Electronic Supplementary Information for

Hybrid capacitive deionization to enhance the desalination performance of capacitive techniques

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$Na_4Mn_9O_{18}$ characterization

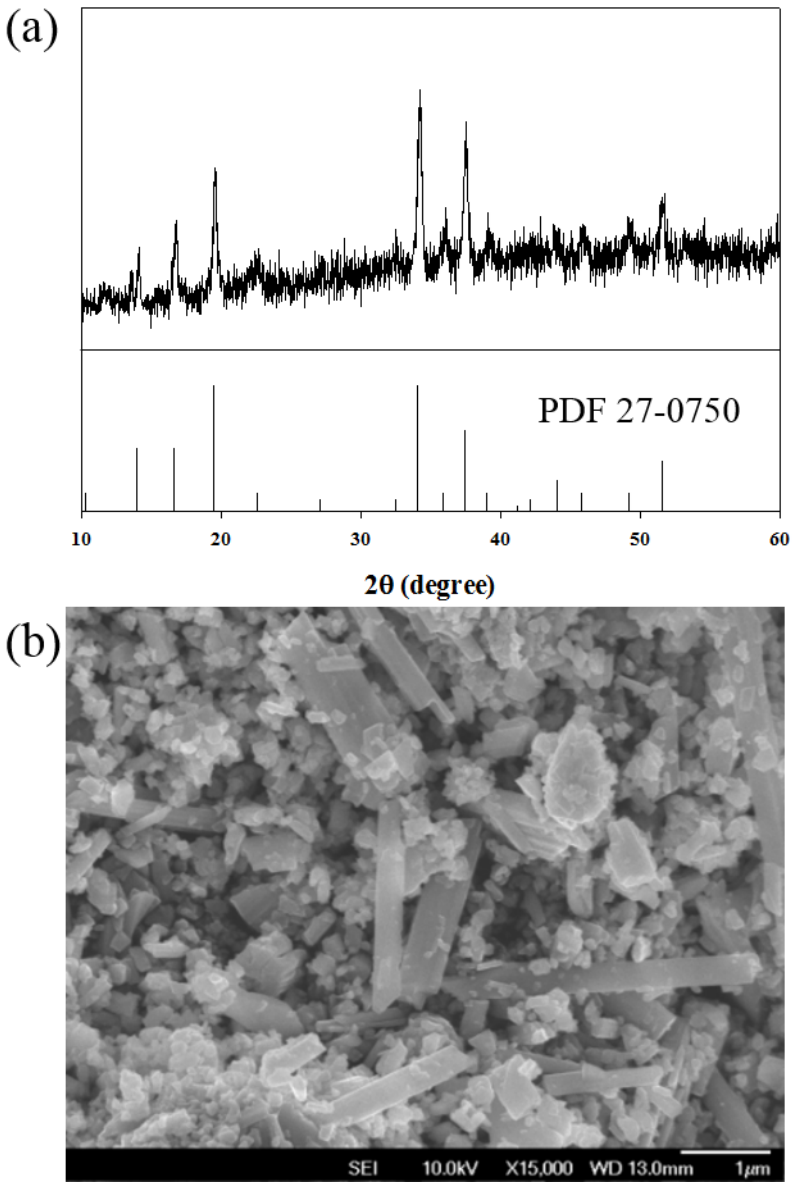


Fig. S1 (a) XRD pattern of synthesized $Na_4Mn_9O_{18}$ with reference to JCPDS (PDF 27-0750) data. (b) SEM image of $Na_4Mn_9O_{18}$.

Ion removal performance of CDI and MCDI systems

The deionization performances of CDI and MCDI were demonstrated in the same reactor, as shown in Fig. 2. The electrodes were disk-shaped (d = 50 mm, thickness: 300 mm) made from the same commercial activated carbon (MSP-20, Kansai Coke and Chemicals) as in the HCDI system. The CDI system constructed from a pair of activated carbon electrodes, graphite sheet, and a nylon spacer (thickness: 200 μm) was used to prevent short-circuiting. The MCDI system contained cation and ion exchange membranes that were placed between the activated carbon electrodes. The ion removal performance of CDI was tested in constant voltage zero-volt desorption mode (CV-ZVD, 1.2 V for 15 min during the ion-adsorption step, and 0 V for 15 min during the ion-desorption step), and MCDI was investigated in constant voltage reverse-volt desorption mode (CV-RVD, 1.2 V for 15 min during the ion-capturing step, and -1.2 V for 15 min during the ion-releasing step). The ion removal capacity was then displayed as the captured the captured sodium chloride mass per total weight of the two activated carbon electrodes (Fig. S3(a)) and NaCl per cell area (cm^2) during the ion-capturing step (Fig. S3(c)). The ion removal rate was finally expressed as the mass of captured ions (mg) per operation time (s) divided by the electrode mass (g) (Fig. S3(b), and divided by the active cell area (cm^2) (Fig. S3(b))

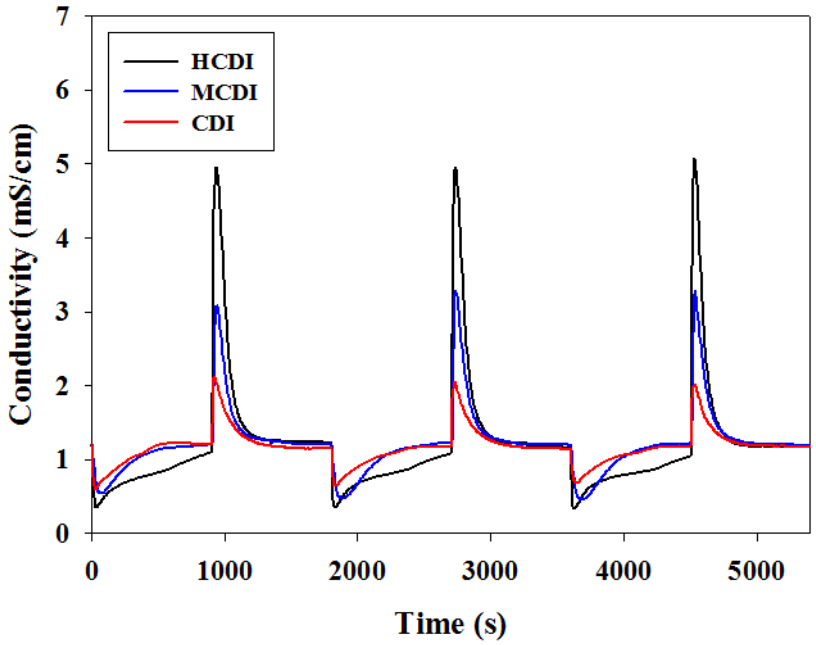
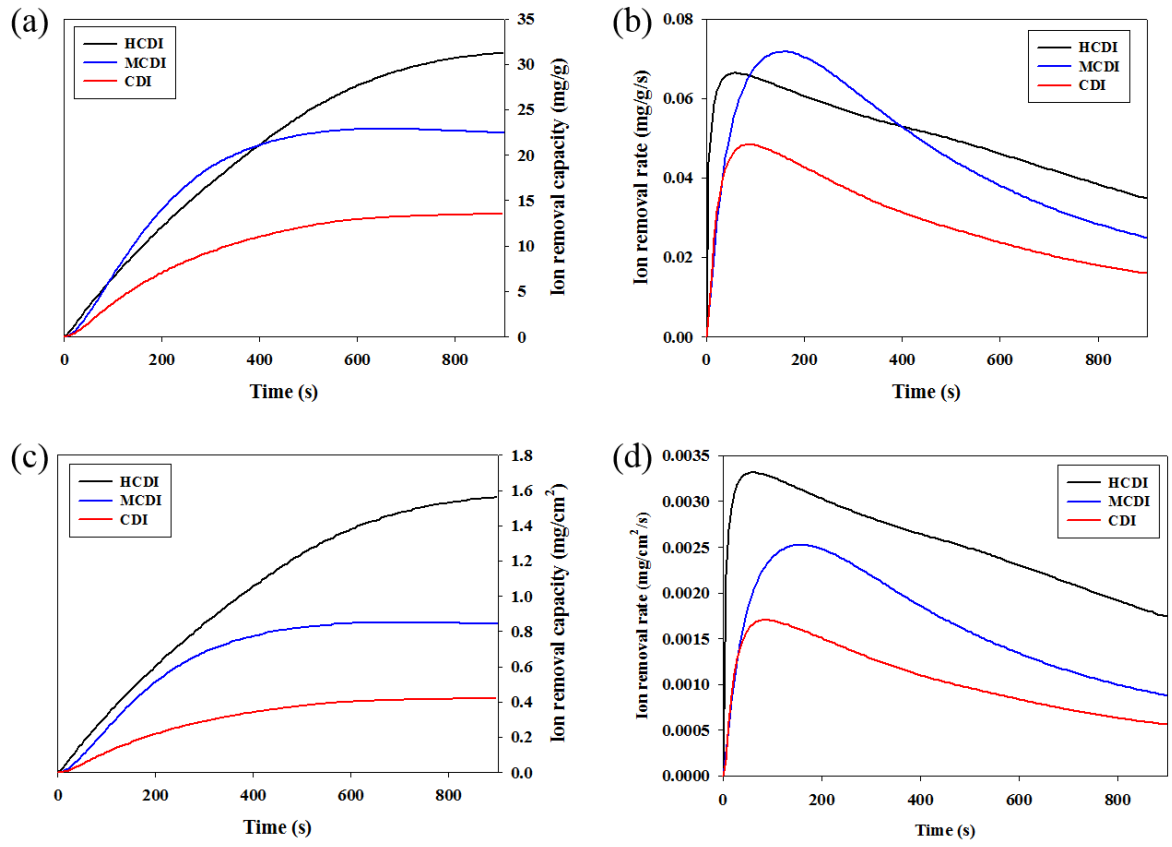


Fig. S2 Conductivity changes of effluent during 3 cycles in 10 mM NaCl in CDI, MCDI, and HCDI systems.



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39 **Fig. S3** Accumulated ion removal capacity and maximum ion removal rates of HCDI, MCDI, and CDI systems

40 during the 3rd ion-capturing step, represented as the mass of deionized ionic charge per total mass of electrodes

41 (a, b), and as the mass of deionized ionic charge per contact cell area (c, d).

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Desalination performance of HCDI system in simulated brackish water

Prior to the application of the HCDI system to actual brackish water, synthetic brackish was first examined. The chemical composition of synthetic brackish water is shown in Table S1. The water quality was similar to the water produced during natural gas operation reported by Pei Xu *et al*.[1] The synthetic water (12 mL) was fed into the HCDI system, which was operated in batch mode at a flow rate of 10 mL/min (1.2 V was applied for 15 min). The concentration of the initial and resultant solutions were analyzed by ion chromatography (ICS-1100, DIONEX).

The ion removal efficiency was obtained from the data shown in Table S1 using equation (1).

$$Removal\ (\%) = \frac{C_t - C_i}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of the source water, and C_t is treated water concentration. The data shows that approximately 50% of the sodium can be deionized using the HCDI system, and that the NMO electrode is effective in removing sodium ion, in addition to potassium, magnesium, and calcium ions by intercalating into the NMO structure. Note that the ion removal efficiency of magnesium ion is higher than potassium and calcium ions, though this difference can be due to the fact that the crystal ionic radius of Mg^{2+} is smaller than both K^+ and Ca^{2+}.[2]

Table S1 Cation concentrations and removal efficiency for initial and deionized water (batch mode operation at 1.2 V for 15 min).

Cation	Na	K	Mg	Ca
Initial concentration (mM)	97.85	0.18	0.46	0.72
Treated water concentration (mM)	48.38	0.14	0.15	0.52
Removal (%)	50.56	21.05	66.93	27.21

Reference

1. R. Xu, J. E. Drewes, D. Heil and G. Wang, *Water Res.*, 2008, **42**, 2605-2617.

2. M. Pasta, C. D. Wessells, Y. Cui and F. La Mantia, *Nano Lett.,* 2012, **12**, 839-843.