



Self-templated fabrication of micro/nano structured iron fluoride for high-performance lithium-ion batteries



Jingru Zhai^a, Zhengyu Lei^a, David Rooney^d, Huaguo Wang^c, Kening Sun^{b,c,*}

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China

^b Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150001, China

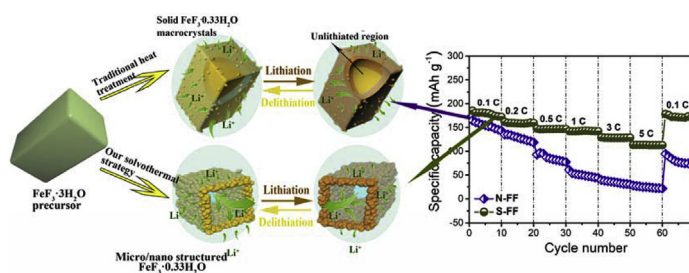
^c State Key Laboratory of Advanced Chemical Power Sources (SKL-ACPS), Zunyi, 563000, China

^d School of Chemistry and Chemical Engineering, Queen's University, Belfast, Northern Ireland, BT9 5AG, UK

HIGHLIGHTS

- Micro/nano structured $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is fabricated using $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ as precursor.
- The formation mechanism in solvothermal reaction is studied and discussed.
- The as-prepared $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ displays excellent lithium storage properties.
- Our strategy could easily be adjusted to synthesize other fluorides.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Lithium-ion batteries
 $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$
 Micro/nano structure
 Self-template

ABSTRACT

Hexagonal-tungsten-bronze-type (abbreviated as HTB) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ has been recognized as a promising high-rate cathode material for lithium-ion batteries. However, rational engineering of advanced structures is highly desirable yet challenging to activate the insulating $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ in practical application. For the first time, a facile and economical solvothermal strategy is demonstrated to synthesize micro/nanostructured $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ through the self-templated morphology evolution and topotactic phase transformation of commercial $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor. Benefiting from the hierarchical structure, the as-prepared $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ exhibits enhanced rate capability and cycle stability compared with the bulk $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ obtained through traditional heat treatment of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$. More interestingly, simple adjustment of the synthesis solvent or temperature enables the fabrication of several iron-based fluorides with uniquely hierarchical morphology, which are still hard to be synthesized under the existing methods.

1. Introduction

Iron trifluoride (FeF_3) has attracted extensive attention as a cathode material for lithium-ion batteries (LIBs) due to its high theoretical specific capacity (237 mAh g^{-1} , $1e^-$ transfer; 712 mAh g^{-1} , $3e^-$ transfer) [1,2]. However, the intrinsically poor electronic conductivity caused by the highly ionic Fe-F bonds leads to a rather low practical

capacity [3]. Generally, nanosizing and/or conductive species coating are regarded as effective strategies to activate the FeF_3 , as it was achieved by several FeF_3 -based composites, including the carbon metal fluoride nanocomposite (CMFNCs) [4,5], FeF_3/C [6,7], FeF_3/CNTs [8], $\text{FeF}_3/\text{PEDOT}$ [9], FeF_3/OMC [10], $\text{FeF}_3/\text{graphene}$ [11,12], $\text{FeF}_3/\text{nickel ammine nitrate}$ [13], etc. On the other hand, the dense crystalline structure of the ReO_3 -type FeF_3 limits the Li^+ diffusivity and thus

* Corresponding author. Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150001, China.
 E-mail address: keningsunhit@126.com (K. Sun).

results in a poor high-rate performance. To further address this issue, FeF_3 derivatives with expanded structure, i.e., H_2O -stabilized ion transport channels, such as HTB- $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ [14,15], pyrochlore $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$ [16] and pyrochlore-like $\text{FeF}_{2.5} \cdot 0.5\text{H}_2\text{O}$ [17] have been successfully designed in ionic liquid (IL) media. Meanwhile, other H_2O -stabilized structures, such as $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ [18,19], $\text{Fe}_{1.9}\text{F}_{4.75} \cdot 0.95\text{H}_2\text{O}$ [20] and $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$ [21] have also been progressively fabricated in water-based synthesis processes. Among them, HTB- $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ with straight 1D tunnels stands out for being structurally more stable during lithiation/delithiation process and it has gradually become the mostly researched insertion fluoride cathode material [22–25]. For example, the zigzag channels in pyrochlore phase have been shown to irreversibly trap Li^+ [16], while for $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, the insertion of Li^+ would destroy the hydrogen bond-stabilized framework and thus release hydration water into the electrolyte [26]. Nevertheless, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is the key precursor for synthesizing other more robust open framework fluorides like TTB-type $\text{K}_{0.6}\text{FeF}_3$ [27].

Despite these advantages, the preparation of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ materials are still very problematic. The existing methods can be classified into two types: (1) Ionic-liquid-assisted “down-up” approach, which can easily build well-defined nanostructures but is too cost for large-scale manufacture. Besides, the poorly-controllable pre-vacuum treatment leads to poor reproducibility and the overall yields are low (ca. 25%) [14,28]. (2) Thermally decomposing an $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor pre-fabricated by $\text{HF}/\text{NH}_4\text{F}/\text{NH}_4\text{HF}_2$ -based aqueous fluorine chemistry under inert gases, i.e., “down-up-down” approach. In this case, an extra ball-milling process may usually be required to reduce the particle size into nanoscale and simultaneously build a conductive network for the target nanocomposites [23,29,30]. Obviously, this latter method suffers from safety issues as well as too complex procedures. No practical application of the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ -based materials would see the light of day if a safe and low-cost synthesis method could not be proposed.

No doubt, nanosizing is a prerequisite for $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ to achieve high capacity. However, nanoscaled materials suffer from some drawbacks including easy aggregation, significant side reactions and so on during cycling, which are unfavorable for the long term stability [31]. Therefore, researchers turn their eyes on micro/nanostructured materials, which integrate the merits of nanostructure and the stability of micron-sized structure, to avoid those shortcomings of nanosized materials [32–34]. Unfortunately, the synthesis of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ with hierarchical structures by economical and safe ways has not yet been developed.

Herein, we report the design and viable preparation of micro/nano structured $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ by a mild solvothermal strategy utilizing commercial $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, simultaneously containing Fe and F elements, and 1-pentanol as the only reactant and solvent for the first time. Accordingly, through systematical investigation of the thermal behavior of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ in solvothermal environment, we propose and discuss a possible formation mechanism of the micro/nanostructured $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$. More interestingly, other promising iron fluoride-based cathode materials with unique morphology, such as hierarchical FeOF nanorods and 3D flowerlike pyrochlore $\text{FeF}_x \cdot 0.5\text{H}_2\text{O}$, which are still hard to be synthesized under the existing methods, could also be obtained by synthesis parameter control.

2. Experimental section

2.1. Materials synthesis

$\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich) and all other chemical reagents (Aladdin) were of analytical grade without any further purification before using.

Synthesis of bulk $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$. In a typical procedure, 167 mg $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ powders were put in an alumina crucible and then the crucible was placed at the center of the tube furnace. After that, the furnace temperature was slowly ramped from 30 °C to 200 °C ($\sim 1^\circ\text{C}$

min^{-1}) and held at 200 °C for 5 h under a flowing nitrogen gas to get $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$.

Synthesis of micro/nano structured $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$. Typically, 167 mg $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ was added to 70 mL 1-pentanol in a 100 mL Teflon-lined stainless-steel autoclave and then heated at 150 °C for 15 h. After the reactor cooled down naturally, the as-synthesized products were collected by vacuum filtration and dried under vacuum conditions at 100 °C overnight.

What's more, we conducted a series of temperature-dependent (120 °C–200 °C) as well as solvent-dependent experiments to further understand and unravel the mechanism of the phase transformation of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, during which five additional alcohols namely, methanol, ethanol, 1-propanol, 1-butanol and ethylene glycol were used as solvents instead of 1-pentanol with other conditions remaining the same.

2.2. Physical characterization

The morphology and microstructure of the samples were confirmed by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010, 15 kV) and transmission electron microscopy (TEM, JEOL JEM-2100, 200 kV). The structure and crystallinity of fluoride samples were checked by powder X-ray diffraction (XRD, Panalytical X'pert pro) with $\text{Cu K}\alpha$ X-ray radiation ($\lambda = 1.5418 \text{ \AA}$). The peak profile and precise lattice parameters of the electrode patterns were determined by Rietveld refinement using the GSAS program. Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 under stable N_2 flow for the precursor with a heating rate of $10^\circ\text{C min}^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis was recorded on a ESCALAB 250Xi (Thermo Fisher Scientific). Raman spectra were recorded on a Renishaw RM 2000 spectrometer (632.8 nm laser). Fourier transform infrared spectroscopy (FTIR) spectra were collected from a Perkin Elmer 100 spectrometer. The atomic modeling was established using Crystal Maker software.

2.3. Electrochemical evaluation

The fluoride samples were mixed with carbon black and polyvinylidene fluoride (PVDF) binder at a weight ratio of 8:1:1 in N-methyl-1-2-pyrrolidinone (NMP) solvent. The as-obtained slurry was coated on an aluminum foil and vacuum-dried at 80 °C for 12 h. Then the electrodes were pressed and cut into disks with diameter of 15 mm. The average loading weight of the active material is $\sim 1 \text{ mg cm}^{-2}$ (weighted by METTLER TOLEDO MS105DU). The CR2025 coin-type cells were assembled in an argon-filled glove box (Mbraun, $\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$) using the prepared disks as the cathode, and metal lithium disks as the anode, Celgard 2400 (polypropylene) was used as the separator, and 1 M of LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylene methyl carbonate (EMC) solvent (1:1:1 in volume) as the electrolyte. The galvanostatic charge/discharge tests over a potential range of 1.7–4.5 V (vs. Li/Li^+) were performed on the Neware CT3008 (Shenzhen Neware Electronic Co., China) battery test system at various current rates (1C is equivalent to 200 mA g^{-1}). Cyclic voltammetry (CV) data were collected on an electrochemical workstation (CHI 660B) at a scanning rate of 0.1 mV s^{-1} between 1.7 and 4.5 V. Electrical impedance spectroscopy (EIS) measurements were carried out using an electrochemical workstation (Princeton Applied Research PARSTAT 2273 advanced electrochemical system) over the frequency range between 100 kHz and 100 mHz with a signal amplitude of 5 mV.

3. Results and discussion

Before treatment, the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor (JCPDS card no. 32–0464, Fig. S1a) consists of mostly smooth prisms along with several irregular blocks with a particle size of around 1–3 μm (Fig. S1b). While after our wet-processing (Fig. 1a, RouteII), the solid prisms evolve into

Download English Version:

<https://daneshyari.com/en/article/7724846>

Download Persian Version:

<https://daneshyari.com/article/7724846>

[Daneshyari.com](https://daneshyari.com)