



Nickel Hexacyanoferrate Nanoparticles as a Low Cost Cathode Material for Lithium-Ion Batteries



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ABSTRACT

Potassium nickel hexacyanoferrate $\text{KNi}[\text{Fe}(\text{CN})_6]$ (NiHCF) was synthesized by a simple co-precipitation method and investigated as a cathode material for lithium-ion batteries. The X-ray diffraction and transmission electron microscopy studies revealed the formation of pure phase of agglomerated NiHCF nanoparticles of about 20–50 nm in size. The material exhibited stable cycling performance as a cathode in a lithium half-cell within a wide range of current densities, and a working potential around 3.3 V vs. Li^+/Li . The lithium ion diffusion coefficient in this system was determined to be in a range of 10^{-9} to 10^{-8} $\text{cm}^2 \text{s}^{-1}$, which is within the values for the cathode materials for lithium-ion batteries with high rate capability. Considering promising electrochemical performance and attractive lithium-ion diffusion properties of this material along with its economical benefits and simplified preparation, NiHCF could be considered as a very promising cathode for large scale lithium-ion batteries.

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1. Introduction

Rapid development and expansion of use of renewable energy sources and electric transport demand means of low cost and reliable energy storage systems. Rechargeable lithium-ion batteries (LIBs) are one of the most promising battery technologies to meet the requirements for such power conversion and storage systems [1,2]. However, the application of LIBs is still limited in electronic devices and electric vehicles due to their high cost preventing LIBs use in large-scale energy storage [3]. Therefore, inexpensive energy storage systems with prolonged cycle life, high power/efficiency and safety are of great demand and interest.

The choice of cathode materials significantly affects the performance and cost of a Li-ion battery [4]. Therefore, using inexpensive cathode materials could significantly reduce the overall cost of LIBs, and, consequently, expand their application for large-scale energy storage. From this point of view, transition metal hexacyanoferrates (MHCFs) could be considered as very promising candidates because they are inexpensive and may offer easy production, and exhibited promising electrochemical

performance [5–10]. MHCFs are the Prussian Blue analogues. They have an open framework represented by a general formula $A_xP/R(\text{CN})_6]$ ($0 < x < 2$); its structure is represented for $\text{KNi}[\text{Fe}(\text{CN})_6]$ in Fig. 1a. P^{+m} and R^{+n} coordinate to the nitrogen and carbon ends of the CN-group respectively, while A alkali metal ions can be intercalated in the interstitial sites that result from the large cages [11]. In 1978, Neff *et al.* reported first the electrochemical reduction and oxidation behavior of the Prussian Blue in 0.1 M KCl solution with rapid color change [8]. Since then, tremendous research have been done on its structure, electronic and optical properties, and redox behavior of Prussian Blue and its analogs (PBAs) [12–23]. $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 3\text{H}_2\text{O}$ was investigated as a potential active material for lithium ion battery by N. Imanishi *et al.* It showed reversible lithium intercalation potential around 3 V vs. Li^+/Li ; it was shown that the zeolitic water in the material structure does not remarkably effect lithium intercalation and the theoretical capacity [5]. The open-frame structure, as shown in Fig. 1a, is stable in both organic and aqueous electrolyte and allows fast intercalation and deintercalation of active cations such as Li^+ [5,24–30], Na^+ [6,31–38], K^+ [6,39], NH_4^+ [15], Mg^{2+} [7,40] due to empty large-ion sites in the structure. Cui *et al.* [6,9] reported five thousand deep cycling of potassium copper/nickel hexacyanoferrate electrode at high current densities (8.3 C) in an inexpensive aqueous electrolyte. Recently, Alveo Energy, an early-stage startup

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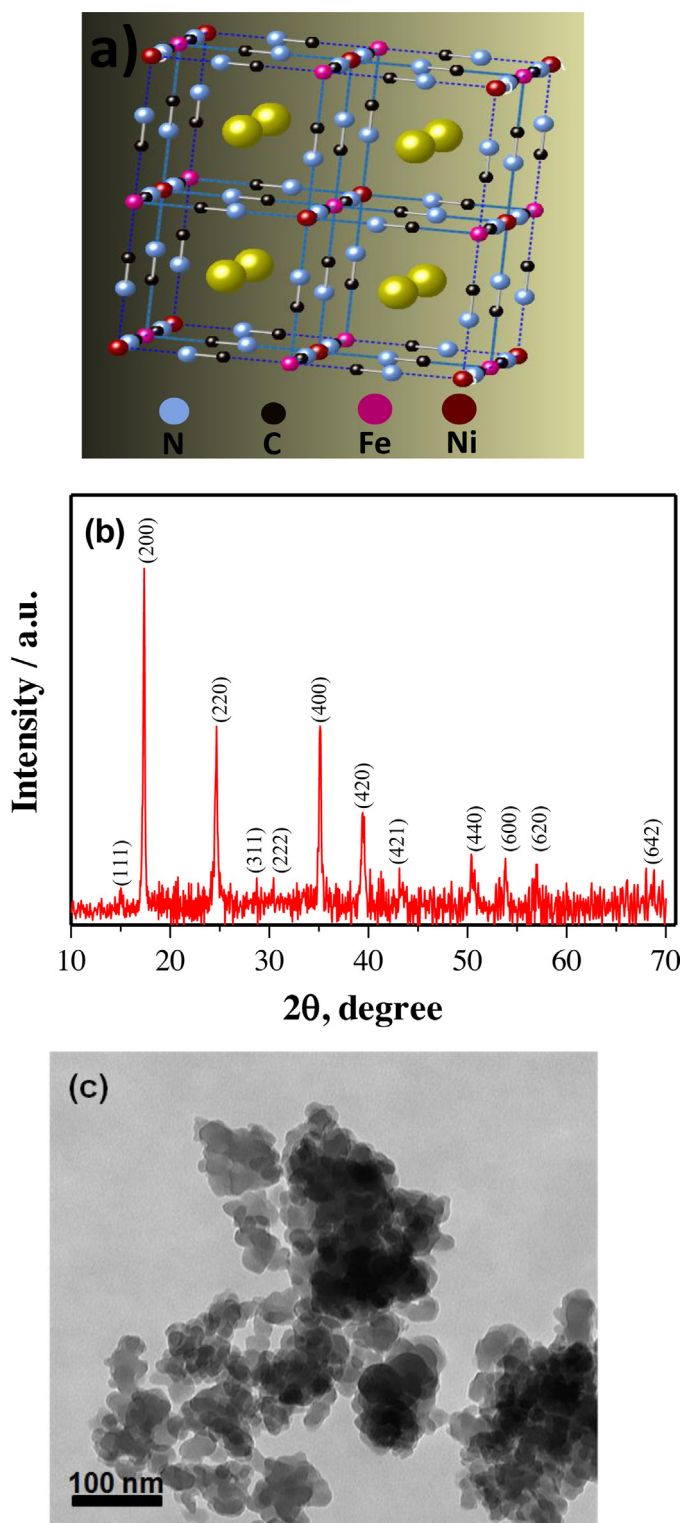


Fig. 1. (a) Schematics of crystal structure of NiHCF, (b) X-ray diffraction patterns, and (c) TEM images of as-prepared NiHCF nanoparticles.

company, has announced the development of low cost aqueous batteries for stationary large-scale energy storages with the MHCf-based cathode [41]. However, aqueous systems have a lower output voltage due to the water stability voltage (stability window) limitations, which would decrease the energy density and power of a battery [42,43].

From a brief review above, it can be seen that the Prussian Blue and its analogues have promising potential to be considered as cathodes for secondary batteries. However, to our knowledge, there is no a systematic research conducted and reported on the MHCfs as cathodes for non-aqueous LIBs including the active ion diffusion properties of MHCfs. In this work, we report on preparation of potassium nickel hexacyanoferrate (NiHCF) via a simple co-precipitation method and its study as a cathode for LIBs, and determination of lithium diffusion coefficient in this system along with investigation of other electrochemical properties of this promising cathode material.

2. Experimental

A simple co-precipitation method was used to synthesize NiHCF [6,15]. The stoichiometric amounts of $\text{Ni}(\text{NO}_3)_2$ and $\text{K}_3\text{Fe}(\text{CN})_6$ (both Sigma Aldrich) were separately dissolved in 250 mL deionized (DI) water. These two solutions were added dropwise into DI water in a round bottom flask under magnetic stirring at 70°C . The yellow color precipitate was filtered, washed and dried in a vacuum oven at 35°C for 72 h and then at 170°C for 3 hours.

The resulting powder was characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical) and transmission electron microscopy (TEM, Libra 120, Carl Zeiss).

The composite cathode was prepared by mixing the as-prepared NiHCF powder with Acetylene Black (AB, MTI Co.) and polyvinylidene difluoride (PVDF, Kynar) in weight ratio NiHCF:AB:PVDF = 8:1:1 in DI water, and coating the resulting slurry onto a graphite paper current collector (Alfa Aesar). Further the electrode was dried at 35°C for 72 h in a vacuum oven. The areal mass loading of NiHCF was around 5 mg cm^{-2} . CR2032 coin cells were assembled in a glove box (MBraun LabMaster), using lithium chips as both reference and counter electrode, Celgard 2400 as a separator and 1 M LiPF_6 in ethylene carbonate:diethyl carbonate:dimethylcarbonate (EC:DEC:DMC) = (1:1:1 vol.) as an electrolyte.

The electrochemical investigation of the cell was carried out using galvanostat/potentiostat VMP3 (BioLogic) and a battery tester Arbin SCTS 4000 (Arbin Instruments). Galvanostatic intermittent titration technique (GITT) was used to determine lithium-ion diffusion coefficient [44,45] as a function of voltage at a range of 2.5–4.0 V vs. Li^+/Li .

3. Results and discussion

3.1. Material Characterization

The XRD patterns of the as-prepared NiHCF could be indexed as a pure Prussian Blue crystal structure, which corresponds to an insoluble analogue of Prussian Blue structure with the $Pm\bar{3}m$ space group with a single cation in the center of the unit cell as shown in Fig. 1a [46]. During co-precipitation formation of NiHCF, Ni^{2+} occupies the nitrogen coordinated Fe^{3+} lattice sites in a face-centered cubic structure as illustrated in Fig. 1a. The sharp, well-defined peaks can be seen in the XRD patterns of the material presented in Fig. 1b, indicating a high crystalline structure of the NiHCF formed. The TEM results (Fig. 1c) have shown that the as-prepared NiHCF consists of agglomerated nanoparticles around 20–50 nm in size.

3.2. Electrochemical performance of NiHCF as a cathode for lithium batteries

Fig. 2 presents the CV curve of a lithium cell with the NiHCF cathode at a scan rate of 0.1 mV s^{-1} and a potential range of 2.0–4.2 V vs. Li^+/Li . It can be seen that the NiHCF cathode exhibits a pair of well distinguished redox peaks around 3.3 V vs. Li^+/Li indicating

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