



## Supplementary Materials

### Text S1. Design and Configuration of Additional Cells

Except for the scaled-up redox-mediated electro dialysis (redox-ED) system, all experiments were performed with small-sized electrochemical cells. Among the three major categories of electrochemical tests in this study, the **Preliminary Study of Water-Softening Redox-ED System** (Section 3.1) and the **Effects of Conductive Ion Exchange Resin** (Section 3.5) used the small-sized cells.

For the **Preliminary Study of Water-Softening Redox-ED System**, three types of cells were used based on preceding research [1]: membrane capacitive deionization (MCDI), multichannel MCDI (MC-MCDI), and preliminary redox-ED (pre-redox-ED) cells. Porous carbon electrodes (Purechem), measuring  $40 \times 40 \text{ mm}^2$ , were employed in these tests.

The MCDI cell comprised two parallel porous carbon electrodes, positioned opposite each other, having an anion exchange membrane (AEM) (ASE, ASTOM) and a cation exchange membrane (CEM) (CSE, ASTOM) between them. A non-conductive spacer measuring  $40 \times 40 \times 0.5 \text{ mm}^3$  was inserted between the membranes to create the feed channel. Both the MC-MCDI and pre-redox-ED cells maintained the same membrane separation, featuring a fully divided feed channel as the middle channel (MC) and two side channels (SCs), each fitted with an AEM and a CEM. Non-conductive spacers, each measuring  $40 \times 40 \times 0.5 \text{ mm}^3$ , separated the electrodes from the adjacent ion exchange membranes (IEM) in the SCs.

For tests in the **Effects of Conductive Ion Exchange Resin**, the same cell configuration was utilized as in the pre-redox-ED cell but with a membrane separation of 16.4 mm. The MC of the resin-redox-ED cell was filled with a well-blended mixture of anion exchange resin (AXR), with a total minimum capacity of 1.3 eq/L ( $\text{Cl}^-$  form) (A400, Purolite), and cation exchange resin (CXR), with a total capacity of 1.9 eq/L ( $\text{Na}^+$  form) (HCR-S/S, DOWEX), in a 1:1 exchange capacity ratio without a spacer. The conductive ion exchange resins (IXRs) were thoroughly dispersed to avoid channeling or any potential damage to the IEMs. The control cell was assembled without IXRs and included a non-conductive spacer measuring  $40 \times 40 \times 16.4 \text{ mm}^3$  inside the MC. In the SCs, each electrode was spaced from the adjacent IEM by a non-conductive spacer measuring  $40 \times 40 \times 0.5 \text{ mm}^3$ .

### Text S2. Electrochemical Ion Removals with Additional Cells

In all electrochemical tests, hard water containing 1.85 mM  $\text{CaCl}_2$  and 0.65 mM  $\text{MgCl}_2$  (*i.e.*, 250 ppm as  $\text{CaCO}_3$ ) served as the feed water. The ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  was adjusted in line with IEC 60734:2012 [2]. Feed solutions were continuously supplied to the feed channels (corresponding to the MCs of MC-MCDI and all redox-ED cells). Flow rates were governed by peristaltic pumps (YZ1515x, Shenchen). Effluents were monitored and analyzed with conductivity (3574-10C, HORIBA) and pH meters (9615S-10D, HORIBA), with data processed as necessary. All electrochemical tests were conducted using a potentiostat (VSP, Biologic), where currents and cell potentials ( $E_{\text{cell}}$ s) were recorded throughout the operations and analyzed subsequently. When a new redox couple solution was prepared, preliminary charging at  $E_{\text{cell}} = +1.2 \text{ V}$  was conducted to balance the species ratio in the SC. Before commencing ion removal steps, the conductivity of the effluent without applied potential was allowed to stabilize. Ion chromatography (IC) was performed utilizing a Thermo Scientific Dionex Aquion Ion Chromatography system with an AS-AP Autosampler (Thermo Fisher Scientific).

For tests in the **Preliminary Study of Water-Softening Redox-ED System**, the cells were operated in single-pass mode with feed flow rates of 2.0 ml/min. In the MC-MCDI, a high-concentration NaCl solution (1.0 M) was circulated in the SC. In the pre-redox-ED, a solution containing a total concentration of 0.1 M ferri-/ferrocyanide redox couple ( $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ , from  $\text{Na}_4\text{Fe}(\text{CN})_6$  salt) and 0.5 M NaCl was circulated in the SC. The SC flow rates of the MC-MCDI and pre-redox-ED cells were maintained at 2.0 mL/min. For ion removal, the MCDI and MC-MCDI cells repeated a cycle of serial charging ( $E_{\text{cell}} = +1.2 \text{ V}$ ; 5 min) and discharging ( $E_{\text{cell}} = 0 \text{ V}$ ; 15 min) steps as required. The pre-redox-ED cell operated continuously at  $E_{\text{cell}} = +1.2 \text{ V}$  for 1 hour. Effluent from the last cycle (or selected cycle of interest) was collected throughout the ion removal phase (*i.e.*, during the charging step) and thoroughly mixed preceding IC analysis.

For tests in the **Effects of Conductive Ion Exchange Resin**, the cells were operated in single-pass modes with two MC feed flow rates ( $v_{\text{MC}}$ 's) of 0.5 and 1.0 mL/min. The SC solution, containing a total concentration of 0.1 M  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (from  $\text{Na}_4\text{Fe}(\text{CN})_6$  salt) and 0.5 M NaCl, was circulated at 5.0 mL/min. Ion removal repeated a cycle of serial charging ( $E_{\text{cell}} = +1.2 \text{ V}$ ; 15 min) and discharging ( $E_{\text{cell}} = -1.2 \text{ V}$  for resin-redox-ED cell, and 0 V for control cell; 15 min) steps for 3 times at  $v_{\text{MC}} = 0.5 \text{ mL/min}$  and 5 times at  $v_{\text{MC}} = 1.0 \text{ mL/min}$ . Effluent was collected from the last, or any selected, cycle during the ion removal step (*i.e.*, charging step) and thoroughly mixed prior to IC analysis.

---

### Text S3. Analytical Methods with Additional Cells

For tests in the **Preliminary Study of Water-Softening Redox-ED System**, the collected conductivity data were converted to ion removal during the charging step (I.R.; %) according to Eq. (S1):

$$\text{I. R. (\%)} = \frac{\text{COND}_0 \times t_{\text{charging}} - \sum_n (\text{COND}_n + \text{COND}_{n-1})(t_n - t_{n-1})/2}{\text{COND}_0 \times t_{\text{charging}}} \times 100 \quad (\text{S1})$$

where  $t_n$  is the time (min) at the  $n$ -th measurement point by the conductivity meter,  $t_{\text{charging}}$  is the duration (min) of the charging step of interest, and  $\text{COND}_0$  and  $\text{COND}_n$  are the effluent conductivities (mS/cm) measured at time  $t=0$  min and  $t_n$ , respectively. The conversion of effluent conductivity to ion concentration was verified through calibration [3]. The charge efficiency (C.E.; %) was calculated using Eq. (S2):

$$\text{C. E. (\%)} = \frac{v \times t_{\text{charging}} \times \sum_i z_i (C_{i,0} - C_{i,\text{charging}})}{f \text{I}t / F} \times 100 \quad (\text{S2})$$

where  $z_i$  is the charge (eq/mol) of the  $i$ -th cation,  $C_{i,0}$  is the concentration (M) of the  $i$ -th cation in the effluent, obtained in a stabilized state without an applied potential,  $C_{i,\text{charging}}$  is the concentration (M) of the  $i$ -th cation in the effluent IC sample during charging,  $v$  is the feed flow rate (L/min) (*i.e.*, MC feed flow rate for MC-MCEDI and pre-redox-ED cells),  $I$  is the current (A) recorded during the corresponding time period for IC sampling, and  $F$  is the Faraday constant (96,485 C/mol). In the C.E. calculation for MC-MCEDI, not only were  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the hard water feed considered, but also  $\text{Na}^+$  that back-diffused from the SCs. The energy consumption for cation removal (E.C.; kWh/kg cation) was calculated using Eq. (S3):

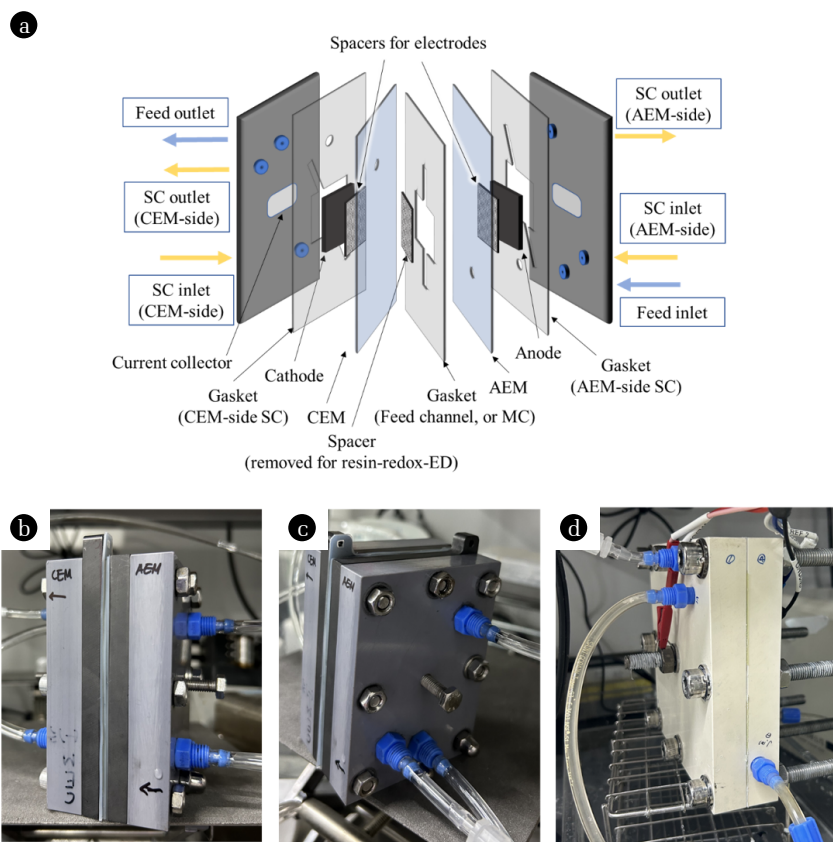
$$\text{E. C. (kWh/kg cation)} = \frac{E_{\text{cell}} \int I dt}{\sum_i [(C_{i,0} - C_{i,\text{charging}}) \times \text{MW}_i] \times v \times t_{\text{charging}}} \quad (\text{S3})$$

where  $E_{\text{cell}}$  is the applied cell voltage (V) and  $\text{MW}_i$  is the molecular weight (g/mol) of the  $i$ -th ion. Other variables remain as previously defined. For tests in the **Effects of Conductive Ion Exchange Resin**, C.E. and T.H.R. were calculated using Eq. (S2) and (S4), respectively:

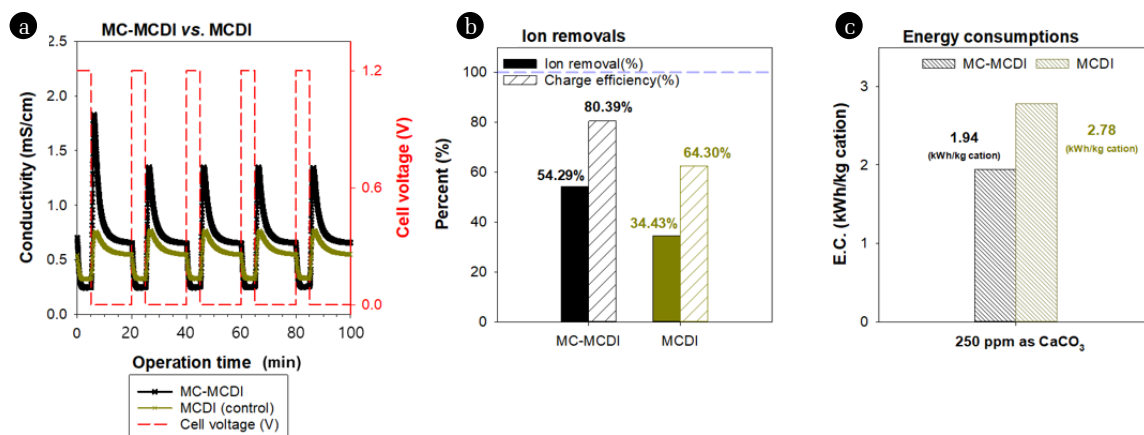
$$\text{T. H. R. (\%)} = \sum_i \frac{(C_{i,0} - C_{i,\text{charging}})}{C_{i,0}} \times 100 \quad (\text{S4})$$

where only  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  removals were considered. Individual ion removal (%) was calculated using Eq. (S5):

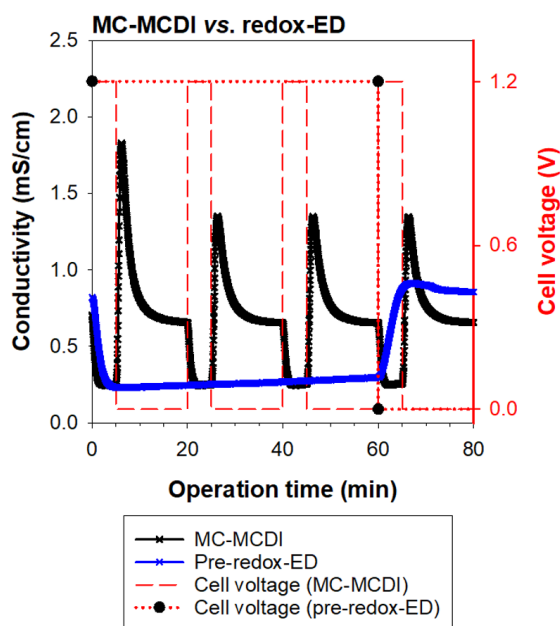
$$i\text{-th ion removal (\%)} = \frac{C_{i,0} - C_{i,\text{charging}}}{C_{i,0}} \times 100 \quad (\text{S5})$$



**Fig. S1.** (a) Basic schematic of the cells used in this study and (b-d) digital images of some cells. In (a), the spacer in the MC was replaced by IXRs to construct the resin-redox-ED cell. The control cell for the resin-redox-ED cell contained the spacer but lacked IXRs. The cells employed in the **Preliminary Study of Water-Softening Redox-ED System** (i.e., MCDI, MC-MCDI, and pre-redox-ED cells) and the **Effects of Conductive Ion Exchange Resin** (i.e., resin-redox-ED and control cells) share the same configuration portrayed in (b) and (c), differing only in certain details (e.g., thickness of the SC and/or the MC). Electrochemical water softening using a scaled-up redox-ED system along with its optimizations was conducted with the cell illustrated in (d).



**Fig. S2.** Comparison of (a) conductivity profiles, (b) ion removals, and (c) E.C. (kWh/kg cation) between the preliminary MC-MCDI and MCDI cells (electrode:  $40 \times 40 \text{ mm}^2$  porous carbon electrode (Purechem); MC feed: 250 ppm as  $\text{CaCO}_3$  hard water; SC feed: 0.5 M NaCl; flow rate: 2.0 mL/min (for all channels); feed channel width: 0.5 mm; charging:  $E_{\text{cell}} = +1.2 \text{ V}$  (for 5 min); discharging:  $E_{\text{cell}} = 0 \text{ V}$  (for 15 min)).



**Fig. S3.** Comparison of effluent conductivity profiles between the MC-MCDI and pre-redox-ED cells (electrode:  $40 \times 40 \text{ mm}^2$  porous carbon electrode (Purechem); MC feed: 250 ppm as  $\text{CaCO}_3$  hard water; SC feed: 0.1 M  $\text{Na}_4\text{Fe}(\text{CN})_6$  and 0.1 M  $\text{NaCl}$ ; flow rate: 2.0 mL/min (for all channels); MC width: 0.5 mm; charging:  $E_{\text{cell}} = +1.2 \text{ V}$  (for 1 h for the pre-redox-ED cell, and 5 min for the MC-MCDI cell); discharging:  $E_{\text{cell}} = 0 \text{ V}$  (for 15 min, only for the MC-MCDI cell)).

## References

- [1] Kim S, Kim C, Lee J *et al.* Hybrid Electrochemical Desalination System Combined with an Oxidation Process. *ACS Sustain. Chem. Eng.* 2017;6(2):1620–1626. <https://doi.org/10.1021/acssuschemeng.7b02789>.
- [2] International Electrotechnical Commission (IEC). IEC 60734:2012 - Household electrical appliances - Performance - Water for testing. Geneva: IEC; 2012.
- [3] Kim N, Hong SP, Lee J, Kim C, Yoon J. High-Desalination Performance via Redox Couple Reaction in the Multichannel Capacitive Deionization System. *ACS Sustain. Chem. Eng.* 2019;7(19):16182–16189. <https://doi.org/10.1021/acssuschemeng.9b03121>.