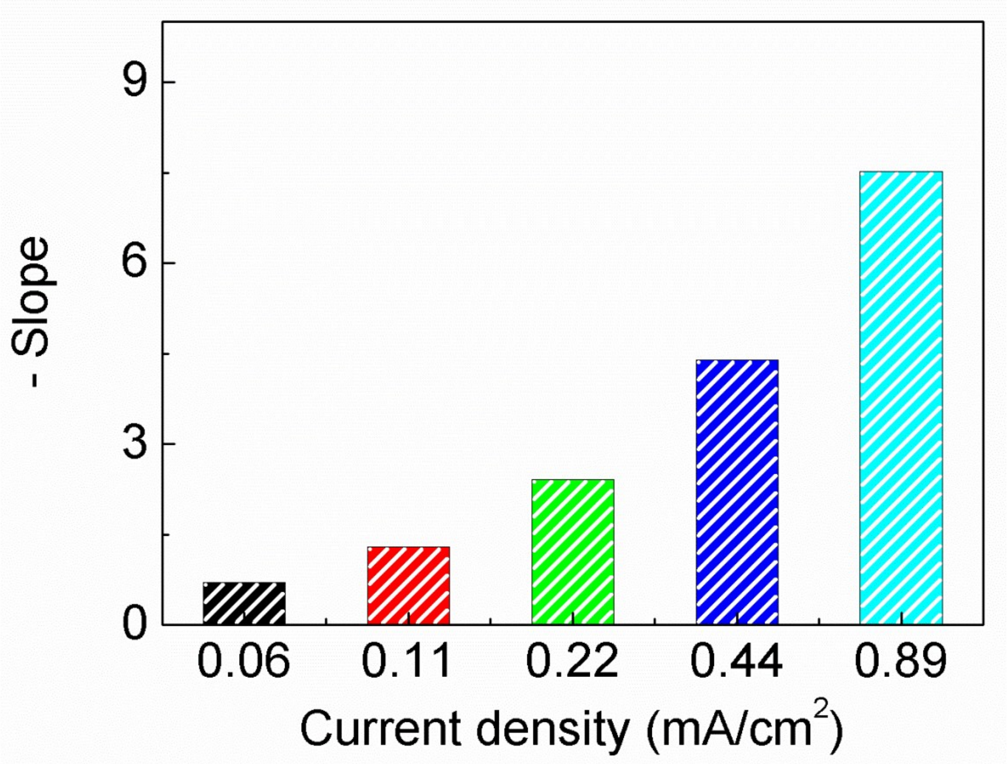

Figure S4, The relation between the current density and negative slope in Figure 2(a)

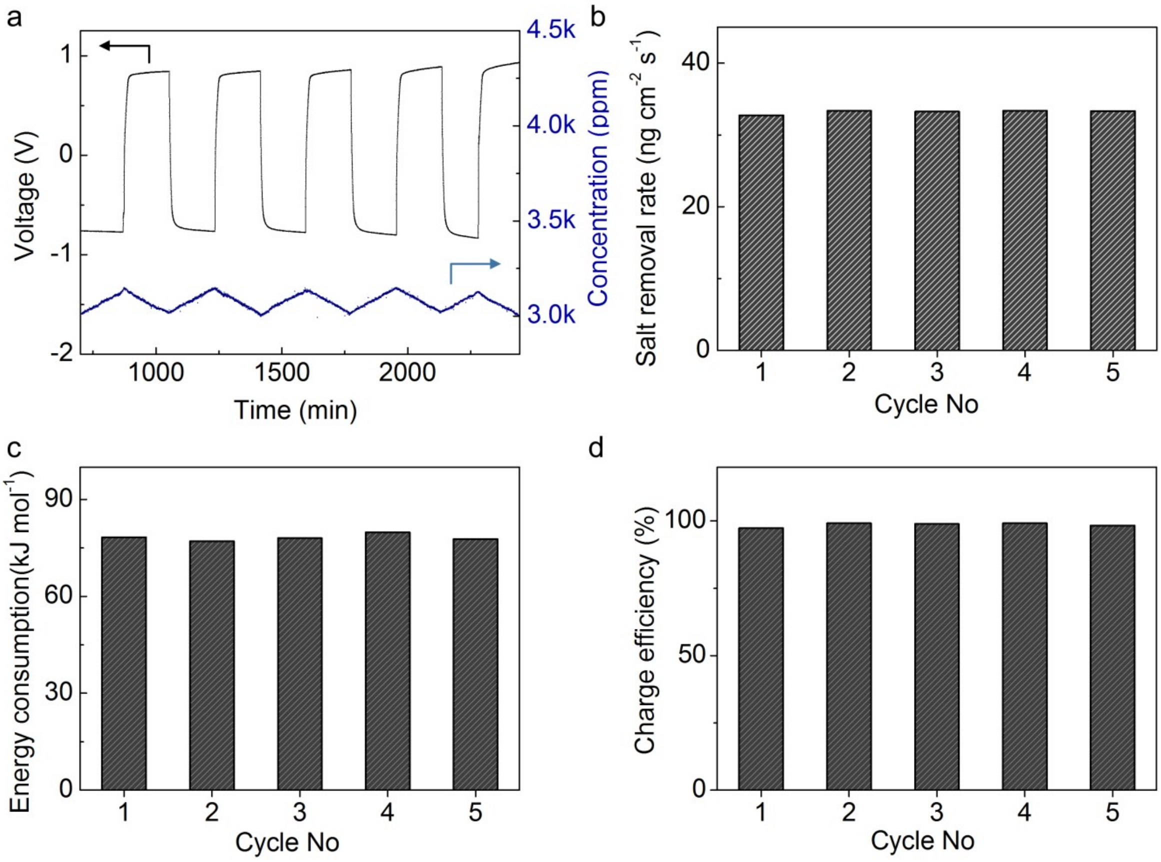

Figure S5 | The cycling performance. (a) the curves of voltage and the corresponding salt concentration change during cycling; the salt removal rate (b), energy consumption (c), charge efficiency (d) during the current variation test. The active electrode area is 3cm*3cm.

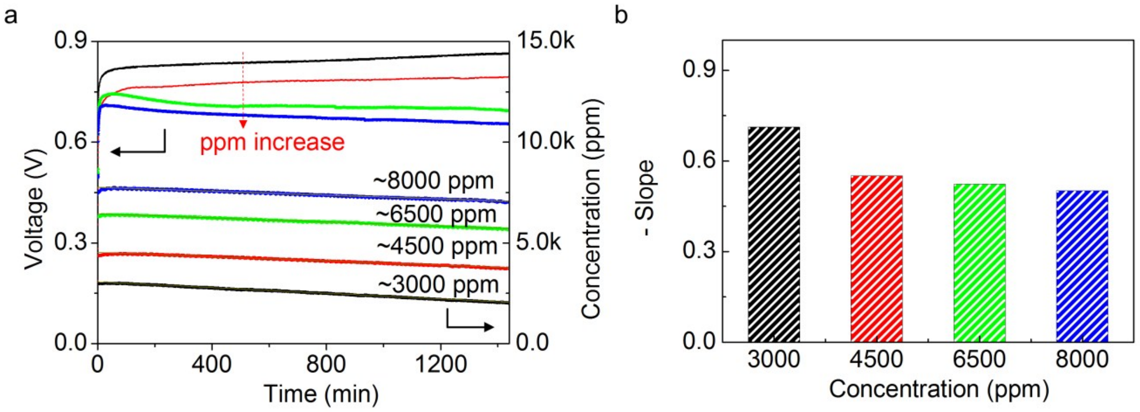

Figure S6. (a) The influence of the salt concentration at 0.06 mA/cm2 current density on the operation voltage and the salt concentration change, (b) The relation between the salt concentration and negative slope

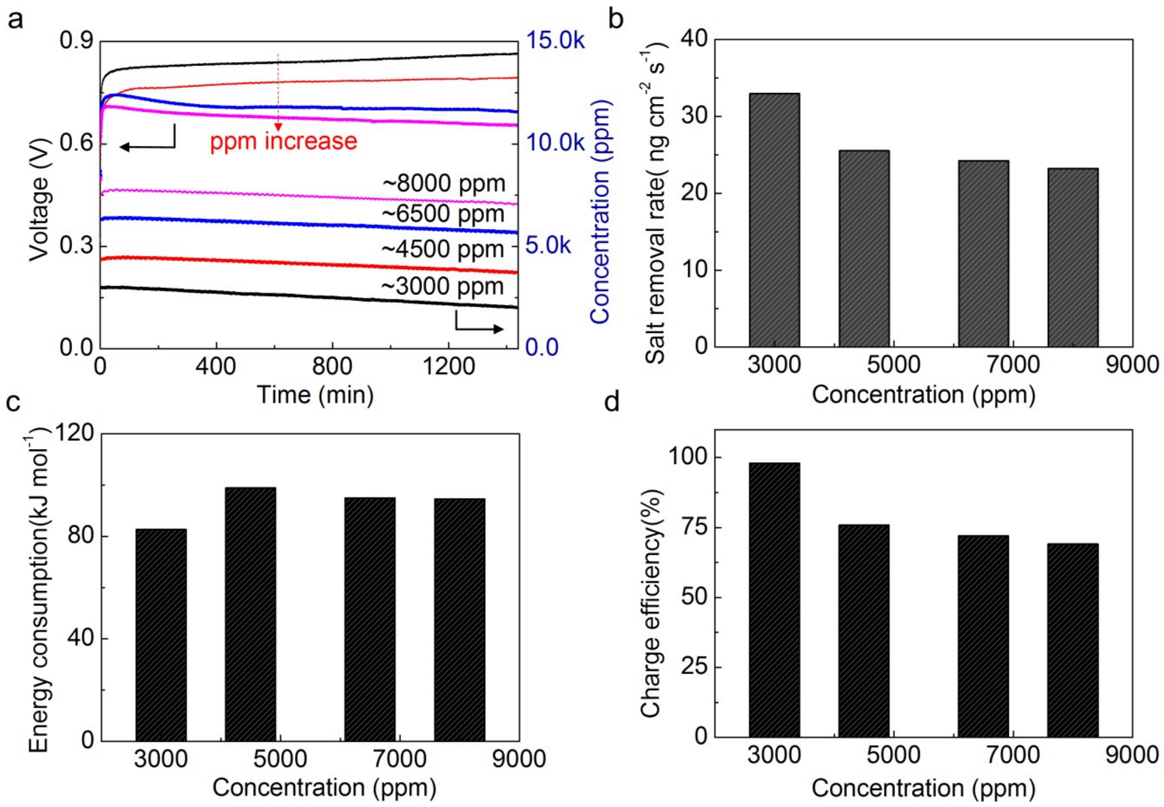

Figure S7 | The influence from salt concentration (a) the curves of voltage and the corresponding salt concentration change at varied concentration; the performance of the salt removal rate (b), energy consumption (c), charge efficiency (d).

Table S1. The feature comparison between reported dual-ion electrochemical desalination and the current molecular redox mediator continuous desalination

	The reported battery desalination[1-14]	**Current molecular redox eletro-mediator desalination**
Mechanism	Salt is released/captured through electrochemical reaction by two individual electrode materials For example[1], the salt desorption process, Chloride electrode: $3BiOCl+3e^{-}\rightarrow Bi+Bi2O3+3Cl^{-}$ Sodium electrode: $Na_{0.44}\ MnO_2\rightarrow Na_{0.44-x}MnO_2+xNa^{+}+xe^{-}$ The salt absorption process, Chloride electrode:$Bi+Bi_2O_3+3Cl\text{-}\rightarrow 3BiOCl+3e\text{-}$ Sodium electrode:$Na_{0.44-x}MnO_2+xNa^{+}+xe^{-}\rightarrow Na_{0.44}MnO_2$ the overall reaction, $3xBiOCl+3Na_{0.44}MnO_2\leftrightarrow xBi+xBi_2O_3+3Na_{0.44-x}MnO_2+3xNaCl$	Salt is captured through redox reaction by one organic molecular the salt removal process Positive electrode: $TEMPO+Cl^{-}\rightarrow TEMPO^{+}Cl^{-}+e^{-}$ Negative electrode: $TEMPO^{+}Cl^{-}+Na^{+}+e^{-}\rightarrow TEMPO+NaCl$ the overall reaction, $TEMPO+Cl^{-}+Na^{+}\rightarrow TEMPO+NaCl$
Salt removal performance	A limited salt removal, determined by the specific capacity of electrode materials	An unlimited salt removal capacity
Desalination mode	Intermittent desalination/salination exchanged mode	Continuous desalination mode
Regeneration	Required	Not Required
Drinking water product	No	Yes
Removal efficiency	Very low	Up to 97.7%
Electrode materials	Two separated electrode materials	One organic molecule by itself redox reaction
Ion exchange membrane	Not necessary	Required

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