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A reversible conversion and intercalation reaction material for Li ion battery cathode



Yongqiang Shen^{a,b}, Xianyou Wang^{a,*}, Hai Hu^a, Miaoling Jiang^a, Shuangying Wei^a,
Yansong Bai^a

^a Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Hunan Province Key Laboratory of Electrochemical Energy Storage and Conversion, School of Chemistry, Xiangtan University, Xiangtan 411105, Hunan, China

^b College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, China

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ABSTRACT

Although FeF_3 and its hydrates have been studied as the cathode materials for Li ion batteries (LIBs), herein the FeF_3 /graphene composite with sheet-like structure is innovatively prepared and used as LIB cathode material. By scanning electron microscope (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), X-ray diffraction (XRD) and electrochemical measurement, the structure and electrochemical performance of the as-synthesized FeF_3 /graphene composite are investigated. The results indicate that the sheet-like structure hybrid is formed by the FeF_3 nanosheets and the graphene sheets. Meantime, we demonstrate that the FeF_3 /graphene composite has good rate capability and cycling performance, whether it is based on conventional intercalation reaction or reversible conversion reactions.

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1. Introduction

Power consumer devices (smartphones, laptops, tablets, etc.) and emerging electrical/hybrid vehicles are driving toward LIBs with high-capacity and high rate performance direction. Therefore, the development of new cathode material, which bases on reversible conversion reaction mechanism and is different from the traditional intercalation materials, is a hotspot and focus of current research. Candidate in a variety of materials, transition metal fluoride, has been considered as a promising new class of cathode materials for LIBs, which exhibits large theoretical capacities and high discharge voltages due to their highly ionic metal-ligand bonds and small atomic weight. But for FeF_3 series compounds, based on the conversion reaction, it needs to consider how to overcome the disadvantage of its severe deterioration and low cycle life [1–3]. And when based on the conventional intercalation reaction, the high ionicity of FeF_3 combined with large bandgap results in poor electrical conductivity [4–6]. Meantime, the dense structure of FeF_3 also deteriorates seriously its electrochemical performance [7]. These faults hinder its practical application as cathode in LIBs. Researchers tried a lot to compensate for the intrinsically poor conductivity such as to use a wide variety of highly conductive carbon (e.g., carbon nanotubes [1,2], activated carbon

[4] and graphene [6,8]) or to change microstructure of FeF_3 [3]. Furthermore, a wide range of hydrated forms of FeF_3 (e.g., $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ [9] and $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$ [10]) have been reported to exhibit a fairly high capacity for LIBs.

In a previous report, we used sol-gel process to synthesize a graphene loading heterogeneous hydrated forms iron based fluoride nanocomposite, and it could deliver a large reversible capacity and excellent cyclic performance for Li-ion batteries [11]. In this work, we report the fabrication of a new sheet-like structure composed of FeF_3 with graphene by sol-gel process (see Supporting Information) and its superior electrochemical properties in LIBs.

2. Results and discussion

Fig. 1a illustrates the preparation process of the FeF_3 /graphene composite with sheet-like structure. As schematically shown in Fig. 1a, firstly, in order to induce surface nucleation of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ on the surface of the graphene, $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, which was quickly formed after HF was added in methanol solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, was aged in sol-gel solution with graphene to generates C–F bonds for nucleation sites. As these C–F bonds were energetically activated, they were expected to act as nucleation sites for $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$. Then $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ induced surface nucleation of iron fluoride due to intermolecular interactions. By controlling the graphene amount, the graphene sheets, which can anchor

* Corresponding author.

E-mail address: wxianyou@yahoo.com (X. Wang).

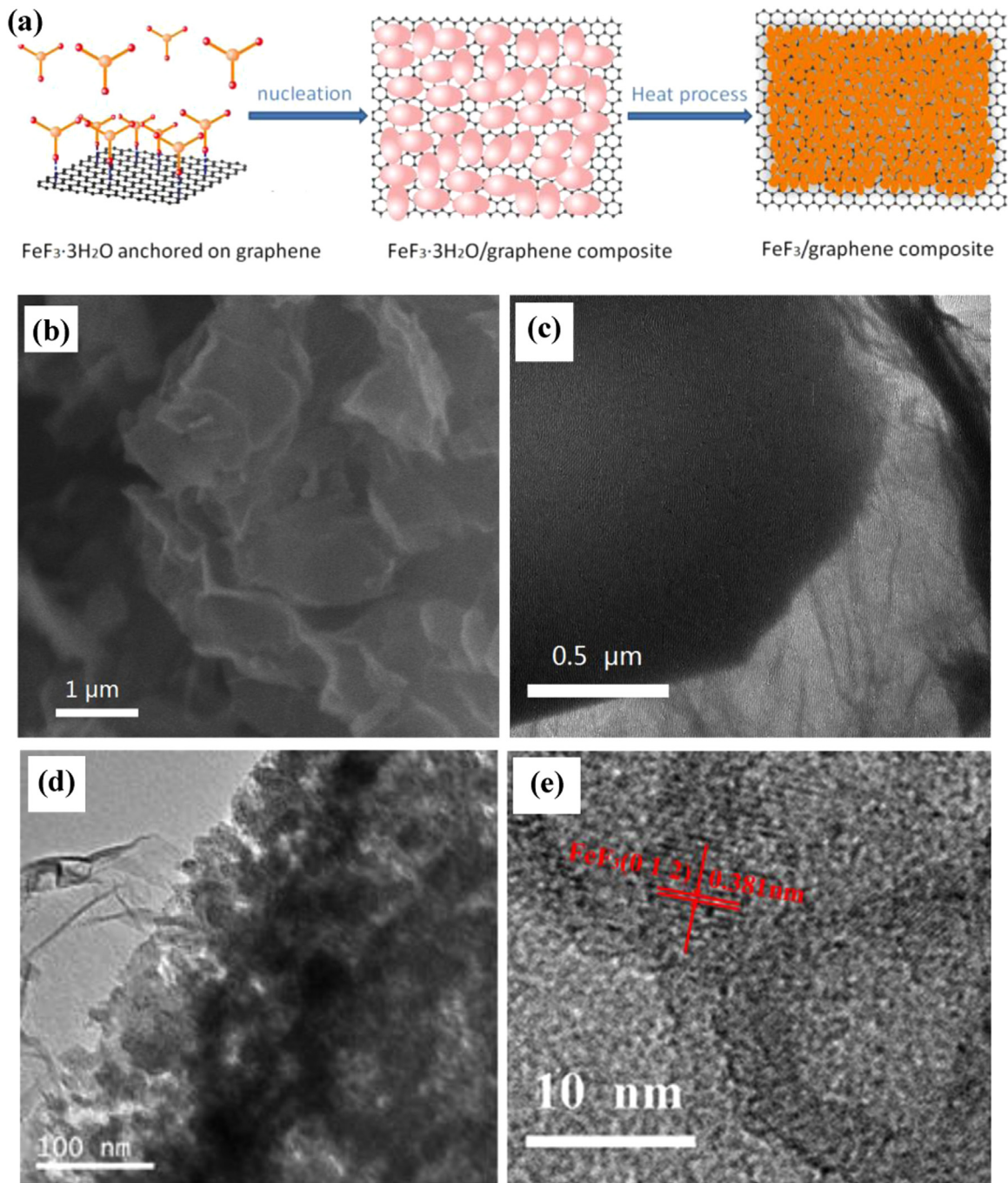


Fig. 1. (a) schematic illustration to form the $\text{FeF}_3/\text{graphene}$ composite with sheet-like structure, (b) SEM image, (c, d) TEM images, and (e) HRTEM images of nanosheets $\text{FeF}_3/\text{graphene}$.

$\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ crystal, can provide more growing spots for $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ crystals and prevent the growth of big fluoride nanocrystals. Thus $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nanocrystals distributed homogeneously on the surface of the graphene sheet, and a $\text{FeF}_3 \cdot 3\text{H}_2\text{O}/\text{graphene}$ composite precursor was obtained. At last, the precursor was heated in a vacuum drying oven at the temperature of 180°C , and along with ascend of the temperature, the large $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ particles gradually removed H_2O molecules to get $\text{FeF}_3 \cdot x\text{H}_2\text{O}$ nanoparticles [11] until the FeF_3 nanosheets, finally suitable heat treatment ensured that the sheet-like $\text{FeF}_3/\text{graphene}$ composite was obtained.

The crystal structures and shapes of the as-synthesized composite were identified by XRD, SEM and TEM analysis. XRD peaks of the fabricated powders before and after heat treatment in

vacuum were identified as those of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (JCPDS no. 32–0464) and FeF_3 (JCPDS no. 33–0647), respectively (Fig. S1, S2 in the Supporting Information). Fig. 1b, c and d show the morphology of the $\text{FeF}_3/\text{graphene}$ composite. The FeF_3 nanosheets are attached on graphene sheets, as expected, which form a sheet-like structure composite. A rough wavy structure could originate from the intrinsic wrinkles and ripples of graphene (Fig. 1b). The sizes of the $\text{FeF}_3/\text{graphene}$ sheets range from several hundred nanometers to a few micrometers. Moreover, different magnification TEM images (Fig. 1c) and d) clearly show that the FeF_3 nanosheets are composed of numerous nanoparticles with various sizes from 10 nm to 100 nm, which stretch outwards from the aggregate core, then present the nanosheets morphology. HRTEM shows that the

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