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Supporting Information for

Enabling Superior Hybrid Capacitive Deionization Performance in NASICON-Structured Na₃MnTi(PO₄)₃/C by Incorporating Two-Species

Redox Reaction

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1. Experimental Section

1.1 Synthesis of NTMP/C

The NTMP/C composites were synthesized by a facile sol-gel method with postannealing. In a typical synthesis, stoichiometric amount of sodium acetate (CH₃COONa), manganese acetate tetrahydrate ((Mn(CH₃COO)₂·4H₂O), ammonium biphosphate (NH₄H₂PO₄) and anhydrous citric acid (C₆H₈O₇) were dissolved into 50 mL deionized water with magnetic stirring. Then the titanium isopropoxide with stoichiometric ratio was added into above mixture. The mixture was heated at 80 °C under stirring to evaporate the water and then further dried in an oven at 100 °C. The resulting material was ground and sintered at 600 °C for 12 h in a tube furnace under argon atmosphere to obtain NTMP/C, the heating rate in the pyrolysis process was 10 °C min⁻¹.

1.2 Materials characterization

The morphologies and structures of the samples were characterized through field emission scanning electron microscopy (FE-SEM, FEI Sirion200) and transmission electron microscopy (TEM, JEM-2010F). The crystal structure and phase composition of the composites were investigated using powder X-ray diffraction (XRD, Bruker D8). Thermogravimetric analysis (TGA) was performed with TG209 (NETZSCH Co.). XPS measurements were performed with an ESCALAB 250 (Thermo Scientific, USA) by using Al K α (hv = 1486.6 eV) X-ray radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-MS) was used to analyze the chemical composition of the NTMP/C samples and concentration of Mn and Ti in the tank after the cyclic test.

1.3 Electrochemical Measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were conducted by using a CHI 660E electrochemical workstation in 1 M NaCl solution. A three-electrode system consisting of a platinum foil as the counter electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and the sample was used as the working electrode. To prepare the working electrodes, a homogeneous slurry of sample, polytetrafluoroethene (PTFE), and carbon black with the mass ratio of 8:1:1 in ethanol was pressed by a rolling mill into a film and dried at 80 °C overnight. The obtained electrodes were pushed onto a titanium mesh which used as current collectors. The specific capacitance (C, F g⁻¹) was calculated from the CV curves as **Equation 1**:

$$C = \frac{\int I dt}{2 \times v \times \Delta V \times m} \tag{1}$$

Where C is the specific capacitance (F g⁻¹), I is the response current density(A), v is the potential scanning rate (V s⁻¹), Δ V is the voltage change (V), and m is the active material mass (g).

1.4 HCDI experiments

To prepare the HCDI electrodes, 82.5 wt% active materials, 10 wt% carbon black, 6 wt% polyvinyl butyral (PVB), and 1.5 wt% polyvinylpyrrolidone (PVP) were mixed together to obtain a homogeneous slurry. Subsequently, the resulting slurry of solids was cast on a graphite paper ($5 \times 7 \text{ cm}^2$) and then dried at 80 °C overnight. The thickness of NTMP/C and AC are 100 and 120 μ m, respectively. A AC electrode, a NTMP/C electrode, and a piece of anion exchange membrane (200 μ m, Hangzhou Iontech Environmental Technology Co., Ltd. Zhejiang, China) were assembled into a HCDI (Figure S3). Different concentrations of NaCl and voltages were employed to investigate the desalination performance of the NTMP/C in various operation conditions. Ion removal step was conducted by applying a voltage (0.4 V to 1.2 V) for a certain time, while the captured ions were released by applying negative voltage (-0.4 V to -1.2 V) for a certain time. A tank (2.5L) of NaCl aqueous solution with different concentrations (100 to 2000 mg L⁻¹, or 1.7 mM to 34.19 mM) was pumped into the CDI setup by a peristaltic pump at a flow rate of 9 mL min⁻¹, and then flowed into another tank. An electrochemical workstation (CHI 660E) was used to supply the needed voltage. The changes of effluent conductivity and pH were recorded by an ion conductivity meter and pH monitor systems. The testing temperature in the capacitive deionization experiments was maintained at 25 °C. The NaCl solution concentration was calculated by a calibration curve according to the conductivity profiles. The ion removal capacity (IRC, Γ , mg g⁻¹), charge consumed (Σ , C g⁻¹), charge efficiency (Λ) and energy consumption (E_{con}, KJ mol⁻¹) were defined as **Equation 2**, Equation 3, Equation 4 and Equation 5, respectively:

$$\Gamma = \frac{\Phi \times \int (C_0 - C_t) dt}{m}$$

$$\Sigma = \frac{\int i dt}{m}$$
(2)
(3)

$$\Lambda = \frac{\Gamma \times F}{M \times \Sigma} \tag{4}$$

$$E_{con} = \frac{M \times U \int i dt}{\Gamma \times m}$$
⁽⁵⁾

Where Φ is the flow rate (mL min⁻¹), C₀ and C_t are the influent and the effluent NaCl concentration (mg L⁻¹), respectively; m is the mass of active material (g); i is the current during the adsorption process (A); U is the voltage during the adsorption process (V); F is the Faraday constant (96485 C mol⁻¹); and M is the molar mass of NaCl (58.5 g mol⁻¹)

	refinement								
space g	space group = R-3c		$R_{p} = 5.03\%$		R _{wp} = 5.47%				
a (Å) :	a (Å) = 8.82621		c (Å) = 21.72350		α (°) = 90				
β(β (°) = 90		γ (°) = 120		V (ų) = 1465.578				
Atom	x	У	z	Mult	Occupancy				
Na1	0.00000	0.00000	0.00000	6	0.883				
Na2	0.63404	0.00000	0.25000	18	0.657				
Mn	0.00000	0.00000	0.14899	12	0.500				
Ti	0.00000	0.00000	0.14899	12	0.500				
Р	0.29771	0.00000	0.25000	18	1.000				
01	0.18350	0.18154	0.08714	36	1.000				
02	0.033322	0.20561	0.19589	36	1.000				

Table S1. Detailed structural information of NTMP/C derived from Rietveld



Figure S1 (a) CV curves of NTMP/C in the (a) negative and (c) positive potential interval with scan rate of 2 mV s⁻¹; (b) Specific capacitance of NTMP/C in the (b) negative and (d) positive potential interval with different scan rates



Figure S2 CV curves of NTMP/C in the (b) negative and (d) positive potential interval with different scan rates



Figure S3 The schematic of the HCDI desalination process



Figure S4 The current response of NTMP/C at different voltage



Figure S5 pH changes of the effluent of NTMP/C at different voltage



Figure S6 (a) pH changes of the effluent, (b) the desalination curve and (c) current response of NTMP/C of 100 adsorption-desorption cycles



Figure S7 The energy consumption of the NTMP/C during cyclic process



Figure S8 Exploration of the desalination process: ex-situ XRD pattern (Partial enlarged view)



Figure S9 Investigation of the Na intercalate/deintercalated process, the (a) Ti 2p and (b) Mn 2p spectra.



Figure S10 EIS of NTMP/C in a three-electrode configuration

Materials	voltag	Current	NaCl	IRC	Cycle	lon removal rate
	e (V)	density	(mg L ⁻¹)	(mg g⁻¹)	number	(mg g ⁻¹ min ⁻¹)
PCN6 ¹	1.2	None	1000	16.29	100	1.5
$3D flower-like MoS_2/rGO^2$	1	None	200	16.82	6	None
3DOM-TIN ³	1.2	None	500	23.6	10	3.2
$K_{0.03}Cu[Fe(CN)_6]_{0.65} \cdot 0.43H_2O^4$	1.2	None	4000	23.2	100	14.4
Na ₂ FeP ₂ O ₇ ⁵	1.2	None	1000	30.2	None	4.86
NTP/M ⁶	1.2	None	1000	25.9	20	10.6
α -MnO ₂ ⁷	1.2	None	880	22.1	20	6.66
$Na_4 Ti_9 O_{20}{}^8$	1.4	None	250	23.5	None	None
rGO/Co ₃ O ₄ -B ⁹	1.6	None	250	18.63	100	None
$L\text{-}S\text{-}\text{Ti}_3\text{C}_2\text{T}_x^{10}$	None	30 mA g ⁻¹	292	72	50	1.65
		1.6 V				
NaOH-Ti ₃ C ₂ T _x ¹¹	1.2	None	500	16.02	None	None
NaMnO ₂ ¹²	1.2	None	20000	40	100	None
Co _{0.5} Ni _{0.5} -Fe ₂ O ₄ ¹³	1.2	None	250	21.84	6	1.2
RGO/Mn ₃ O ₄ ¹⁴	1.2	None	1000	34.5	20	1.14
porous $Ti_3C_2T_x$	1.2	None	10000	45	60	None
MXene aerogel ¹⁵						
CuFe@NiFe PBA ¹⁶	None	0.5 mA cm ⁻¹	2900	71.8	50	None
MnO ₂ -1h ¹⁷	1.2	None	500	21.32	None	0.7
Mo _{1.33} C-MXene ¹⁸	0.8	None	35100	15	40	None
NiHCF/rGO-10 ¹⁹	1.2	None	500	22.8	100	None
FePO ₄ ²⁰	1.2	None	2340	50.13	10	4.74
NTP/C ²¹	1.6	None	1000	66.9	30	None
Co _{0.5} Ni _{0.5} Fe ₂ O ₄ ²²	1.2	None	250	21.84	6	1.2
NTMP/C (this work)	1.2	None	2000	72.2	100	21.6

Table S2. Comparison of various reported electrodes applied for CDI

	Mn ³⁺ /(Mn ³⁺ + Mn ²⁺)	Ti ⁴⁺ /(Ti ³⁺ + Ti ⁴⁺)		
Pristine	0.306	0.475		
Intercalation-1 st	0.261	0.367		
Deintercalation-1 st	0.368	0.531		
Intercalation-3 th	0.275	0.364		
Deintercalation-3 th	0.365	0.525		

Table S3 The proportion of Mn^{3+} and Ti^{4+} in NTMP/C during the desalination process

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