



Enhancing cycling performance of FeF₃ cathode by introducing a lightweight high conductive adsorbable interlayer



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ABSTRACT

Iron fluorides, as a kind of high specific capacity conversion-type cathode materials for lithium rechargeable batteries, are attracting an increasing number of researchers. However, their practical applications are hindered by the poor electrical conductivity and the volume effect during cycling. In this work, a lightweight porous hollow carbon nanofiber (PHCNF) interlayer is proposed to coat on the original FeF₃ cathode to solve these problems. This interlayer is synthesized through a facile carbonizing-activating process using polypyrrole (PPy) as raw material, and plays a difunctional role in trapping the escaped FeF₃ particles and improving the electrical conductivity of electrode. By introducing the high conductive coating layer, an extremely high specific capacity of 217 mAh g⁻¹ for 40 cycles in the 2–4.5 V region is achieved, which is close to the theoretical specific capacity of 237 mAh g⁻¹ for FeF₃. Also, a superior power capability is retained delivering a reversible specific capacity of 193 mAh g⁻¹ at 200 mA g⁻¹ and 101 mAh g⁻¹ even at 1000 mA g⁻¹.

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1. Introduction

Recently, with the vigorous development of portable electronic devices, lithium rechargeable batteries are now considered as one of the dominant power sources for a variety of electric storage applications due to their high storage capacity, and long cycle life [1–3]. However, current state-of-the-art Li-ion batteries could not satisfy the fast-growing demand for higher specific capacity, power density and safety. To further improve the performance of lithium ion batteries, the research for new type electrode material, especially cathode materials, for Li-ion batteries has been highlighted. The theoretical capacity of traditional cathode materials (such as LiFePO₄, LiCoO₂) is often low (140–170 mAh g⁻¹), because of the intercalation reactions based on single or less electron reaction [4,5]. Accordingly, an effective strategy for high capacity electrodes is to utilize conversion reaction with multi-electron transfer [6–15]. during the conversion reactions, phase transitions occur with the general equation as follows: MX_m + nLi ↔ M + nLiX_{m/n}, where M is transition metal, X is anion.

Among kinds of the conversion-type compounds, metal

fluorides such as NiF₂ with an average discharge charge voltage of 2.96 V and a theoretical specific capacity of 554 mAh g⁻¹ [16], CoF₂ (2.85 V, 553 mAh g⁻¹) [17], CuF₂ (3.55 V, 528 mAh g⁻¹) [18,19], FeF₂ (2.66 V, 571 mAh g⁻¹) [20,21], FeF₃ (2.74 V, 712 mAh g⁻¹) [22,23], etc have been investigated as cathode materials for Li-ion batteries, owing to their high operating voltages and high theoretical specific capacities. A representative example is iron trifluoride (FeF₃), the electrochemical reaction mechanism of which was proposed by Badway [24–26], which can be described as a two-step reaction. With the initial insertion of Li⁺, the intercalated “LiFeF₃” is formed. A first voltage plateau is around 3.4 V, and then the second plateau of around 2.1 V appears with the conversion reaction producing Fe and LiF. These two step reactions involve three-electron transfer, so it is generally acknowledged that FeF₃ has a high theoretical specific capacity of 237 mAh g⁻¹ (one-electron transfer) testing between 2.0 and 4.5 V, this voltage range is similar to some other high capacity conversion-type cathode materials, such as vanadium oxides [27,28]. Furthermore, a larger theoretical specific capacity of 712 mAh g⁻¹ (three-electron transfer) can be achieved testing between 1.5 V and 4.5 V region [29–32]. Moreover, the peculiarities of low toxicity, low cost and better cyclability than other metal fluorides, make FeF₃ a very promising candidate of the cathode materials for Li-ion batteries.

Nevertheless, several drawbacks, such as high ionicity and poor

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structural stability, prevent FeF_3 from its practical application as a cathode material. The high ionicity of FeF_3 induces a large band gap, thus FeF_3 , like most metal fluorides, invariably exhibits insulating behavior, giving rise to large hysteresis voltage, poor cycling and rate capability. What is worse, the pulverization of electrodes, resulting from the large volume effect accompany with the structural changes during battery operation, severely degrades the cyclability of the conversion-type FeF_3 cathode [20]. To address the above-mentioned issues, various measures were taken, which could be mainly summed up in three aspects: i) Rational morphologies designing and nanocrystallization of FeF_3 . Rational designed morphologies could alleviate the volume effect and shorten the ion transport path, while nanoscaled crystallite dimension could significantly improve the reaction activity of the FeF_3 particles. For example, Ma et al. prepared a three-dimensionally ordered macroporous FeF_3 hybrid structure which delivered a reversible capacity of 190 mAh g^{-1} for 30 cycles at 20 mA g^{-1} [22]. ii) Fabrication of FeF_3 based composite with conductive carbonaceous materials [23,33]. The building of the carbonaceous conductive framework could effectively improve the cyclability and rate performance of the composite materials. Kim et al. fabricated FeF_3 nanoflowers on CNT branches, sustained a reversible capacity of nearly 200 mA g^{-1} for 30 cycles at 20 mA g^{-1} [23]; Liu et al. synthesized uniform iron fluoride nanocrystals on reduced graphene oxide sheets, a capacity of 205 mA g^{-1} for 30 cycles at 45 mA g^{-1} was achieved [33]. iii) Element doping. Smaller band gap can improve the electronic conductivity of FeF_3 itself and alleviate the sluggish kinetics of FeF_3 , in addition, doping element can effect microcrystal growth. For example, Bai et al. prepared $\text{Fe}_{(1-x)}\text{Ti}_x\text{F}_3$ by a hydrothermal method, which retained the specific capacity of 174 mAh g^{-1} at 23.7 mA g^{-1} [34]. Overall, a majority of research focus on the fabrication of FeF_3/C composite to modify the cyclability and rate performance of FeF_3 , and some good results are achieved. But the current resulting reversible capacities are not satisfactorily high, and the cycle performance still need to be improved, which may be partially responsible for the pulverization phenomenon of FeF_3 based composite cathodes, since it still exists in the case of low carbon content.

Considering that the electrode pulverization is difficult to avoid for conversion-type cathode materials. A macroscopic electrode structure was designed by introducing an interlayer inserted between electrode and separator by our group [35], and an excellent performance was achieved which retained an ultrahigh capacity of 600 mAh g^{-1} at 100 mA g^{-1} for 60 cycles. Unfortunately, the proportion of interlayer in electrode remains to be further reduced. In this work, a lightweight conductive interlayer between active material and separator is designed to apply to conversion-type cathode materials, simply by coating the surface of FeF_3 cathode with a porous hollow carbon nanofiber (PHCNF) film directly. The coating film is thick in order to ensure a high proportion of active material, which accounted for only 27.9 wt% of the whole cathode (cathode layer and interlayer). A schematic illustration of the designed cell configuration and the preparation process of PHCNF are shown in Scheme 1. The PHCNF can be synthesized through a facile carbonizing-activating process using PPy as raw material. The as-synthesized PHCNF possesses a three dimensional cross-linked network structure with a large specific surface area, which comes from the porous hollow structure of every carbon fiber. The hollow structure can reduce the weight of the interlayer, and the highly porous structure can provide abundant accommodate space for the escaped FeF_3 nanoparticles also benefit the electrolyte permeation. The cross-linked conductive carbon network plays a key role in stabilizing the electrode structure and reducing the internal resistance of the battery simultaneously. Thus the “double-layer” electrode configuration provides an effective way to resolve the

problems of volume effect and electrode pulverization, from which most conversion-type electrodes are suffering [36].

The application of the carbon nanofiber interlayer enables the pure FeF_3 cathode to retain an extremely high reversible specific capacity of 217 mAh g^{-1} after 40 cycles at 20 mA g^{-1} , which is close to the theoretical specific capacity of 237 mAh g^{-1} of FeF_3 . The specific energy is also retained at more than 612 Wh kg^{-1} under these conditions. To the best of our knowledge, this is the highest specific capacity and energy among the ever published results under the same test conditions. Interestingly, the composite cathode also deliver an excellent rate performance, reversible capacities of 193 mAh g^{-1} , 174 mAh g^{-1} and 101 mAh g^{-1} are achieved at 200 mA g^{-1} , 400 mA g^{-1} and 1000 mA g^{-1} , respectively. It should be noted that the outstanding performance of the novel design of electrode configuration may well prove the possibility of conversion-type compounds being used as commercial electrode materials for Li rechargeable batteries.

2. Experimental

2.1. Synthesis of iron fluoride (FeF_3)

FeF_3 powders were synthesized by a facile liquid-phase method. Firstly, 70 mL FeCl_3 (0.02 M) ethanol solution was prepared in Teflon-lined autoclave, then, 30 mL HF solution (40%) was added into FeCl_3 ethanol solution dropwise, after stirring, the bright yellow solution gradually became colorless. After another stirring for 0.5 h , the Teflon-lined autoclave was sealed and heated in an oven at $60 \text{ }^\circ\text{C}$ for 10 h . The generated pink precipitate was collected and washed with absolute ethanol for several times, following by drying at $80 \text{ }^\circ\text{C}$ for 8 h to get $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ powders as precursor. After another drying at $120 \text{ }^\circ\text{C}$ for 48 h , the FeF_3 light green powders were obtained.

2.2. Synthesis of the PHCNF

The porous hollow carbon nanofiber was prepared from polypyrrole nanofiber. The polypyrrole nanofiber was synthesized by our previous work [37,38]. Briefly, 7.3 g CTAB and $13.7 \text{ g ammonium persulfate}$ was dissolved in 120 mL HCl solution (1 M), respectively. After stirring in ice bath for 0.5 h , a white reactive template was achieved. Then, $8.3 \text{ mL pyrrole monomer}$ was added slowly, the black precipitate was obtained after 24 h stirring at $0\text{--}5 \text{ }^\circ\text{C}$. After collecting and washing for several times with deionized water and absolute ethanol, the black precipitate was during at $80 \text{ }^\circ\text{C}$ in an oven for 12 h . Then, the as-synthesized polypyrrole nanofiber was heated at $700 \text{ }^\circ\text{C}$ for 2 h under a N_2 atmosphere for carbonization. The as-obtained carbon nanofiber and KOH were mixed with a mass ratio of $3:1$ in ethanol and deionized water mixed solution. After drying, the mixture was heated at $700 \text{ }^\circ\text{C}$ for 1 h in N_2 atmosphere for activation, and then the product was washed to ensure that the chloride ions was removed completely. Finally, the porous hollow carbon nanofiber (PHCNF) doped with nitrogen were obtained after drying in an oven overnight at $80 \text{ }^\circ\text{C}$.

2.3. Materials characterization

The phases of the synthesized materials were characterized by transmission electron microscopy (TEM, JEM-2100F, Japan), scanning electron microscope (SEM, Nova NanoSEM230, USA), and X-ray diffraction (XRD, Rigaku-TTRIII, Japan). Elemental analysis was made by an energy dispersive spectrometer (EDS). The pore diameter distribution, total pore volume and specific surface area were identified through a Surface Area and Porosity Analyzer (ASAP 2020HD88, USA). Digital photos were taken with a digital camera

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