

# Electronic Supplementary Material

## Enabling nickel ferrocyanide nanoparticles for high-performance ammonium ion storage

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### Experimental

#### Samples Characterization

The prepared samples were investigated by using X-ray diffraction analyzer (Bruker D8 Advanced), thermogravimetric analysis (NETZSCH STA449 F3), confocal Raman spectrometer (WITec ALPHA300 with a 532 nm excitation laser), inductively coupled plasma-optical emission spectroscopy (AGILENT ICP-OES 730), scanning electron microscopy (Hitachi SU-70), Fourier transform infrared spectroscopy (Nicolet 6700), and X-ray photoelectron spectroscopy (XSAM800 Ultra spectrometer). The electronic

conductivities of the prepared samples are tested by using multimeter (VICTOR VC890C).

### **The detailed calculation about the contributions of capacitive process and diffusion-limited process for the capacity**

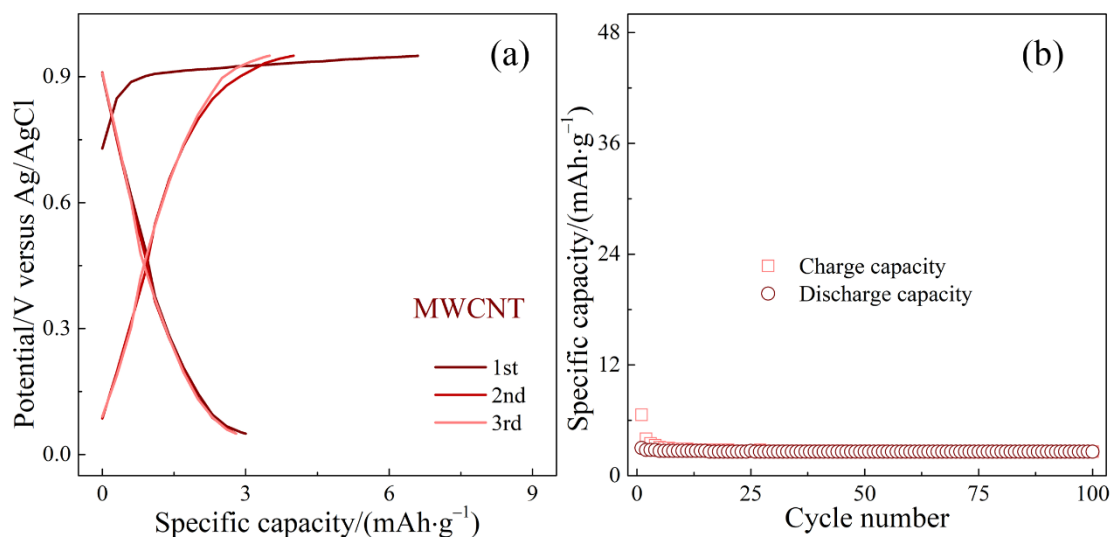
The current ( $i$ ) in CV test obeys the power-law formula based on the following Eq. (1):

$$i = av^b \quad (1)$$

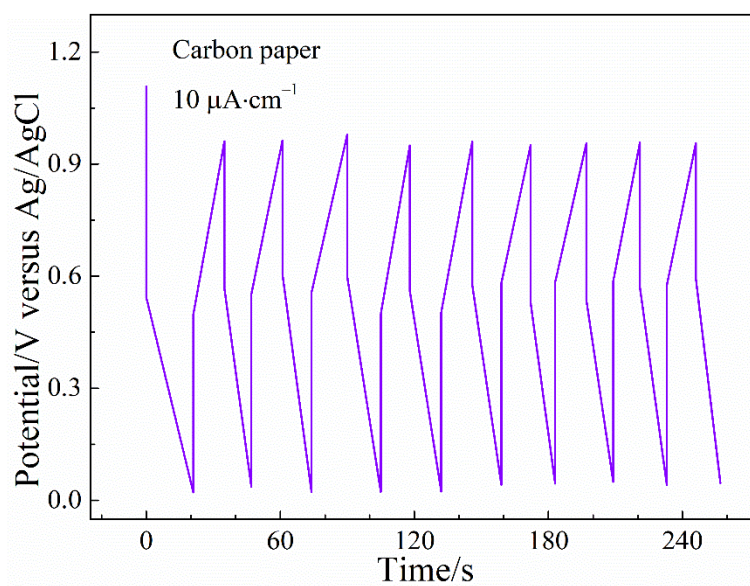
In this equation,  $a$  and  $b$  are variable parameters,  $v$  is scan rate. The value of  $b$  could assess the behavior of cell. If  $b$  is close to 0.5, it suggests a semi-infinite linear diffusion process. If  $b$  is close to 1.0 it suggests the capacitive process. The value of  $b$  comes from the slope of the plot of  $\log i$  versus  $\log v$ . In our work,  $b$  value for anodic sweep calculated from the  $\log(i)$  versus  $\log(v)$  are 0.92 and 0.91 for  $\text{Ni}_2\text{Fe}(\text{CN})_6$  and  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$ , respectively, indicating capacitance-dominant kinetics. The surface capacitance ( $k_1$ ) and diffusion-controlled contributions ( $k_2$ ) can be quantified according to Eq. (2) and (3) [35–38]:

$$i = k_1v + k_2v^{0.5} \quad (2)$$

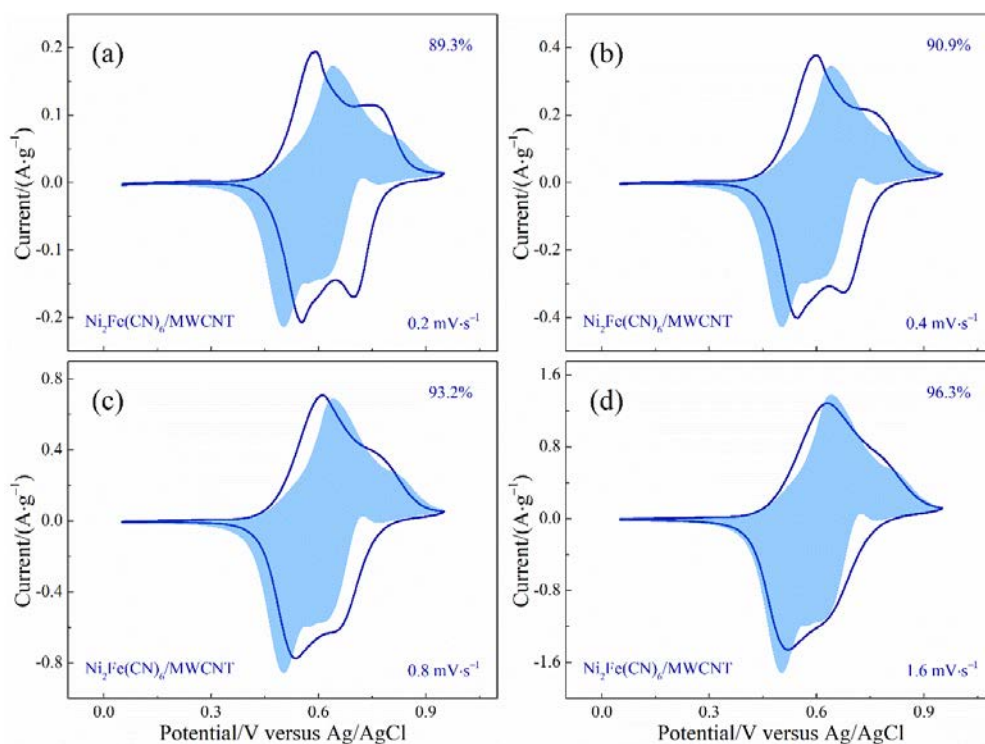
$$i/v^{0.5} = k_1v^{0.5} + k_2 \quad (3)$$



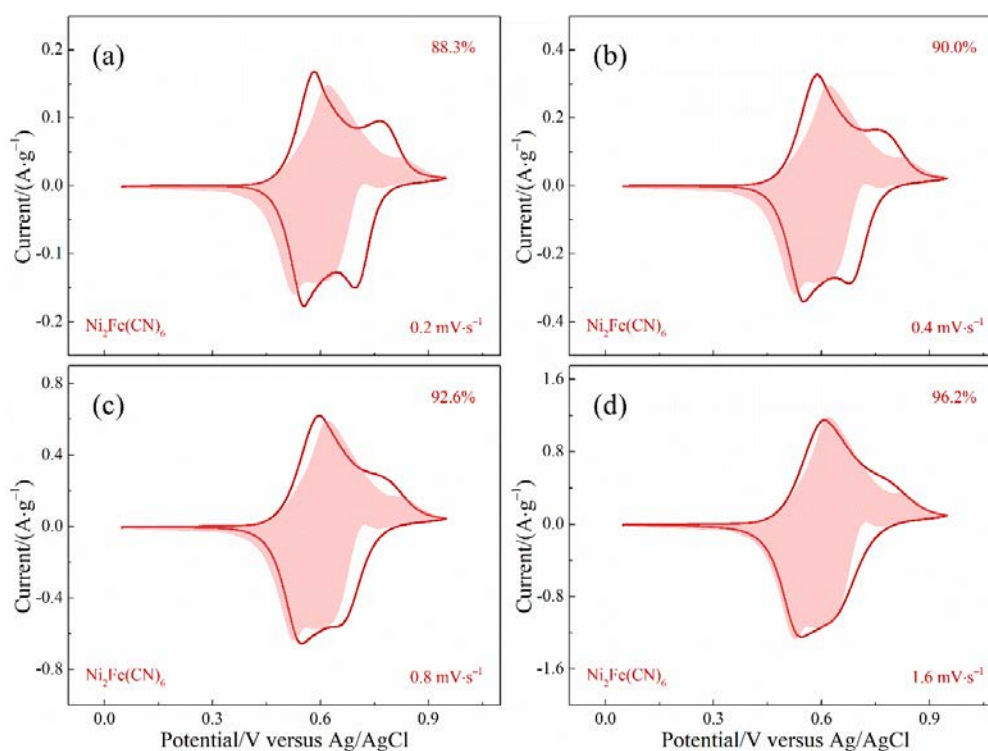
**Fig. S1** (a) Discharge-charge profiles of MWCNT at  $60 \text{ mAh g}^{-1}$ . (b) Cycling performance of MWCNT at  $60 \text{ mAh g}^{-1}$ .



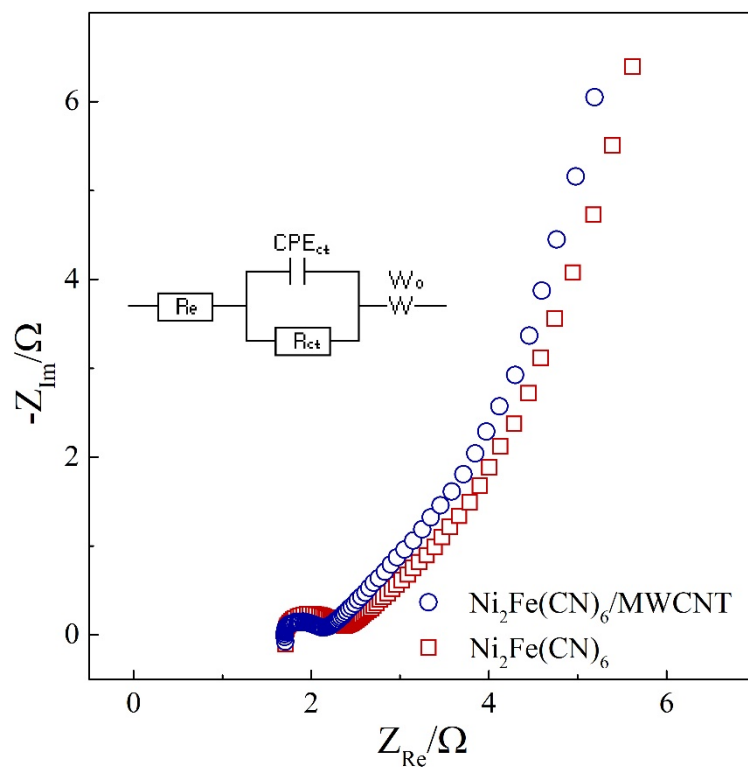
**Fig. S2** Discharge-charge profiles of carbon paper at  $10 \mu\text{A cm}^{-1}$ .



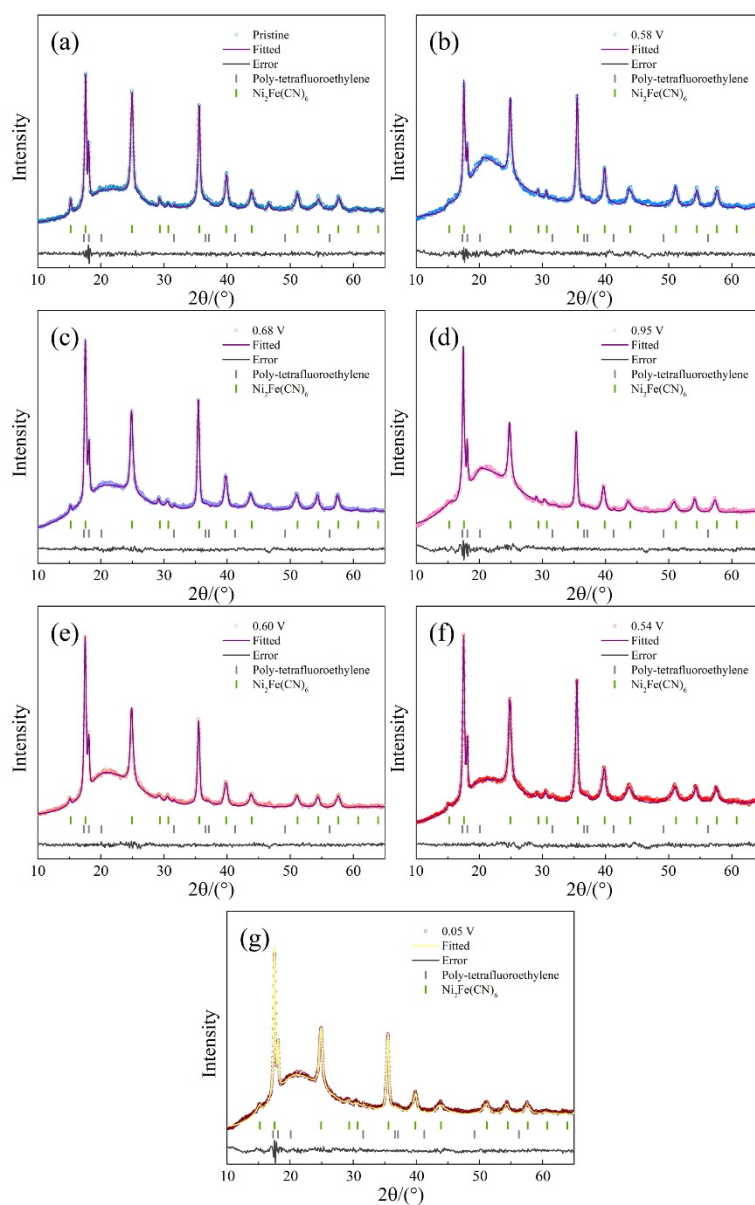
**Fig. S3** Capacitive contribution of  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$  at (a) 0.2, (b) 0.4, (c) 0.8, and (d)  $1.6 \text{ mV s}^{-1}$ .



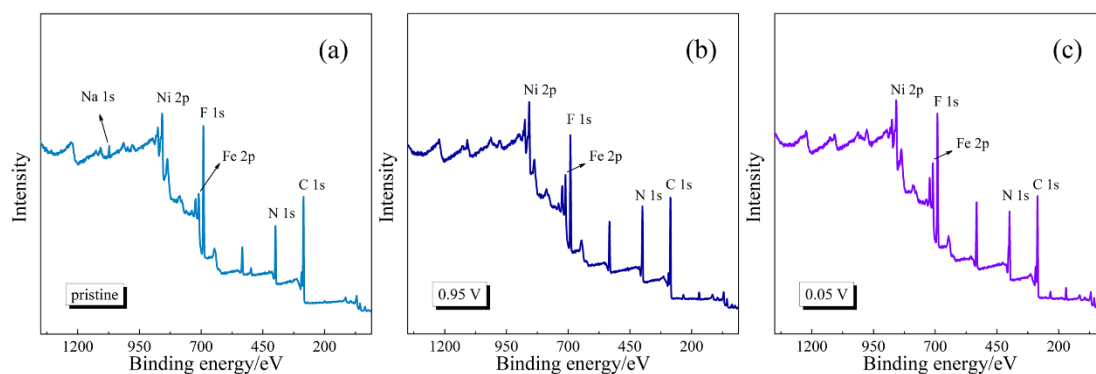
**Fig. S4** Capacitive contribution of  $\text{Ni}_2\text{Fe}(\text{CN})_6$  at (a) 0.2, (b) 0.4, (c) 0.8, and (d)  $1.6 \text{ mV s}^{-1}$ .



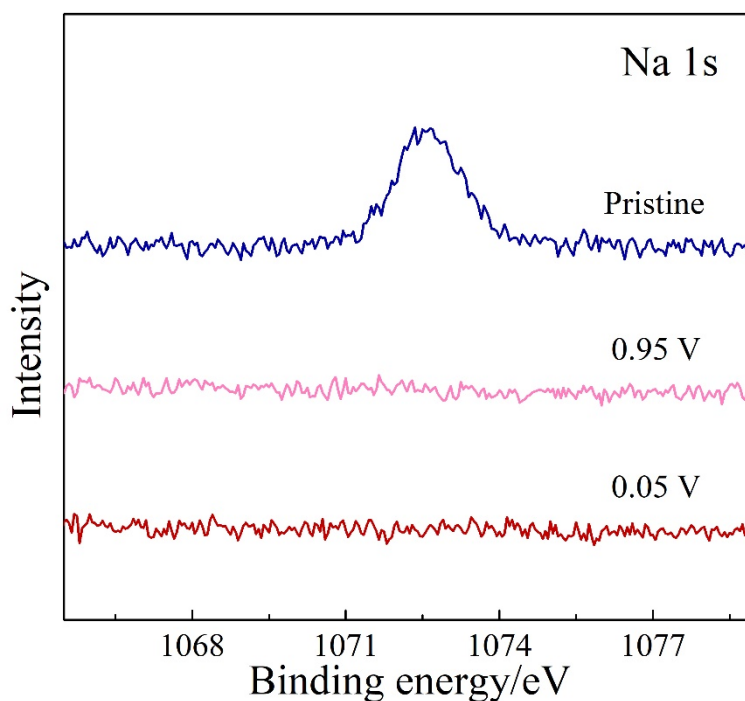
**Fig. S5** Electrochemical impedance spectroscopy spectra of  $Ni_2Fe(CN)_6/MWCNT$  and  $Ni_2Fe(CN)_6$ . The inset shows an equivalent circuit.



**Fig. S6** Rietveld refined ex situ XRD patterns of  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$  with experimental data at various states: (a) pristine, (b) charge to 0.58 V, (c) charge to 0.68 V, (d) charge to 0.95 V, (e) discharge to 0.60 V, (f) discharge to 0.54 V, and (g) discharge to 0.05 V.



**Fig. S7** Sum XPS spectrum of  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$  during cycling. (a) pristine electrode; (b) 0.95 V; (c) 0.05 V.



**Fig. S8** XPS spectra of Na 1s peaks for  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$  electrode at different charge state.

**Table S1.** ICP-OES analysis of  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$ ,  $\text{Ni}_2\text{Fe}(\text{CN})_6$  and  $\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$  after ion-exchange.

Sample	Na	Ni	Fe
$\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$	2.5628%	26.4805%	12.7654%

$\text{Ni}_2\text{Fe}(\text{CN})_6$	3.1617%	26.7969%	12.8653%
$\text{Ni}_2\text{Fe}(\text{CN})_6/\text{MWCNT}$ after ion-exchange	0.0182%	24.3140%	13.1440%

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Terminology for Eq. 1:

- $I_p$       the peak current density
- $n$         the charge transfer number
- $F$         the Faraday's constant
- $C$         the concentration
- $S$         the surface area of the electrode
- $R$         the gas constant
- $T$         the absolute temperature
- $D$         the diffusion coefficient
- $v$         the square root of the scan rate