



Short communication

Sodium titanium hexacyanoferrate as an environmentally friendly and low-cost cathode material for sodium-ion batteries



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HIGHLIGHTS

- A novel PBA-type cathode with titanium is used for sodium ion batteries.
- The $Ti^{2+/3+}$ and $[Fe(CN)_6]^{4-/3-}$ couples provide two sites for Na^+ ion storage.
- An initial discharge capacity of 92.3 mAh g^{-1} is obtained at 50 mA g^{-1} .

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ABSTRACT

A new type of Prussian blue analog, sodium titanium hexacyanoferrate, has been synthesized with good electrochemical performance using an environmentally friendly, solution precipitation method. Because of the hydrolysis reaction of titanium, it has been proved that the synthetic reaction is sensitive to heat, and the best reaction temperature is $60 \text{ }^\circ\text{C}$. The resulting particles belong to a well-defined open framework with cubic structure. Because of the two sodium storage sites provided by the low-spin $[Fe(CN)_6]^{4-/3-}$ couple and high-spin $Ti^{3+/4+}$ couple, sodium titanium hexacyanoferrate exhibits a high specific capacity over 90 mAh g^{-1} , and two pairs of clear charge/discharge platforms at $3.0 \text{ V}/2.6 \text{ V}$ and $3.4 \text{ V}/3.2 \text{ V}$, respectively. The results show that this material can be applied as a low-cost cathode electrode with good electrochemical performance for sodium ion batteries.

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1. Introduction

Increasing numbers of energy storage systems (ESSs) are required for persistent power supply [1]. Rechargeable batteries play an important role in ESSs, and Li-ion batteries have become a primary support for energy markets. However, the available amounts of Li resources are unable to meet the demands for future yield of Li-ion batteries [2]. The shortage of Li resources may restrict the development of Li-ion batteries. Compared with Li-ion batteries, room-temperature Na-ion batteries are more suitable for large-scale ESSs because of their low cost and abundant resources [3].

At present, great studies have been devoted to explore anode materials of Na-ion batteries, such as hard carbon [4], alloy materials [5] and titanate [6]. Although many kinds of Na-ion battery cathode material are being studied, the Na-storable cathodes are developed with no breakthrough. Among of them researchers paid close attention to three-dimensional framework structure materials, including sodium super ionic conductor (NASICON) structures [7] and metal-organic frameworks (MOFs) [8]. In fact, as one class of MOFs, Prussian blue (PB) and its analogues (PBAs) have been selected as excellent candidates for clean energy storage.

In previous work, $Na_4Fe(CN)_6/C$ gave a new thought that stable performance of materials with a cheaper and simpler synthesis method should be pursued for the PB and PBAs development [9]. Through continuous exploration, some important factors were found to affect the performance of PB and its analogues. The first is the numbers of vacancies and coordination water in materials [10–12]. The existence of vacancies and interstitial water may cause

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collapse of $-\text{Fe}-\text{C}\equiv\text{N}-\text{Fe}-$ skeleton and distortions of lattice during Na^+ ions insertion/extraction, resulting in poor electrochemical performances. In order to reduce vacancies and increase sodium ion content, the reducing agent can be added into the reaction solution [11]. Secondly, the electrochemical performances of PBAs are influenced by different transition metal elements in their host frameworks [13]. For instance, nickel ferricyanides provide a zero-strain structure for large numbers of Na^+ ions insertion/extraction [14]. However, nickel in PBAs is electrochemically inert without redox active sites, resulting in a low theoretical capacity [15]. In contrast, sodium manganese ferrocyanides have two redox couples of $[\text{Fe}(\text{CN})_6]^{4-/-3-}$ and $\text{Mn}^{2+/-3+}$, contributing to a high discharge capacity of 110 mAh g^{-1} [16]. Owing to the valence state change of manganese ions, crystal structure will collapse during the operating process [17]. A similar situation occurs in other materials, such as cobalt hexacyanoferrate and copper hexacyanoferrate et al. [18,19].

Herein, we report a new class of PBA structure by simply replacing the transition metal with Ti and the new compound was named sodium titanium hexacyanoferrate (NTH). The synthesis conditions were optimized into a reaction for 6 h at 60°C through an environmentally friendly aqueous reaction. The well-defined face-centered cubic structure of NTH particles provides enlarged ionic channels where sodium ions could effectively diffuse. Because of the introduction of Ti^{4+} ions, the NTH electrode exhibits a good electrochemical performance with both high capacity and good cycling stability. During the process of Na^+ ions insertion/extraction, there are two redox couples at 2.6/3.0 V and 3.2/3.4 V, corresponding to high-spin $\text{Ti}^{3+/-4+}$ couple and low-spin $[\text{Fe}(\text{CN})_6]^{4-/-3-}$ couple, respectively. According to these advantages, NTH-based sodium batteries should thus be appropriate for large-scale ESSs application.

2. Experimental section

2.1. Materials synthesis

NTH was prepared by a simple aqueous precipitation reaction [20]. First, 100 mL of 0.05 M TiCl_3 solution and 100 mL of 0.05 M $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ solution were mixed drop by drop in 200 mL of deionized water, the resulting solution was continuously stirred at either 60°C or 80°C for 6 h. The as-prepared samples were aged for another 24 h to obtain uniform particle sizes. Afterwards, the samples were separated by high-speed centrifugation, washed with deionized water and ethanol many times, and then dried at 60°C in a vacuum oven for 24 h. The samples prepared at 60°C and 80°C were labeled NTH-60 and NTH-80, respectively.

2.2. Material characterization

The crystalline structure of the samples was characterized by powder X-ray diffractometry (XRD), carried out using a Japanese Hitachi Rigaku-D/Max-2550 PC type diffractometer with monochromatized $\text{Cu K}\alpha$ radiation. The morphological appearance and size of the particles were investigated using a Hitachi S-4800 scanning electron microscopy (SEM) with an accelerating voltage of 20 kV. The distributions and contents of product elements were roughly surveyed by energy dispersive spectroscopy (EDS) using the Hitachi S-4800. The chemical compositions were examined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for Na, Ti, and Fe using a VISTA-MPX device and elemental analysis instrument (EA, Vario EL Cube) for C, N and H. TG curves were acquired on a NETZSCH STA449F3 instrument at a heating rate of 5°C min^{-1} under an N_2 environment. Fourier transform infrared (FT-IR) spectra were obtained to detect cyanide ligands and

hydroxyl in NTH using a Bruker Alpha (ATR-Ge, $400\text{--}4000 \text{ cm}^{-1}$). In order to detect the valence states of Ti and Fe in the materials, X-ray photoelectron spectroscopy (XPS) test was carried out on a PHI QUANTERA-II instrument. The electron spin resonance (ESR) spectra were recorded on a JEOL JES-FA200 spectrometer at 300 K.

2.3. Electrochemical measurements

The electrochemical characterization of the NTH cathode was carried out using button cells assembled in an Ar-filled glove box with water/oxygen contents lower than 1 ppm. A slurry of NTH powder, acetylene black, and poly(vinyl difluoride) at a weight ratio of 7:2:1 was coated onto aluminum foils to prepare the working electrode. The Na-ion half-cell consisted of a Na metal anode, a glass fiber separator (GF/D, Whatman), and the prepared working electrode. The electrolyte was prepared using 1 M NaPF_6 dissolved in ethylene carbonate and diethyl carbonate at a 1:1 volume ratio. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) curves were carried out on a CHI 660e electrochemical workstation (ChenHua Instruments Co. Wuhan). Galvanostatic charge/discharge experiments were conducted at room temperature on a LAND cyler (Wuhan Kingnuo Electronic Co. Wuhan). The potentials throughout the paper are referenced to the Na/Na^+ couple.

3. Results and discussion

The morphology features and elemental compositions of the NTH samples synthesized at different temperatures can be clearly visualized from their SEM and EDX images, respectively. NTH-60 sample exhibits cubic morphology with clear boundaries at a size of 100–150 nm, as shown in Fig. 1(a). Most of them with regular cubes and uniform size are evenly distributed. The well-defined cubic crystal structure is beneficial to provide a stable reaction place and a three dimensional path for Na^+ insertion/extraction. In contrast, NTH-80 sample presents non-uniform and irregular small particles at a size of 30–80 nm, as shown in Fig. 1(b). Besides, the agglomeration phenomenon in the tiny particles of NTH-80 might reduce the contact area between the material and the electrolyte, leading to a longer insertion/extraction path and poor rate capability.

Preliminary analysis of element contents for NTH samples synthesized at different temperatures was investigated by EDS. The EDS spectrums reveals that NTH-60 and NTH-80 samples with chemical compositions of Na, Ti, Fe, C, N and O elements have been successfully synthesized. Combined with a rough quantitative analysis, the different peak intensities of two samples indicate higher content of Ti in NTH-60 sample than that in NTH-80 sample.

When the TiCl_3 solution and $\text{Na}_4\text{Fe}(\text{CN})_6$ solution were mixed at room temperature, the resulting solution presented a blood red color without any precipitate. After heat treatment, it can be seen from Fig. 1(c) that the color of the precipitate changed from green (in the web version) to blue with the increased temperature. Based on the results, the composition of materials in the synthesis process could be judged preliminarily through their color, which might control the extent of reaction conveniently. On the other hand, different colors illustrate the end-products with different chemical composition.

The elemental contents in the samples were further determined using ICP-AES, and the results are shown in Table 1. The precise chemical formulas of NTH-60 and NTH-80 samples are calculated to be $\text{Na}_{0.66}\text{Ti}[\text{Fe}(\text{CN})_6]_{0.92} \cdot \square_{0.08}$ and $\text{Na}_{0.7}\text{Ti}[\text{Fe}(\text{CN})_6]_{0.9} \cdot \square_{0.1}$ (\square = vacancy in framework), respectively. According to the results, it can be seen that the contents of Ti and Fe in NTH-60 were much higher than those in NTH-80, especially Ti element, which is

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