

Nickel Hexacyanoferrate/Carbon Composite as a High-Rate and Long-Life Cathode Material for Aqueous Hybrid Energy Storage

Dapeng Zhang,^a Junshu Zhang,^a Zengxu Yang,^a Xiaochuan Ren,^b Hongzhi Mao,^a Xianfeng Yang,^c Jian Yang,^{a,*} and Yitai Qian^{a,d}

^[a] Key Laboratory of Colloid and Interface Chemistry, Ministry of Education School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, P.R. China.

^[b] Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, Wuhan 430074, P. R. China.

^[c] Analytical and Testing Centre, South China University of Technology, Guangzhou 510640, P. R. China.

^[d] Hefei National Laboratory for Physical Science at Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P. R. China.

Experimental section

Material synthesis

NiHCF Cathode: The chemicals and solvents were purchased from Sinopharm Chem. Reagent Co. Ltd. and used without any further purification, except carbon powders from MTI Corporation. Firstly, 400 μL of ethylene diamine (en) was dissolved in a mixed solvent of 50 mL deionized water and 50 mL absolute ethanol. Then, 50 mL of 0.04 M NiCl_2 was added dropwise at room temperature, producing the complex of $[\text{Ni}(\text{en})_2]^{2+}$. After 100 mg of carbon powders was added, the solution was sonicated for 30 min to generate a good suspension. 50 mL of 0.02 M $\text{K}_3\text{Fe}(\text{CN})_6$ was added with vigorous stirring. After 24 hours, 2 mL of HCl (37 %) was introduced to remove en molecules encapsulated or adsorbed in the product, followed by a stirring for 30 min. The as-obtained black precipitate was filtered, washed by deionized water and absolute ethanol, and dried in air at 60 °C overnight. The obtained product was denoted as eNiHCF/C in the text. When carbon powders were removed from the protocol and the other chemicals were kept as the same, the resultant product was named as eNiHCF. The comparison between eNiHCF/C and eNiHCF would clarify the influence of carbon on electrochemical performances. When both carbon powders and en molecules were removed from the protocol, the product was denoted as NiHCF, where the precipitation happened very fast. The comparison between eNiHCF and NiHCF would offer us the opportunity to understand the influence of en molecules on electrochemical performances of NiHCF.

rGO Anode: Graphite oxide (GO) was synthesized by modified Hummers' method [1]. Then, GO at a concentration of 2 mg mL^{-1} was sealed in a Teflon-lined autoclave and maintained at 180 °C for 24 h. The resultant powders were washed and dried by freeze-drying.

Structural characterization

Powder X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Bruker D8 Advance, Germany), using Cu K_α line ($\lambda=1.5418 \text{ \AA}$) as the radiation source. TEM images and element mapping were recorded on a transmission electron microscope (JEOL JEM-1101, Japan), and a high-resolution transmission electron microscope (JEOL JEM-2100F, Japan). The contents of C, H, N were detected by an elemental analyzer (Elementar Vario EL CUBE, Germany). The contents of K, Ni and Fe, were obtained by a Flame Atomic Adsorption Spectrometer (Flame AAS, Persee TAS-990, China).

Electrochemical measurements

Electrochemical properties of eNiHCF/C, eNiHCF, and NiHCF, were evaluated in a typical three-electrode setup, using a platinum mesh as the counter electrode, a saturated Ag/AgCl electrode as the reference electrode and 1M NaNO_3 as the electrolyte. As to the working electrode, it was made of 70 wt% eNiHCF or NiHCF, 15 wt% carbon powders, 5 wt% conducting graphite and 10 wt% polyvinylidene fluoride (PVDF). When eNiHCF/C was the active material, carbon powders were removed from the recipe, because they were already added in the synthesis of eNiHCF/C. So, the recipe was changed to 85 wt% eNiHCF/C, 5 wt% conducting graphite and 10 wt% PVDF. These materials were milled in a trace of N-methyl-pyrrolidinone (NMP) and then deposited onto a carbon paper (NOS1005, Ce Tech, Taiwan), followed by a drying at 60 °C in air. ASSCs based on

eNiHCF/C as the cathode and rGO as the anode were also tested. However, nickel mesh rather than carbon paper, was used as the current collector for eNiHCF/C, with its mass loading at $\sim 2 \text{ mg cm}^{-2}$. On the side of anode, a slurry was made of 80 wt% rGO, 10 wt% carbon powders and 10 wt % polytetrafluoroethylene on a stainless steel. After dried in air overnight, the electrode was treated by a static pressure of 10 MPa for 1.5 min to improve the contact of rGO with stainless steel.

Galvanostatic charge-discharge profiles were measured by a battery test system (LAND CT2001A, China). Cyclic voltammograms (CV) were obtained on an electrochemical workstation (CHI760E, ChenHua Instruments Co., China). Electrochemical impedance spectra (EIS) were acquired from another electrochemical workstation (Autolab PGSTAT302N, Switzerland).

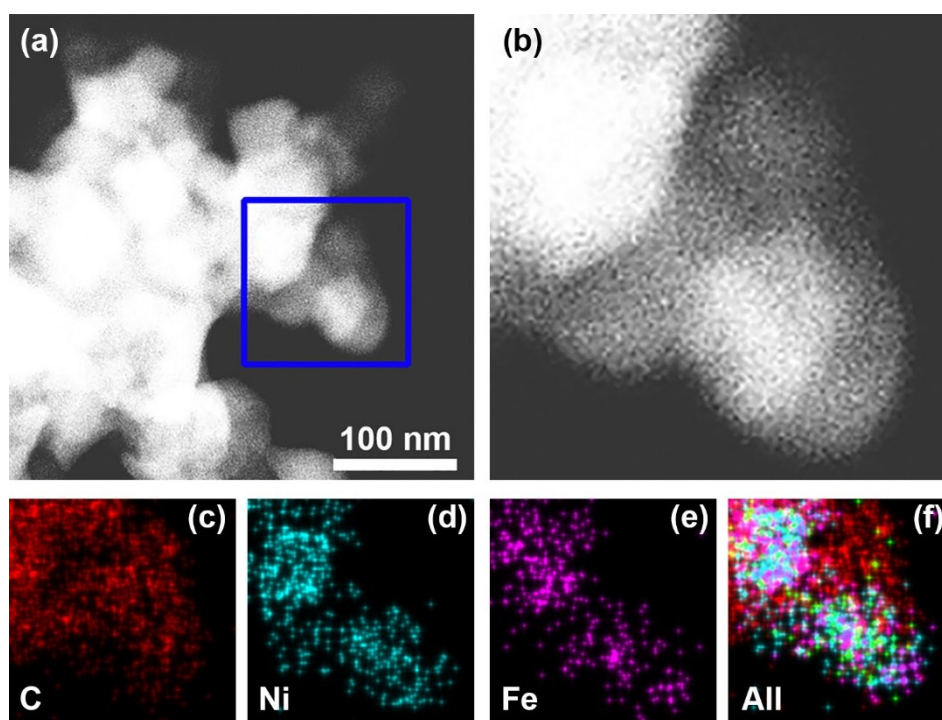


Fig. S1 (a, b) Dark-field TEM images and (c-f) elemental mapping of eNiHCF/C.

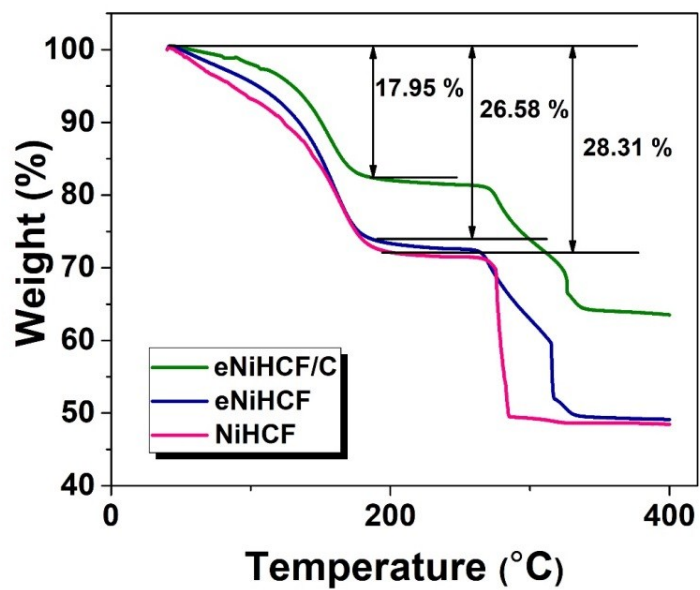


Fig. S2 TGA curves of eNiHCF/C, eNiHCF and NiHCF.

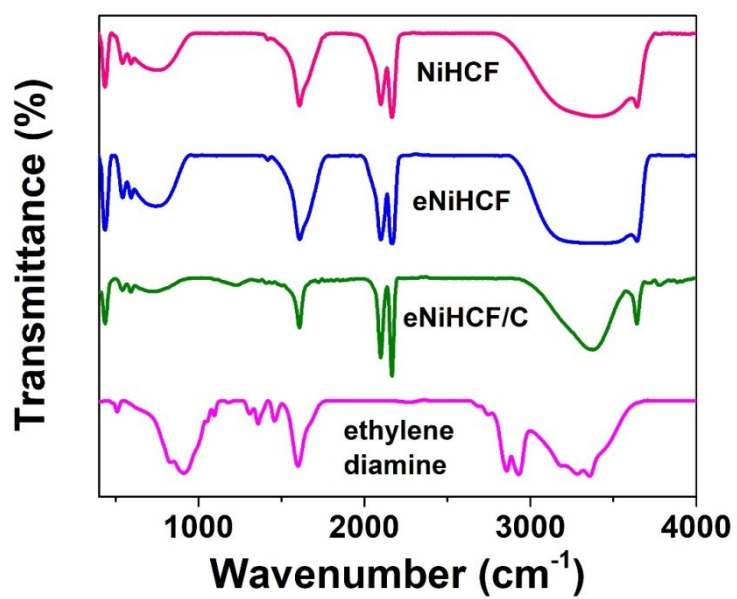


Fig. S3 FTIR spectra for NiHCF, eNiHCF, eNiHCF/C and ethylenediamine.

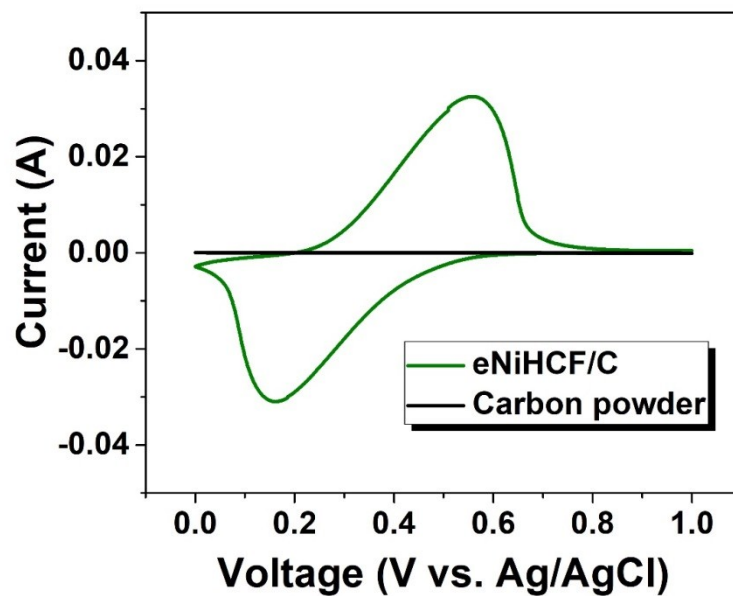


Fig. S4 CV curves of eNiHCF/C and carbon particles at a scan rate 5 mV s⁻¹.

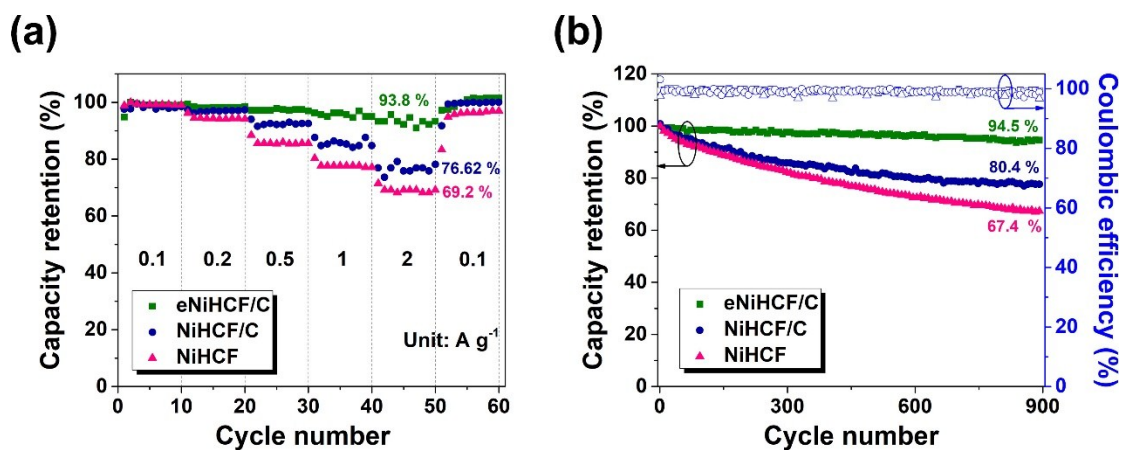


Fig. S5 (a) Rate and (b) cycle performances of eNiHCF/C, NiHCF/C and NiHCF.

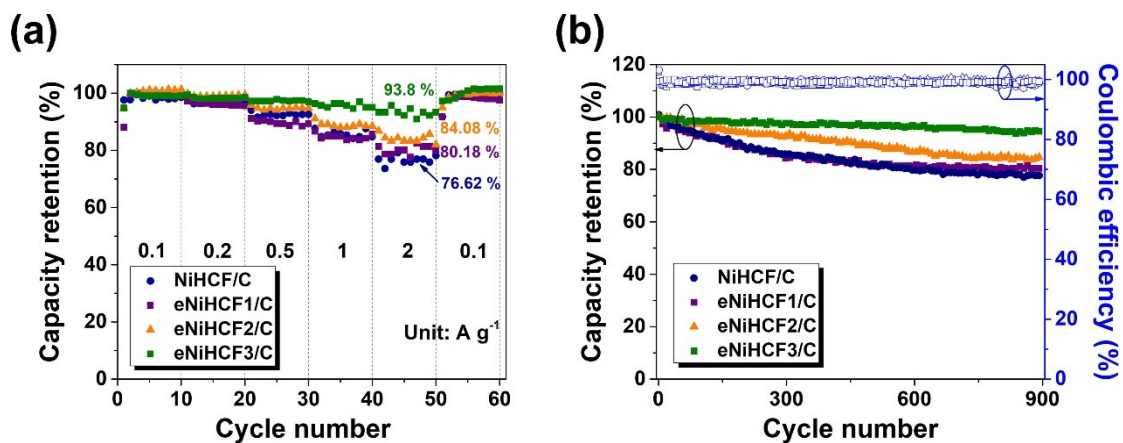


Fig. S6 (a) Rate and (b) cycle performances of NiHCF/C, eNiHCF1/C, eNiHCF2/C and eNiHCF3/C.

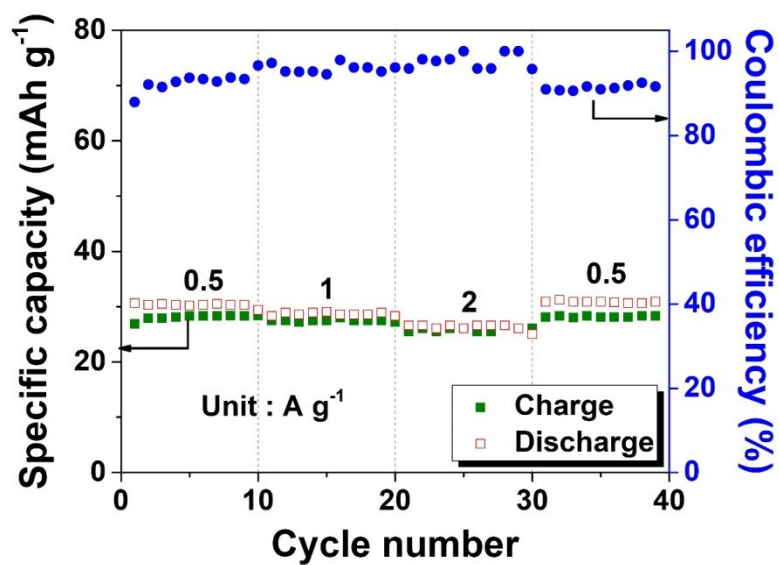


Fig. S7 Rate performance of rGO anode.

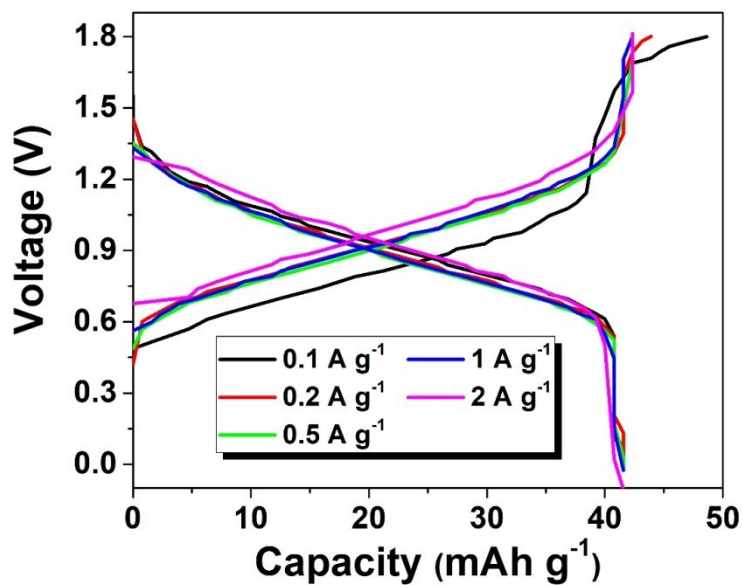


Fig. S8 Galvanostatic discharge/charge profiles of eNiHCF/C//rGO at different rates.

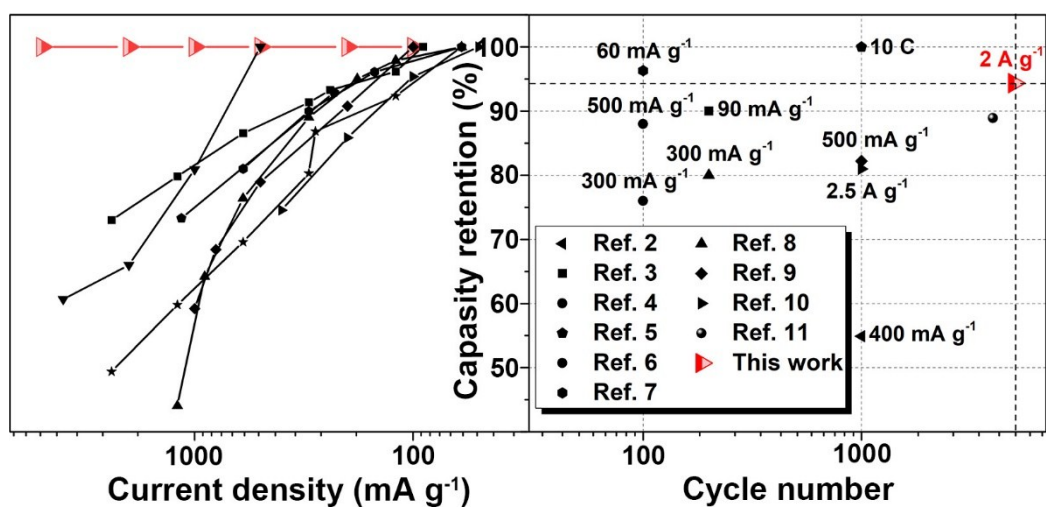


Fig. S9 Comparison of electrochemical property of PBA-electrode batteries and supercapacitors between this work and previous report.

Table S1
analysis
eNiHCF/C.

Elements	N	C	H
Content (wt, %)	15.19	35.10	2.818

Elements
result of

The mass fraction of carbon powder can be calculated by following mathematic form:

$$\omega_{Carbon\ powder} = \omega_C - \frac{\omega_N}{M_N} \times M_C$$

Table S2 Metal contents in eNiHCF/C, eNiHCF, and NiHCF measured by flame atomic absorption spectra.

Element	K (ppm)	Ni (ppm)	Fe (ppm)
eNiHCF/C	0.226	1.362	1.138
eNiHCF	0.183	0.914	0.754
NiHCF	0.213	1.341	1.022

Table S3 The comparison between the eNiHCF/C and pervious reports

Materials	Capacity	Rate performance /current density	Cycle stability /cycle number (current density)	Ref.
FeHCF	144 mAh g ⁻¹	82 % / 2.5 A g ⁻¹	83 % / 500 (1.25A g ⁻¹)	12
VHCF	94.1 mAh g ⁻¹	62 % / 1.76 A g ⁻¹	79 % / 250 (1.76 A g ⁻¹)	13
Cu _{0.56} Ni _{0.44} HCF	52 mAh g ⁻¹	—————	91 % / 2000 (500 mA g ⁻¹)	14
Na ₂ Ni[Fe(CN) ₆]	65 mAh g ⁻¹	93.8 % / 0.65 A g ⁻¹	87 % / 500 (325 mA g ⁻¹)	15
Na ₂ Cu[Fe(CN) ₆]	58.5 mAh g ⁻¹	85.5 % / 3 A g ⁻¹	93 % / 500 (300 mA g ⁻¹)	16
CuHCF	46 mAh g ⁻¹	—————	81.8 % / 50 (20 mA g ⁻¹)	17
eNiHCF/C	46.4 mAh g ⁻¹	93.8 % / 2 A g ⁻¹	94.5 % / 900 (0.5 A g ⁻¹)	This work

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