Supporting Information

Novel Resin Composite Electrodes for Selective Removal of Sulfate by the Capacitive Deionization Process

Kuichang Zuo,^{1,3} Jun Kim,^{1,3} Amit Jain,^{2,3} Tianxiao Wang,¹ Rafael Verduzco,^{2,3*} Mingce Long⁴, Qilin Li^{1,3*}

¹ Civil and Environmental Engineering, Rice University, MS 319, 6100 Main Street, Houston 77005, USA

² Department of Chemical and Biomolecular Engineering, Rice University, MS 362,
6100 main Street, Houston 77005, USA

³ NSF Nanosystems Engineering Research Center Nanotechnology-Enabled Water

Treatment, Rice University, MS 6398, 6100 Main Street, Houston 77005, USA

⁴ School of Environmental Science and Engineering, Shanghai Jiao Tong University,

800 Dongchuan Road, Shanghai 200240, China

*Corresponding author:

Qilin Li: <u>qilin.li@rice.edu</u> (Email), 713-348-2046 (Tel) Rafael Verduzco: <u>rafaelv@rice.edu</u> (Email), 713-348-6492 (Tel)

QPVA solution preparation

The anion-exchange binder was comprised of quaternized polyvinyl alcohol (QPVA, Figure S2).¹ KOH (50 mol % relative to PVA repeat units) and glycidyl trimethyl ammonium chloride (GTMAC, 50 mol % relative to PVA repeat units) were added to a 6 wt % PVA solution in DI water. Next, the mixture was heated at 70 °C for 4 h while stirring continuously. The resulting mixture was precipitated in pure ethanol and dried overnight under vacuum to obtain QPVA as a white solid. This product was redissolved in deionized water at 90 °C, and the pH was lowered to 5.0 by adding 1.0 M HCl solution.

Tests of SO₄²⁻ selectivity on resin particles

The selectivity of original unpulverized resin particles was evaluated in batch beaker experiment. During experiments, 0.05, 0.1, 0.2, 0.4 and 0.6 g resin were added in 50 mL binary solution containing 5 mmol/L NaCl and 5 mmol/L Na₂SO₄. The resins and solutions were mixed thoroughly using magnetic stirs, and water samples (0.5 mL at each time) were taken at 0.5 h, 1.0 h, 2.0 h, 12.0 h, and 24.0 h to ensure saturation of the resin. After that, the water samples were analyzed using IC, and the SO_4^{2-} selectivity (*S*) was defined in Eq. S1.

$$S_{\text{SO}_{4}^{2^{-}}} = \frac{V_{\text{final}}(C_{\text{SO}_{4}^{2^{-}},\text{initial}} - C_{\text{SO}_{4}^{2^{-}},\text{final}}) / C_{\text{SO}_{4}^{2^{-}},\text{initial}}}{V_{\text{final}}(C_{\text{CI}^{-},\text{initial}} - C_{\text{CI}^{-},\text{final}}) / C_{\text{CI}^{-},\text{initial}}}$$
(1)

where $C_{SO_4^2, initial}, C_{CI^-, initial}, C_{SO_4^2, final}, C_{CI^-, final}$ (mmol/L) are the initial and final SO₄²⁻ and Cl⁻ concentrations respectively; V_{final} is the final volume of saltwater.



Figure S1 Fabrication process of resin coated activated carbon electrode using flow coating method. (A) Graphite sheet was fixed on glass plate as current collector; (B) Graphite sheet was put on the flow coater before coating; (C) Adding activated carbon slurry as electrode material; (D) Coating activated carbon on graphite sheet; (E) Coating resin slurry on the top of carbon layer that has dried for 30 min at room temperature; (F) The prepared resin coated electrode after being crosslinked at 70 °C for overnight. AC: activated carbon; *v*: moving speed (mm/s); *h*: gap between top coating blade and bottom graphite (or AC layer when coating resin slurry).



Figure S2 Synthesis of quaternized PVA (QPVA).



Figure S3 Electrodialysis cell for separate experiments. (A) Photograph and (B) schematic diagram of the electrodialysis cell; (C) Sum of concentration of Cl⁻ and SO_4^{2-} in anion donation and accepting chambers. CEM: cation exchange membrane; Resin-MF: resin coated microfiltration membrane; Acc-Cha: ion accepting chamber; Don-Cha: anion donation chamber.

Size Distribution by Intensity



Figure S4 Size distribution of resin powder after pulverized by cryogenic milling.



Figure S5 Zeta potential of resin powder.



Figure S6 Removal behavior of Cl⁻ and SO₄²⁻ with various amount of resin in 50 mL of binary solution containing 5 mmol/L NaCl and 5 mmol/L Na₂SO₄. (A) Equilibrium concentrations; (B) SO₄²⁻ adsorption and selectivity.



Figure S7 QPVA coated electrode has a dense and homogeneous polymeric coating on the top of activated carbon electrode.



Figure S8 Electrochemical impedance spectroscopy of uncoated, QPVA coated, and resin/QPVA coated electrode.



Figure S9 Performance of uncoated, QPVA coated and resin/QPVA coated electrode during 27 h of operation. (A) Current production; (B) Conductivity evolution.



Figure S10 pH change of the uncoated, QPVA coated and resin/QPVA coated electrode during operation



Figure S11 Performance of CDI with anode coating with various amount of resin slurry. (A) Conductivity change during desorption period; (B) Average adsorption and desorption current; (C) Total salt removal and release during adsorption and desorption period respectively.



Figure S12 Performance of resin/QPVA coated electrode with various $CI:SO_4^{2-}$ concentration ratios. (A) Conductivity change; (B) Current generation and salt removal; (C) Charge efficiency; (D) Ion removal and SO_4^{2-} selectivity. Arrows in panel B and C represent corresponding axis.



Figure S13 The resin/QPVA coated electrode after long term operation.

References

1. Tian, G. Y.; Liu, L.; Meng, Q. H.; Cao, B., Preparation and characterization of cross-linked quaternised polyvinyl alcohol membrane/activated carbon composite electrode for membrane capacitive deionization. *Desalination* **2014**, *354*, 107-115.