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Insoluble metal hexacyanoferrates as supercapacitor electrodes

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ABSTRACT

Nano-sized insoluble iron, cobalt and nickel hexacyanoferrates (Mhcf) were prepared by a simple co-precipitation method. The potential of using these materials for supercapacitor was examined by cyclic voltammogram and constant charge/discharge. Due to the different types of the second metal (M), the Mhcf electrodes showed different electrochemical capacitive performances. The specific discharge capacitances of Fehcf, Nihcf and Cohcf electrodes at the current density of 0.2 A g^{-1} were 425 F g^{-1}, 574.7 F g^{-1} and 261.56 F g^{-1}, respectively. Meanwhile, the Mhcf electrodes showed good cyclic performance.

1. Introduction

Electrochemical supercapacitors are charge-storage devices that possess ideally high power density, excellent reversibility and long cycle life [1]. They have attracted a lot of attention in power source applications such as hybrid electric vehicles [2]. Up to date, amorphous $RuO_2 \cdot \chi H_2O$ was reported as the most promising electrode material for supercapacitor with a specific capacitance of 720 F g^{-1} [3]. But the high cost and environmental toxicity of this material limits its extensive use in commercial applications. Efforts have been made to find a cheap and environmentally friendly material with good electrochemical performance to replace RuO_2.

Recently, transition metal hexacyanoferrates have raised renewed and growing interest in the electrochemical field such as rechargeable batteries [4,5], due to their unique structural characteristics such as three-dimensional network and tunnel structure, as well as the low cost and environmental toxicity [6]. Anna Lisowaka-Oleksiak et al. [7] prepared metal hexacyanoferrate network inside polymer matrix for electrochemical capacitors with high capacitance, which resulted from the presence of inorganic networks. But the two-step electrochemical deposition of these hybrid films was relatively complicated, and it was hard to calculate the specific capacitance per weight of the electrodes. In this work, a series of cheap insoluble transition metal hexacyanoferrates (Mhcf) such as iron, nickel and cobalt hexacyanoferrate were prepared by a simple co-precipitation method. Cyclic voltammogram and constant charge/discharge were employed to assess the potential application of those materials as active electrode materials of supercapacitor in 1M KNO_3 solution.

2. Experimental

All reagents used in this experiment were of analytical grade without further purification. A typical experiment procedure was as follows: $M_3[Fe(CN)_6]_k$ (Mhcf in short) was synthesized by adding 0.03 mol MCl_k into stoichiometric amount of $K_3[Fe(CN)_6]$ slowly. $MCl_k \cdot 6H_2O$ were (a) $FeCl_3$, (b) $NiCl_2$ and (c) $CoCl_2$, respectively. The mixture was stirred for 30 min under room temperature. When finished, the precipitates were centrifuged and washed with deionized water for several times, and finally dried at 80 °C for 8 h. The colors of corresponding products were green, brown and purple. The formation of those materials could be expressed as follows:

$$3MCl_k + kK_3[Fe(CN)_6] \rightarrow M_3[Fe(CN)_6]_k + 3kKCl.$$

X-ray powder diffraction data were collected on a Rigaku D/max2550VB$^+$18 kw with Cu $K\alpha$ radiation, scan range from 10° to 90°. The morphology of the as-prepared particles was characterized using a JE01-1230 transmission electron microscope. The chemical composition of the Fehcf product was analyzed by Thermo-NORAN energy dispersive spectrometer (EDS).

The $M_3[Fe(CN)_6]_k$ electrode was prepared by mixing 75 wt.% $M_3[Fe(CN)_6]_k$ powders, 20 wt.% acetylene black and 5 wt.% PTFE binder. The mixture was pressed onto stainless steel grids which served as current collector, and dried at 80 °C under vacuum for 12 h. The electrochemical behavior of $M_3[Fe(CN)_6]_k$ was characterized by cyclic voltammetry and charge–discharge tests. The experiments were carried out in a conventional three electrode electrochemical cell. The prepared $M_3[Fe(CN)_6]_k$ electrode was

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used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode and a platinum foil of convenient area was set as the counter electrode. The electrolyte in this experiment was 1M KNO_3. Cyclic voltammetry (CV) and charge–discharge tests were performed using a CHI660 workstation (Shanghai, China).

3. Results and discussion

3.1. Material characteristics

Fig. 1A showed the diffraction patterns of the Mhcf products: (a) Fehcf, (b) Nihcf, (c) Cohcf. All the peaks of Fig. 1A (a) can be indexed as face-centered-cubic phase with a lattice parameter of 10.21 Å. Berlin green $Fe[Fe(CN)_6]$ and Prussian blue $Fe_4[Fe(CN)_6]_3$ were isostructural compounds, thus the two compounds cannot be differentiated through only X-ray diffraction (XRD) measurements [8]. Therefore, EDS spectrum was supplemented to further characterize the composition of the Fehcf products. The EDS spectrum (Fig. 1B) showed the presence of Fe, C and N with an atomic ratio of 1:3:3, which matches well with that of Berlin green $Fe[Fe(CN)_6]$. The Cu signal is attributed to the copper substrate in the TEM measurement. All the peaks of Fig. 1A (b) can be indexed as cubic $Ni_3(Fe(CN)_6)_2(H_2O)$ with a lattice parameter of 10.23 Å, which was in good agreement with the values from the standard card (JCPDS No. 82-2283). All the peaks of Fig. 1A (c) can be indexed as cubic $Co_3(Fe(CN)_6)_2(H_2O)$ with a lattice parameter of 10.296 Å, which was in consistent with the values from the standard card (JCPDS No. 82-2284).

The morphology of the Mhcf products was investigated by TEM. The TEM image of Fehcf was shown in Fig. 2a. As shown in Fig. 2a, the Fehcf sample consisted of spherical-like particles with size of around 60 nm. Shown in the inset in Fig. 2a was the photograph of Fehcf suspended in water. The green color of the suspension further confirmed the formation of Berlin green $Fe[Fe(CN)_6]$. As shown in Fig. 2b and c, the Nihcf product consisted of particles with the average diameter of 20 nm, while the average size of Cohcf was around 15 nm. Shown in the insets in Fig. 2b and c were the photographs of Nihcf and Cohcf products suspended in water, with the color of brown and purple, respectively.

3.2. Electrochemical properties of Mhcf

Fig. 3 showed the cyclic voltammetry of Mhcf in 1 M KNO_3 aqueous electrolyte at the potential scanning rate of 5 mv s^{-1}. As shown in Fig. 3, all the as-prepared Mhcf exhibited stable redox couples in 1 M KNO_3 solution. The redox peak profiles were symmetric, indicating the good reversibility of the electrochemical reaction on the Mhcf electrodes. The shape of the curves revealed that the capacitance characteristics were distinguished from that of electric double-layer capacitance, in which case the shape of the curves was normally close to an ideal rectangular shape, indicating that the capacity was mainly resulted from the pseudocapacitive capacitance. As for Fehcf, there were sharp anodic and cathodic peaks at the potential of around 0.1 V, which may be

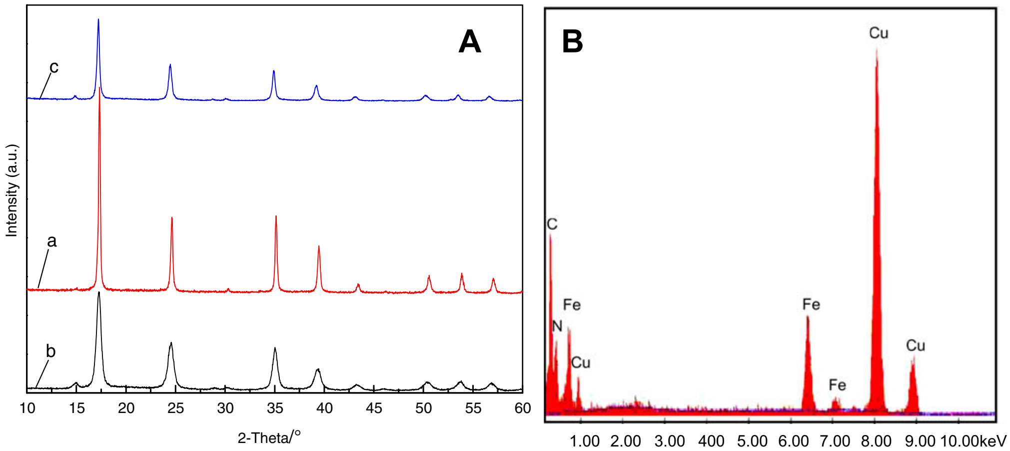

Fig. 1. XRD patterns (A) of the Mhcf products: (a) Fehcf, (b) Nihcf, (c) Cohcf. (B) EDS spectrum of the Fehcf product.

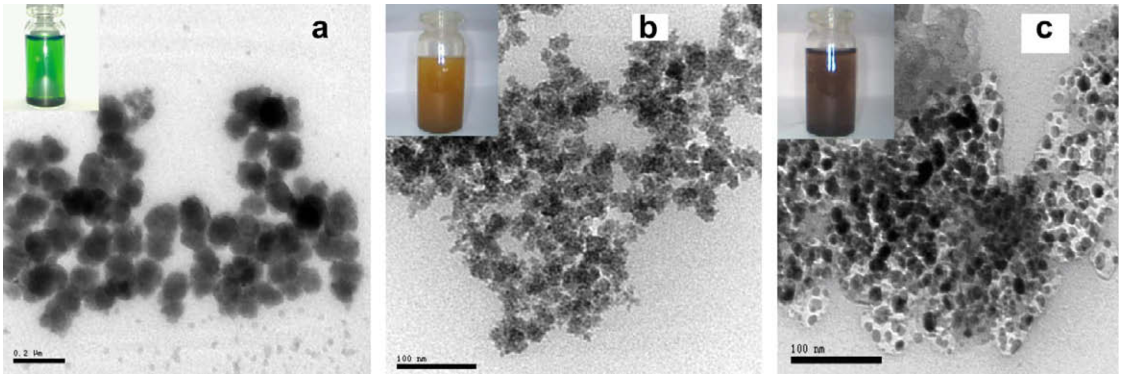

Fig. 2. TEM images of Mhcf: (a) Fehcf, (b) Nihcf, (c) Cohcf. The inset in (a), (b) and (c) was the photograph of Fehcf, Nihcf and Cohcf products suspended in water, respectively.