



Ag nanoparticles promoted LiFePO₄F nanospheres cathode with superior cycling stability for lithium-ion batteries

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ABSTRACT

Tavorite-like structure LiFePO₄F has been recently studied as potential alternative cathode materials for lithium-ion batteries due to its outstanding structural stability, abundant resources and remarkable safety. However, its poor electronic conductivity and lithium-ion diffusion coefficient leads to the unsatisfactory cycling stability and rate capabilities of LiFePO₄F. Herein, Ag decorated LiFePO₄F nanospheres have been synthesized for the first time via a precipitation method with *in-situ* reduction of Ag⁺, simultaneously improving electronic conductivity and lithium-ion diffusion coefficient. The Ag nanoparticles with size of ~10 nm are *in-situ* grown on the surface of LiFePO₄F nanospheres with impressive electrochemical performance. It delivers a high discharge capacity of 148.7 mAh g⁻¹ (very close to the theoretical capacity of 152 mAh g⁻¹) at 0.1 C. It is worth mentioning that the Ag-decorated LiFePO₄F nanospheres reveal superior cycling stability. The initial discharge capacities of Ag-decorated LiFePO₄F reaches up to 120.3 mAh·g⁻¹ at 0.5 C, and the capacity retention is as high as 96.1% after 300 cycles, which is remarkable higher than that of pure LiFePO₄F nanospheres with initial discharge capacity of 110.2 mAh·g⁻¹ and capacity retention of 83.1% after 300 cycles. Furthermore, the Ag-decorated LiFePO₄F displays the average discharge potential loss of only 0.7% which is lower than pure LiFePO₄F of 4.7% after 300 cycles, and the corresponding specific energy retention ratio of 95.5% which is higher than that of 80.1%.

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1. Introduction

In recent years, lithium-ion batteries have been intensively utilized in portable electronics and large-scale smart grids [1,2]. In the compositions of lithium-ion batteries, cathode materials play the key roles in electrochemical performance of the batteries. Among the developed cathode candidates, the tavorite-like structure LiMPO₄F (M = V, Mn, Fe, Co, Ni ...) cathode materials have been considered as a promising alternative cathode material for lithium-ion batteries due to its outstanding safety and low cost [3]. This kind of cathode materials is comprised of 1D chains of corner-sharing metal octahedral (MF₂O₄) inter-connected by phosphate

tetrahedral (PO₄), while the intersecting channels that house the lithium-ion afford open pathways for 3D ion transport [3,4]. For comparison, olivine structure LiMPO₄ (M = Fe, Mn, Co, Ni) cathode materials display limitation of 1D lithium-ion diffusion pathway [5–8]. Consequently, the ionic conductivity of LiFePO₄F (~1 × 10⁻⁷ s cm⁻¹ at 300 K) is higher than that of LiFePO₄ (~1 × 10⁻⁹ s cm⁻¹ at 300 K) [5,6,8].

LiFePO₄F was firstly reported by Barker's group without electrochemical performance, the calculated theoretical capacity is 152 mAh g⁻¹ [7]. Subsequently, LiFePO₄F has been explored as cathode materials for lithium ion batteries due to its potential structure stability. LiFePO₄F is isostructural with the natural mineral tavorite LiFePO₄·OH, which belongs to a triclinic structure (space group P-1) [4,5,8]. However, it presents a poor electronic conductivity which is ascribed to specific 1D chains for electron transport [9], leading to unsatisfactory electrochemical performance [4,5,10,11]. Up to now, a great deal of efforts has been

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devoted to improve the electronic conductivity of LiFePO_4F .

Generally, an effective strategy is coating with carbon derived from organic carbon source. Meanwhile the coated carbon is beneficial to restrict the agglomeration of nanoparticles during the sintering process [10]. But the Fe^{3+} in LiFePO_4F is easily turned into Fe^{2+} in the carbonthermic reduction process resulting in the existence of impurity. Therefore, LiFePO_4F usually was ball-milled with inorganic carbon such as super carbon and acetylene black in the past [5,8,11–13]. However, as fragil nanostructures such as nanosheets, nanofibers and hierarchical structure are susceptible to damage during the physical mixture process. Moreover, the carbon can not be uniform coated on the surface of active nanoparticles which limits the enhancement of the electrochemical performance.

Another approach is decorated using high electronic conductivity of metal such as Ag and Cu etc. under a moderate synthetic condition via an *in-situ* grown method [14–17]. Especially, as Ag possesses outstanding electronic conductivity [18], it has been exploited in various of electrode materials for lithium ion batteries with improved electrochemical performance, for instance LiV_3O_8 [19], LiCoO_2 [20], $\text{BaLi}_2\text{Ti}_6\text{O}_{14}$ [21], LiMn_2O_4 [22,23], LiFePO_4 [24,25], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [26], $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [27], CuCr_2O_4 [28] and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [29]. However, to our best knowledge, there are rarely reported about improve the electrochemical performance of LiFePO_4F via Ag decoration.

Herein, Ag-decorated LiFePO_4F nanospheres as a novel cathode material for lithium ion batteries were prepared via a simple precipitation method. Ag nanoparticles were *in-situ* grown on the surface of LiFePO_4F nanospheres to overcome its poor electron conductivity. The as-synthesized material reveals greatly improved electrochemical performance over those of pure LiFePO_4F nanospheres benefiting from not only high electron conductivity but also enhanced lithium ion diffusion coefficient. We believe that the high conductivity metal such as Ag modification is a promising strategy to effectively promote electrochemical performance of LiFePO_4F for next-generation lithium-ion batteries.

2. Experimental

2.1. Materials synthesis

Synthesis of FePO_4 nanospheres: The FePO_4 nanospheres were prepared via a chemically induced precipitation method. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.02 mol) and $\text{NH}_4\text{H}_2\text{PO}_4$ (0.02 mol) were dissolved in deionized water (500 mL), respectively. The $\text{NH}_4\text{H}_2\text{PO}_4$ solution was added slowly into the $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ solution to form a uniform sol using peristaltic pump under vigorous stirring at 20°C . Then 5 mL H_2O_2 solution (30 wt%) was added dropwise into the above mixed solution. A light yellow amorphous $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$ precipitation was formed until stirring for 2 h. After repeatedly washing by deionized water, centrifugation and drying, the obtained $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$ precursor was dehydrate at 750°C for 8 h under air to form FePO_4 nanospheres.

Synthesis of LiFePO_4F nanospheres: The LiFePO_4F nanospheres were prepared via a solid-state route method. The obtained FePO_4 nanospheres were mixed with LiF (mole ratio 1:1) using a mechanical grinder for 2 h. After that, the mixture was placed in tube oven heating in Ar atmosphere at 575°C for 60 min. Followed by cooling and grinding, the LiFePO_4F nanospheres were synthesized.

Synthesis of Ag-decorated LiFePO_4F nanospheres: The as-synthesized LiFePO_4F nanospheres was dispersed in distilled water and sonicated for 30 min to get a uniform suspension solution. Then, the uniform suspension solution was transferred to the solution of silver nitrate. Next, glucose solution was added to the above mixture solution, followed by dramatically stirring for 2 h at room temperature. After that, the precipitates were separated by

centrifugation, washed with deionized water and ethanol for several times. Finally, the obtained Ag-decorated LiFePO_4F nanospheres were dried in vacuum at 100°C for 12 h. The weight ratio of Ag and LiFePO_4F powder was controlled to be 1:99.

2.2. Physical characterization

Phase identification was performed with an X-ray diffractometer (XRD, D/Max-3C, Rigaku) and a graphite monochromator at 36 kV, 20 mA using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology and microstructure of the synthesized samples were analyzed by scanning electron microscope (SEM, JSM-6610LV, JEOL) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The energy dispersive analysis of X-ray spectrum (EDX) was used to determine the content of Ag.

2.3. Electrochemical measurements

For electrochemistry studies, the synthesized LiFePO_4F was ball-milled with acetylene black for 2 h, while the Ag decorated LiFePO_4F sample was ground with acetylene black using mortar. The cathode electrode loaded on the Al foil was composed of a mixture of active material, carbon black and polyvinylidene fluoride (PVDF) with the weight ratio 7:2:1, using N-methyl-pyrrolidone (NMP) as a solvent. And then, the loading mass of the active material is typically $1.5\text{--}2.0 \text{ mg cm}^{-2}$. The electrolyte was 1 M LiPF_6 solution in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 by volume, Merck). The Celgard 2400 was used as a separator and lithium was as the counter and reference electrode. The coin-type cells (CR2025) were assembled in an argon-filled glove box (Super 1220/750/900, Mikrouna) with O_2 and H_2O lower than 5 ppm. The cells were aged for 12 h before tests.

The galvanostatic charge-discharge measurements were performed at different rate in a voltage range of 1.5–4.0 V using a constant-current-constant-voltage method on the battery test system (CT-3008-5V, Neware). The electrochemical impedance spectroscopy (EIS) measurement was conducted by using an electrochemical workstation (VersaSTAT3, Princeton), with an excitation potential of 5 mV and the frequency range of 0.01–100000 Hz. All the tests were performed at room temperature.

3. Results and discussion

3.1. Structural and morphology analysis

The overall fabrication procedure of Ag-decorated LiFePO_4F

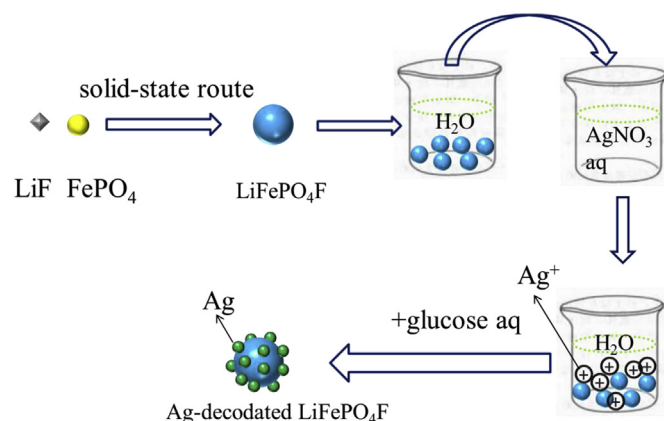


Fig. 1. Schematic fabrication procedure of the Ag-decorated LiFePO_4F nanospheres.

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