



## Short communication

# A new gridding cyanoferrate anode material for lithium and sodium ion batteries: $\text{Ti}_{0.75}\text{Fe}_{0.25}[\text{Fe}(\text{CN})_6]_{0.96} \cdot 1.9\text{H}_2\text{O}$ with excellent electrochemical properties



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## HIGHLIGHTS

- A cyanoferrate  $\text{Ti}_{0.75}\text{Fe}_{0.25}[\text{Fe}(\text{CN})_6]_{0.96} \cdot 1.9\text{H}_2\text{O}$  can be used as a new anode material.
- The cyanoferrate reacts with lithium following a conversion reaction mechanism.
- The cyanoferrate can store much more lithium than sodium.

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## ABSTRACT

A novel air-stable titanium hexacyanoferrate ( $\text{Ti}_{0.75}\text{Fe}_{0.25}[\text{Fe}(\text{CN})_6]_{0.96} \cdot 1.9\text{H}_2\text{O}$ ) with a cubic structure is synthesized simply by a solution precipitation method, which is first demonstrated to be a scalable, low-cost anode material for lithium-ion batteries exhibiting high capacity, long cycle life and good rate capability. Nevertheless, it has a low capacity of about  $100 \text{ mAh g}^{-1}$  as an anode material for sodium-ion batteries.

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## 1. Introduction

Prussian Blue (PB),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , the oldest and most studied mixed-valence material of this type, has an archetypal hexacyanometalate framework structure [1–3]. Materials with the PB structure may be described in terms of the general formula  $\text{A}_x\text{PR}(\text{CN})_6$ , where nitrogen-coordinated transition metal cations (P) and hexacyanometalate complexes ( $\text{R}(\text{CN})_6$ ) form a face-centered cubic open framework containing large interstitial A-sites [4,5], which contains open  $\phi 1004$  channels (0.32 nm in diameter) and interstitial sites (0.46 nm in diameter) [6]. The electrochemical activities of PB and its analogues were investigated

as cathode materials of mainly sodium-ion batteries several years ago, such as  $\text{FeFe}(\text{CN})_6$  [7],  $\text{NaFeFe}(\text{CN})_6$  [8,9],  $\text{NaMnFe}(\text{CN})_6$  [10–13],  $\text{NaMnMn}(\text{CN})_6$  [14] and so on [15–18], which show reversible intercalation and de-intercalation of lithium or sodium ions. Nevertheless, such a PB-analogue has never been investigated as an anode material due probably to its relatively high working potential.

In this work, by using a simple solution precipitation method and introducing a  $\text{Ti}^{4+}/\text{Ti}^{3+}$  redox couple, we synthesize a gridding material  $\text{TiFe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  [19], and demonstrate for the first time that it can be used as a new anode material working at relatively low potentials for lithium-ion or sodium-ion batteries. For lithium-ion batteries, it can deliver a reversible capacity of  $350 \text{ mAh g}^{-1}$  with excellent cycling and rate performances.

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## 2. Experimental section

The single-crystal titanium hexacyanoferrate nanoparticles were prepared simply by a solution precipitation method. Typically, 50 mL 0.1 M tetrabutyl titanate ethanol solution was slowly added to 100 mL 0.1 M  $\text{Na}_4\text{Fe}(\text{CN})_6$  aqueous solution containing 1.5 M HCl under continuous stirring to generate a precipitate. The resulting suspension was maintained at 60 °C for 6 h under  $\text{N}_2$  atmosphere. The as-obtained dark green precipitate was centrifuged and washed for several times with deionized water and acetone, and finally dried in a vacuum oven at 70 °C for 12 h.

The crystalline structure of the sample was characterized by using a x-ray diffractometer (Philips X'Pert Pro Super,  $\text{Cu K}\alpha$  radiation). The XRD pattern was collected in a range of  $2\theta$  values from 10° to 70° at a scanning rate of 10°  $\text{min}^{-1}$ . The morphology of the sample was studied by scanning electron microscopy (SEM, Sirion 2000, FEI). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific) and X-Ray fluorescence (XRF-1800) measurements were performed to obtain information on the surface compositions of the particles. Thermal analysis (TGA) was performed at a heating rate of 2 °C  $\text{min}^{-1}$  in the temperature range of 30–700 °C in nitrogen atmosphere (DTG-60H, Shinadzu).

The electrochemical properties of the obtained cyanoferrate-based material was evaluated in coin-type cells. The electrode laminate was prepared by mixing the active material (70 wt%), acetylene black (15 wt%) and PVDF (15 wt%) in *N*-methyl-pyrrolidinone into an electrode slurry and then the slurry was cast on a copper foil collector. The mass loading of the active material within the laminate was about 2  $\text{mg cm}^{-2}$ . The coin-cells (CR2032 size) were assembled in an argon-filled glove box with above laminate as the working electrodes. For making lithium-ion half cells, metallic

lithium disks were used as the counter electrodes and 1 M  $\text{LiPF}_6$  in a 1:1 (w/w) mixture of EC and DEC solution as the electrolyte and Celgard 2400 membrane as the separators. For making sodium-ion half cells, handmade Na disks were used as the counter electrodes, 1.0 M  $\text{NaClO}_4$  in a 1:1 (w/w) mixture of EC and DMC solution as electrolyte and glass fiber (whatman Gf/D) as the separators. The cells were tested on a multi-channel battery test system (NEWARE BTS-610) with galvanostatic charge and discharge in different selected voltage ranges. The electrodes for ex-situ XRD test were obtained by disassembling the lithium half cells at different states of charge (SOC) or depths of discharge (DOD) and washed by DMC.

## 3. Results and discussion

The X-ray diffraction pattern of the synthesized titanium cyanoferrate powder is shown in Fig. 1a. All diffraction peaks of  $\text{TiFe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  are weak but can be well indexed to a face-centered cubic structure with a space group  $\text{Fm}\bar{3}\text{m}$  (JCPDS no. 23-0605). Its lattice parameter,  $a$ , is calculated as 1.01 nm. The schematic illustration of the crystal structure for  $\text{TiFe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  are show in the inset of Fig. 1a. In this structure, nitrogen-coordinated  $\text{Ti}^{4+}$  ions (red color) and hexacyanometalate complexes ( $\text{Fe}(\text{CN})_6$ ) (blue color) form a face-centered cubic open framework. SEM shows that this material consists of large, porous agglomerations of 20–50 nm nanoparticles (Fig. 1b). The surface electronic state of this sample was examined by XPS. The XPS spectrum of Fe 2p and Ti 2p (Fig. 1c) indicates that there are four Fe-related peaks with binding energy at 709.1, 710.7, 721.9 and 724.7 eV, corresponding to  $\text{Fe}^{\text{II}}2\text{p}_{3/2}$ ,  $\text{Fe}^{\text{II}}2\text{p}_{1/2}$ ,  $\text{Fe}^{\text{III}}2\text{p}_{1/2}$ , and  $\text{Fe}^{\text{III}}2\text{p}_{3/2}$ , respectively [20]. There are two more Ti-related peaks (i.e. doublet) at 458.8 and 464.6 eV, that correspond to  $\text{Ti}^{\text{IV}}2\text{p}_{3/2}$  and

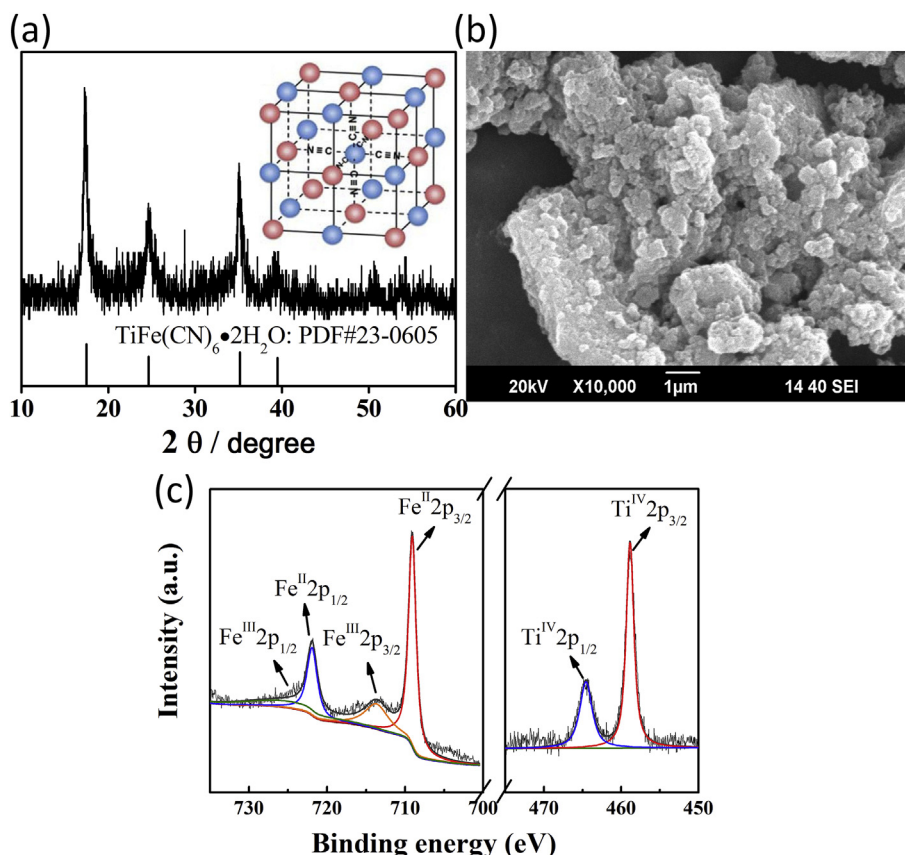


Fig. 1. a) XRD pattern and b) SEM image of the TFCN sample. The inset in a) shows the schematic crystal structure. c) XPS spectrum of Fe 2p and Ti 2p.

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