



A three-dimensional interlayer composed of graphene and porous carbon for Long-life, High capacity Lithium-Iron Fluoride Battery



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ABSTRACT

We design a macroscopic structure composing of porous carbon and graphene sheets, which are coated onto a cellulose paper as an interlayer inserted between electrode and separator. The interlayer mainly acts as a divertor to accommodate the discharge products breaking away from the electrode by mechanical degradation or cathode dissolution during cycling and keeps the close contact with current collector.

Iron fluoride is a new-type lithium storage material developed in recent years, which can act as a cathode material candidate for the rechargeable lithium ion battery due to their large theoretical capacity and relatively high operating potential. Specifically, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, which possesses unusual tunnel structure, is attracting more and more attentions. However, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ suffers from the poor electronic conductivity and volume effect during cycling, causing the large capacity fading. In this study, we design a macroscopic structure composing of porous carbon and graphene sheets, which are coated onto a cellulose paper as an interlayer inserted between electrode and separator. The interlayer can not only enhance the electronic conductivity, but also absorb the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ nanoparticles breaking away from the Al foil due to the volume effect upon cycling. When the interlayer is applied in battery, discharge capacities of 600 and 460 mAh g^{-1} can be achieved at the rates of 100 and 600 mA g^{-1} after 60 cycles, respectively. Furthermore, the capacity of 435 mAh g^{-1} can be still retained at a high rate of 1000 mA g^{-1} after 250 cycles. The results demonstrate a potential feasibility for the porous carbon/graphene sheets to be applied to obtain a high-performance lithium-iron fluoride battery.

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1. Introduction

Energy crisis is becoming more and more severe since the growing consumption of fossil fuel in recent years. Although some renewable resources have been found, the utilization of these energy is difficult due to the instability and diffusion in space. Thus, the demand for an energy storage system with a high specific capacity is increasing [1]. Lithium ion battery is a promising candidate which has drawn immense attentions due to the high energy density and conversion efficiency [2–4]. However, the state-of-the-art cathode materials, such as LiCoO_3 and LiFePO_4 , deliver only a actual specific capacity below 160 mAh g^{-1} , which can not meet the demands of electric vehicles and energy storage systems [5–7]. As a conversion-type cathode material, transition metal fluorides can provide a large specific capacity and relatively high operation voltage [8]. Specifically, considerable attentions

have recently been focused on iron fluoride due to the high theoretical specific capacity of 712 mAh g^{-1} in the range of 1.5–4.5 V, electromotive force value of 2.7 V and low cost. Among the plentiful polymorphs of iron fluoride, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is prominent on account of the unusual tunnel structure, which is favorable for more Li-ion insertion [9].

Despite the theoretically attractive features of iron fluoride, the electronically insulating behavior introduced by the large bandgap affects the utilization of the active iron fluoride material [10]. Consequently, great efforts have been made to overcome the poor electrical conductivity by fabricating FeF_3/C nanocomposites [11], which are based on the high electrochemical activity and conductivity of carbon [12–14], for example, the $\text{FeF}_3/\text{graphite}$ nanocomposites prepared by mechanical ball-milling of the as-prepared FeF_3 nanopowders with graphite [15], FeF_3 nanoparticles deposited on carbon nanotube (CNT) surface [16] and FeF_3 -graphene composite [17]. Besides the fabrication of FeF_3/C nanocomposites, designing favorable morphologies is another approach to overcome the restrictions [18,19]. The poor electrochemical performance can be improved by fabricating the porous

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FeF_3 nanospheres [20], FeF_3 nanowires [21], and $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ with microporous morphology [22]. Enhancing the temperature of the battery operation is also an effective pathway to get a remarkable specific capacity, owing to the impact of temperature on the activity of iron fluoride [23]. A comparison of the electrochemical performance about above researches is shown in Table S1 (see the Supporting Information).

In spite of some achievements attained by the preparation of FeF_3/C nanocomposites or designing favorable morphologies, these modifications can not realize the desired specific capacity and cycling performance for practical applications. Indeed, the previous researches commonly exhibit a below-hundred cycle, and the capacity reveals a rapid degradation. When operated on the appropriate temperature, the battery can exhibit a higher specific capacity. However, the temperature spot can not be kept in the practical application. Another issue, which is not brought to enough attentions, is the large volume change during charge/discharge, limiting the cycle performance of iron fluoride [24]. Moreover, a new finding that the substantial discharge product (such as LiF and Fe) shall dissolve into electrolyte in initial conversion reaction was recently reported [25]. To further improve the performance of iron fluoride cathode material, the volume expansion and cathode dissolution should be also considered besides enhancing the electronic conductivity of iron fluoride. Based on these issues, we designed a conductive interlayer consisting of porous carbon and graphene sheets (GS), which are coated on the cellulose paper as an interlayer inserted between $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ electrode and electrolyte. The interlayer mainly acts as a divertor to accommodate the discharge products breaking away from the electrode by mechanical degradation or cathode dissolution during cycling and keeps the close contact with current collector to retain the electrochemical activity of these portion of active material, which is expected to improve the cycle performance. With these considerations, the interlayer needs to provide high electronic conductivity, abundant pore volume and reasonable pore distribution. Hence, GS is chosen as conductive component, and porous carbon with rich pore structure acts as carrier. Fig. 1 shows the interlayer structure in battery. The porous carbon/GS (PGS) was fabricated by a hydrothermal treatment combining GO and hydrochars, followed by a heat treatment at 800°C . GS component which is dispersed throughout the interlayer, can greatly enhance the electron conductivity of electrode to improve the utilization of active material. Meanwhile, the porous carbon can not only adsorb the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ stripping from the electrode due to volume expansion, but also capture the dissolved species, which greatly improves the storage capability

and cycle performance. Furthermore, it does not need to include complicated modification for $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ particles, but to insert a simply constructed porous interlayer, which is firstly applied to the lithium-iron fluoride battery.

2. Experimental

2.1. Preparation of the materials

The $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ powder was prepared by a low-temperature method in which FeCl_3 was added firstly into the excessive HF solution. Then the mixture was put in an ice-bath with a constant stirring for 24 h at 2°C . After that, the white powders could be obtained. To obtain the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ powders, the white powders must be heated at 120°C for 24 h in air. When the colour turned to palegreen, the well-dispersed $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ grains could be obtained. Graphite oxide was prepared based on the modified Hummer's method [26]. The detailed steps could be seen in Supporting Information. The PGS was synthesized through a hydrothermal method, followed by a high temperature activation step at 800°C . In a typical synthesis procedure, we dissolved firstly 4.8 g of sucrose into the 77 ml of dispersed GO solution with a concentration of 2.4 mg mL^{-1} , followed by a magnetical stir of 4 h at room temperature. Then the aqueous mixture was poured into Teflon-lined stainless steel autoclave and maintained for 12 h at 180°C . The black powders could be obtain after the resulting precipitate was filtered off, washed thoroughly with deionized water and dried at 60°C . Then, it was activated using potassium hydroxide as activating agent at a ratio of 1:5. The mixture of KOH and the black powders was dissolved in a mix solution of ethanol and deionized water, which was stirred for 10 min before being dried at 120°C . The dried mixture was heated at a heating rate of 5°C min^{-1} and maintained at 800°C for 2 h in a muffle furnace filled with argon. The PGS could be obtained after washing the resulting product with diluted hydrochloric acid and deionized water.

2.2. Characterization

The morphology and structure of the prepared samples were characterized using scanning electron microscope (SEM, Nova NanoSEM230) and transmission electron microscopy (TEM, JEOL JEM-2100F). The structure and composition of the samples were performed by X-ray diffraction (XRD, Rigaku-TTRIII) with $\text{Cu K}\alpha$ radiation at a scanning rate of 8° min^{-1} , and the Raman spectra was obtained using a LabRAM HR800 from HORIBA JOBIN YVON. The

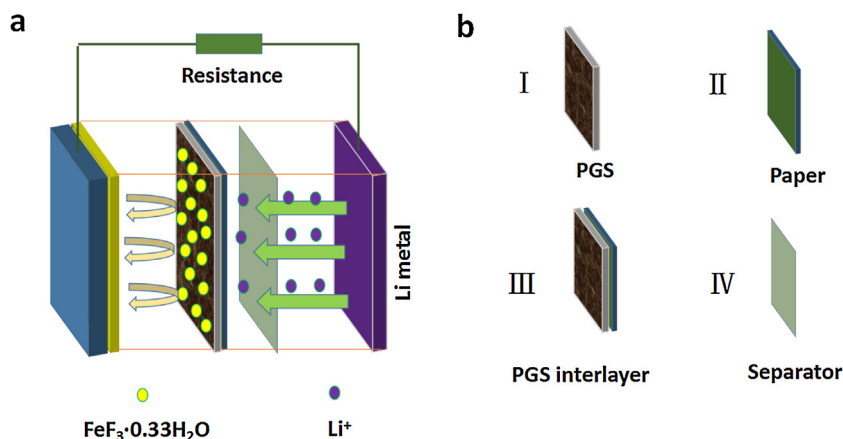


Fig. 1. a) Schematic of a Li- $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ battery with PGS interlayer. b) The Schematic of four compositions in the battery.

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