Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

CNT Modified Two-Phase Manganese Hexacyanoferrate for a Superior Cathode of Sodium-Ion Batteries

Ying Li[1], Kwok-ho Lam[1,*], and Xianhua Hou[2,*]

[1]Department of Electrical Engineering, Research Institute for Smart Energy, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

[2]School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006, People's Republic of China

*E-mail: kokokh.lam@polyu.edu.hk; houxh@scnu.edu.cn

1. Supplementary Experimental Information

1.1 Materials preparation

Materials: All chemical reagents including sodium hexacyanoferrate decahydrate ($Na_4Fe(CN)_6·10H_2O$, ≥99.0%), potassium hexacyanoferrate trihydrate ($K_4Fe(CN)_6·3H_2O$, ≥99.5%), sodium chloride (NaCl, 99.8%), manganese chloride anhydrous ($MnCl_2$, ≥99.0%), polyvinylpyrrolidone (PVP), and multiwall carbon nanotubes (CNT, 99.9%) were purchased from Aladdin and used without further purification. All the aqueous solutions were prepared with deionized (DI) water.

Synthesis of KNa-MnHCF@CNT: The pre-treatment of the purchased CNT was conducted by using HNO_3 and H_2SO_4 at 80 ºC for 3h. Then the oxidized CNT (25 mg) were dissolved in 25 mL DI water and ultrasonicated for 30 mins with a small amount of surfactant (PVP) to improve the dispersion of CNT in DI water. The $MnCl_2$ (3 mmol) was added into the above solution as Solution A. Solution B (25 mL) and Solution C (25 mL) were prepared by adding $Na_4Fe(CN)_6 \cdot 10H_2O$ (0.75 mmol) and $K_4Fe(CN)_6 \cdot 3H_2O$ (0.75 mmol), respectively, with the amount of NaCl. After that, Solution C was dropwise added into Solution B using the peristaltic pump (1 mL min^{-1}) under vigorous magnetic stirring at room temperature. At the same time, Solution B was dropwise added into Solution A under the same speed. The mixed solution was then stirred for 20 h and aged for 24 h before collected by vacuum filtration and washed with DI water and ethanol for several times. The obtained precipitate was dried in a vacuum oven at 100 ºC for 24 h. To avoid the light-induced redox action of $[Fe(CN)_6]^{4-/3-}$, the operation before vacuum filtration was performed under dark environment. The as-prepared sample was named as KNa-MnHCF@CNT. KNa-MnHCF was prepared as the control sample using the same procedures but without the addition of CNT and surfactant.

1.2 Materials characterizations

The crystalline structure of the obtained samples and cycled electrodes were characterized using X-ray diffraction (XRD) analysis with Cu$K\alpha$ (λ = 1.540598 Å) radiation (SmartLab; Rigaku, Tokyo, Japan), 0.01° scan step, and continuous scanning type in the 2θ range of 10°–60°. The chemical compositions of the prepared powder samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700ce). The samples for ICP-MS measurements were prepared by dissolving the dried particles in 100 ml of HNO_3 (0.1M). To investigate the water content, thermogravimetric analysis (TGA) data was collected on a TGA/DSC3+ (Mettler Toledo) instrument by raising the temperature from room temperature to 500 ℃ at a heating rate of 5 ℃/min under N_2 flow. The surface morphologies of the samples were observed by a field-emission scanning electron microscope (FESEM, TESCAN MAIA3) and high-resolution field-emission transmission electron microscope

(HRTEM, FEI Tecnai G2 F30, 300kV). The line scanning and element analysis of the samples were examined using scanning electron microscope (SEM, Hitachi SU8200) with energy disperse spectroscopy (EDS, Bruker Quantax) and a FlatQUAD detector. The chemical states of metal ions and surface elements compositions were conducted by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI).

1.3 Electrochemical measurements

All electrochemical performance was evaluated with CR2025-type coin cells with a metallic sodium plate as the counter electrode. The working electrode was prepared by mixing the active material with conductive agent (Super P) and binder (PVDF) at a certain weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP) to form slurry. The resultant slurry was coated on aluminium (Al) foil and dried in a vacuum oven at 120 ^{o}C for overnight. A porous glass fiber was used as the electrode separator. The electrolyte was a 1 M $NaClO_4$ solution in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a volume ratio of 1:1 with the addition of 5% fluoroethylene carbonate (FEC). CR2025-type coin cells were assembled in an Ar-filled glove box ($H_2O \leq 0.5$ ppm, $O_2 \leq 0.5$ ppm) (MBRAUN, Germany) for electrochemical measurements. The cells were galvanostatically charged and discharged on a battery testing system (LAND CT-2001A, China) with various current densities between 2.0 and 4.2 V at room temperature. Cyclic voltammogram (CV) measurements of the cells were performed on an electrochemical workstation (BioLogic, VMP-300, French) at a scanning rate of 0.1 mV s^{-1} from 2.0 to 4.2 V. Electrochemical impedance spectra (EIS) were tested by the VMP-300 electrochemical workstation at a frequency range from 0.01 Hz to 100 kHz with a voltage amplitude of 5 mV.

1.4. Supplementary experimental images and Tables.

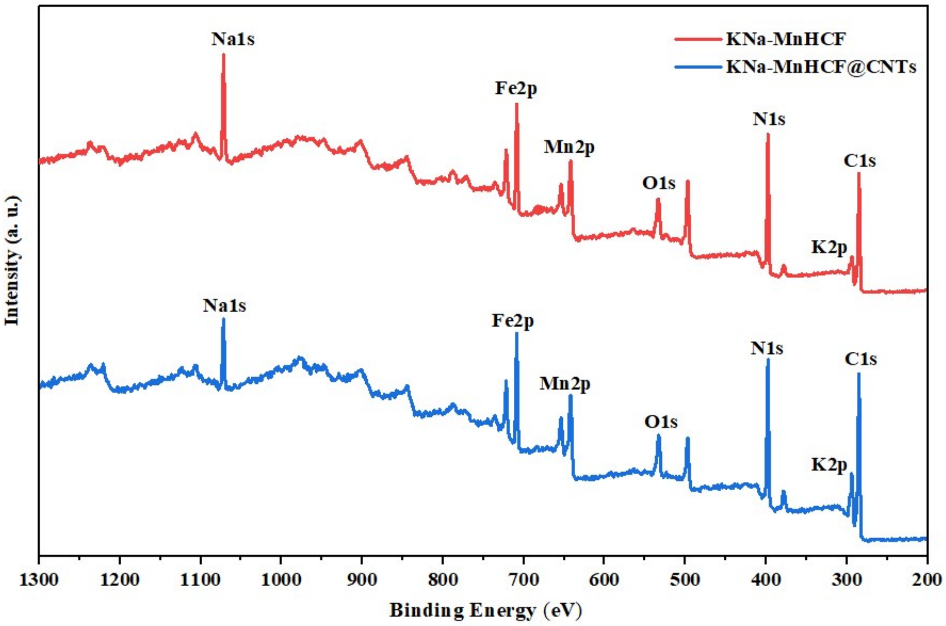

Fig. S1 The full XPS spectra of the KNa-MnHCF and KNa-MnHCF@CNT samples.

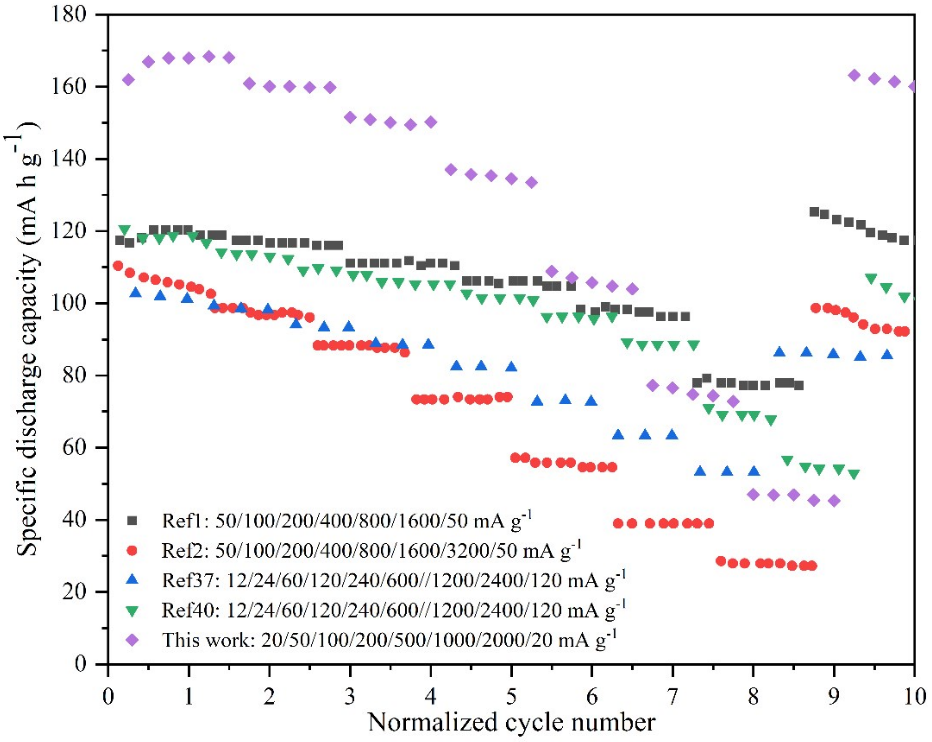

Fig. S2 Rate performance of KNa-MnFe(CN)$_6$@CNT and other PBAs materials from references.

Table S1. The ICP results of the KNa-MnHCF and KNa-MnHCF@CNT samples.

Sample	Weight %				Atomic %				Relative atomic ratio			
	K	Na	Fe	Mn	K	Na	Fe	Mn	K	Na	Fe	Mn
KNa-MnHCF	3.87	8.36	14.30	14.97	9.90	36.36	25.60	27.25	0.36	1.34	0.94	1.00
KNa-MnHCF@CNT	13.28	3.21	13.84	14.5	33.96	13.96	24.78	26.39	1.29	0.53	0.94	1.00

Table S2. The surface elements compositions of XPS results of the KNa-MnHCF and KNa-MnHCF@CNT samples.

Sample	Atomic %					
	K	Na	Fe	Mn	C	N
KNa-MnHCF	3.54	8.23	7.47	6.48	41.51	32.77
KNa-MnHCF@CNT	5	4.91	6.53	5.65	48.16	29.74

Table S3. The electrochemical performance comparison between this work and report work (1 C = 120 mA g^{-1}).

Sample	**Initial discharge capacity**	**Initial coulombic efficiency**	**Capacity retention**
s-PBMN[1]	120 mA h g^{-1} at 50 mA g^{-1}	98.1%	91.7% after 400 cycles
HCS-PBMN[2]	123 mA h g^{-1} at 50 mA g^{-1}	93%	82.3% after 600 cycles
g-(Ni0.1Mn0.9)HCF[36]	110 mA h g^{-1} at 0.2 C	<50%	95% after 100 cycles
C2-NaMn[37]	101.7 mA h g^{-1} at 0.1 C	95%	——
	89.9 mA h g^{-1} at 2 C	——	80.5% after 100 cycles
NMHFC@PPy[40]	124 mA h g^{-1} at 0.1 C	72%	——
	113.4 mA h g^{-1} at 2 C	——	67% after 200 cycles
NaK-MnHCF@3DNC[42]	211 mA h g^{-1} at 20 mA g^{-1}	83.6%	68% after 100 cycles
KNMF-3[43]	127.2 mA h g^{-1} at 40 mA g^{-1}	92%	85% after 100 cycles
KNa-MnHCF@CNT	164.5 mA h g^{-1} at 20 mA g^{-1}	96.3%	82.0% after 100 cycles
(this work)	77.3 mA h g^{-1} at 1 A g^{-1}	——	——