Supporting Information

for Adv. Sci., DOI 10.1002/advs.202201678

Efficient and Durable Sodium, Chloride-doped Iron Oxide-Hydroxide Nanohybrid-Promoted Capacitive Deionization of Saline Water via Synergetic Pseudocapacitive Process

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S1. Experiments

**Material characterization:** Elemental composition and surface state of the Cl-FeOOH, Na-FeOOH, and FeOOH samples were detailly studied by X-ray photoelectron spectroscopy (XPS), which was implemented on a VG Scientific ESCALAB Mark II spectrometer, and the spectra were calibrated with the C-C peak of 284.8 eV. To further characterize the phase composition, X-ray diffraction (XRD) test was carried out with a Rigaku D/MAX-RB X-ray diffractometer using the Cu Kα (40 kV, 20 mA) radiation and a secondary beam graphite monochromator. The surface chemical composition was identified using Fourier-transform infra-red spectroscopy (FT-IR, Bruker VERTEX70, Germany) operated at room temperature. Morphology and microstructure of FeOOH hybrid samples were observed via field emission scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F20). Raman spectra were obtained on an optical microscope with the excitation of 514.5 nm line from an Ar+ ion laser (Spectra Physics). Nitrogen adsorption-desorption isotherms were provided by ASAP 2020 Brunauer-Emmett-Teller (BET) analyzer, and specific surface area and pore volume properties were calculated by the BET method along with the estimated pore size distribution via Barrett-Joyner-Halenda (BJH) model.

**Electrochemical performance measurements:** Cyclic voltammetry (CV) plot was tested on the electrochemical workstation (CHI 660E) in a standard three-electrode system consisting of prepared electrode, graphite paper, and saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively, and the specific capacitance \( C_m, \text{ F g}^{-1} \) was calculated by Equation S1.

\[
C_m = \frac{Q}{mv \Delta V}
\]  

(S1)

where \( m, \Delta V, \) and \( v \) indicated the active mass, chosen potential range, and running rate, respectively. The \( Q \) was the integrated CV curve area.
GCD measurements were conducted using an automatic LAND battery test instrument (Land CT2001A) to evaluate both capacitive property and cycling performance. Coulomb efficiency ($\eta, \%$) was obtained by the ratio between $t_d$ and $t_c$. The $t_c$ was the charging time, and $t_d$ suggested the discharging time.

$$\eta = \frac{t_d}{t_c} \times 100$$  \hspace{1cm} (S2)

The relationship between peak current ($I$) and scan rate ($v$) in the CV curves can be described as follows:

$$I = a v^b$$  \hspace{1cm} (S3)

where the $b = 0.5$ corresponded to the ion intercalation process, and $b = 1$ implied the capacitance-like behavior.

Capacity contribution can be calculated based on CV results:

$$I (V) = k_1 v + k_2 v^{1/2}$$  \hspace{1cm} (S4)

where $v$ was the scan rate, $k_1 v$ stood for the contribution of capacitive-controlled current, and $k_2 v^{1/2}$ reflected the contribution of diffusion-controlled current.\(^{[1-2]}\)

The electrochemical impedance spectroscopy (EIS) was performed in a frequency window of 10 mHz to 100 kHz under a voltage amplitude of 5 mV. The diffusion coefficient ($D_{Na^+}$, cm\(^2\) s\(^{-1}\)) was calculated by Equation S5 and S6

$$D_{Na^+} = \frac{0.5 \pi^2 \tau^2}{c^2 F^2 A^2}$$  \hspace{1cm} (S5)

$$Z_{re} = \sigma \omega^{-1/2}$$  \hspace{1cm} (S6)

where $F$ was the Faraday constant, $R$ was the gas constant, $T$ was the absolute temperature, $c$ was the Na\(^+\) concentration, $A$ was the electrode surface area, $\sigma$ was the Warburg factor, and $Z_{re}$ was the real part impedance.

Desalination behavior measurements: Charge efficiency ($A$) was quantitatively determined according to Equation S7.

$$A = \frac{F \times \Gamma}{\Sigma}$$  \hspace{1cm} (S7)

where $F$ (C mol\(^{-1}\)), $\Gamma$ (mol g\(^{-1}\)), and $\Sigma$ (C g\(^{-1}\)) depicted Faraday constant, salt adsorption capacity, and charge density, respectively.

The energy consumption ($E$, Wh g\(^{-1}\)) was obtained as follows.
\[ E = v \int i dt / (C_0 - C) V \]  

where the \( v \) indicated a driven potential of 1.2 V, \( \int i dt \) corresponded to the integrated value of the current transient vs. running time plot, and \( V \) (mL) was the rotational solution volume. \( C_0 \) and \( C \) (mg L\(^{-1}\)) were initial and final concentrations, respectively.
**Figure S1.** High-resolution N1s XPS spectra of three as-fabricated samples with (a) and without (b) the PVP additive.

**Figure S2.** XRD patterns of three as-fabricated samples without the PVP additive.
Figure S3. SEM images of three as-fabricated samples without the PVP additive: a,b) bare FeOOH, c,d) Na-FeOOH, and e,f) Cl-FeOOH.

Figure S4. N$_2$ adsorption-desorption isotherms of bare FeOOH, Na-FeOOH, and Cl-FeOOH.
**Figure S5.** Pore size distribution plots by the BJH method of a) bare FeOOH, b) Na-FeOOH, and c) Cl-FeOOH.

**Figure S6.** CV curves at different scan rates: a) bare FeOOH, b) Na-FeOOH, and c) Cl-FeOOH.
Figure S7. a) CV curves of the Na-FeOOH electrode at various scan rates from 0.4 to 5 mV s\(^{-1}\); b) Log\((i_p)\) vs. Log\((v)\) plots; c) CV curve with the pseudocapacitive contribution fraction (purple region) at scan rate of 5 mV s\(^{-1}\).

Figure S8. a) CV curves of the Cl-FeOOH electrode at various scan rates from 0.4 to 5 mV s\(^{-1}\); b) Log\((i_p)\) vs. Log\((v)\) plots; c) CV curve with the pseudocapacitive contribution fraction (purple region) at scan rate of 5 mV s\(^{-1}\).
Figure S9. The real part impedance ($Z'$) vs. squared root of the angular frequency ($\omega^{-1/2}$) in Warburg region plots of bare FeOOH, Na-FeOOH, and Cl-FeOOH.

Figure S10. GCD profiles at different current loads: a) bare FeOOH, b) Na-FeOOH, and c) Cl-FeOOH.
**Figure S11.** Transient current vs. running time plot of the asymmetric Na-FeOOH//Cl-FeOOH cell during the CDI process.

**Figure S12.** Dynamic solution conductivity vs. running time plots of the asymmetric Na-FeOOH//Cl-FeOOH cell in NaCl solution with different concentrations: a) 300 mg L\(^{-1}\) and b) 100 mg L\(^{-1}\).

**Figure S13.** CDI cycling plot of the asymmetric Na-FeOOH//Cl-FeOOH cell.
**Figure S14.** PH vs. running time plot of Na-FeOOH//Cl-FeOOH cell in NaCl solution of 500 mg L\(^{-1}\).

**Figure S15.** XRD patterns before and after the CDI process: a) Na-FeOOH and b) Cl-FeOOH.

**Figure S16.** SEM images after the CDI process: a,b) Na-FeOOH and c,d) Cl-FeOOH.
Table S1. Texture properties and element contents determined by XPS and ICP-OES analyzes of three as-prepared samples.

| Samples        | S_{BET} (m^2 g^{-1}) | V_{Birch} (cm^3 g^{-1}) | D_{pore} (nm) | Na content (wt%) (XPS) | Cl content (wt%) (ICP-OES) |
|----------------|------------------------|-------------------------|--------------|------------------------|---------------------------|
| Na-FeOOH       | 64.22                  | 0.17                    | 1.35         | 0.28                   | 0.24                      |
| Cl- FeOOH      | 51.41                  | 0.09                    | 1.35         | -                      | -                         | 4.34                      |
| FeOOH          | 74.87                  | 0.08                    | 1.35         | -                      | -                         | -                         |

Table S2. Comparative CDI results among different materials.

| Samples            | NaCl concentration (mg L^{-1}) | Voltage (V) | Adsorption capacity (mg g^{-1}) | Ref.       |
|--------------------|--------------------------------|--------------|----------------------------------|------------|
| P-AC               | 1000                           | 1.2          | 22.7                             | S3         |
| Li_{4}Ti_{5}O_{12}@C NFAs | 100                          | 1.4          | 25                               | S4         |
| Na_{0.71}CoO_{2}   | 500                            | 1.2          | 34.8                             | S5         |
| ce-MoS_{2}        | 400                            | 1.2          | 8.81                             | S6         |
| HC@MnO_{2}        | 500                            | 1.2          | 30.7                             | S7         |
| VN/NCQDs          | 500                            | 1.4          | 23.71                            | S8         |
| NP-EHPCs          | 500                            | 1.2          | 24.14                            | S9         |
| Na-FeOOH          | 500                            | 1.2          | 32.13                            | This work  |
| Cl-FeOOH          | 500                            | 1.2          | 30.22                            | This work  |

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