



# Solid-state attachments of Ag nanoparticles onto the surfaces of LiFePO<sub>4</sub> cathode materials for Li storage with enhanced capabilities

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## ABSTRACT

Ag@LiFePO<sub>4</sub> cathode materials have been prepared successfully by performing solid-state reactions between AgNO<sub>3</sub> and the ascorbic acid in the presence of LiFePO<sub>4</sub> powders at ambient temperature. Metallic Ag nanoparticles of *ca.* 10 nm in diameter can be produced with the environmental benign approach and efficiently attached onto the surfaces of commercial LiFePO<sub>4</sub> cathode materials. The as-prepared composites show highly enhanced electrochemical performances in storing Li with *ca.* 22% increase in their discharge specific capacity from 128 to 156 mAhg<sup>-1</sup> at C/10 rate, after loading Ag additive of 2 wt%. The coulombic efficiency of the composites can retain 97%, after cycling for 80 times. They can also remain up to 94 mAhg<sup>-1</sup> of their discharge specific capacity at high rate of 5 C, which is almost twice higher than that of LiFePO<sub>4</sub> cathode materials.

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## 1. Introduction

LiFePO<sub>4</sub> is one of the most promising cathode materials for its excellent Li storing features, such as good reversibility, high thermal and chemical stability, low cost and nontoxicity [1,2]. The pristine LiFePO<sub>4</sub> cathode materials, however, exhibit poor electrochemical performances, because of their low intrinsic electronic conductivity and low Li<sup>+</sup> diffusion coefficient [3]. These unfortunately lead to their initial capacity loss and poor rate capability in storing Li. In order to improve the electrochemical properties of LiFePO<sub>4</sub> materials, extensive efforts have been made to overcome their limitations related to electronic and ionic transportations through doping with foreign materials, decreasing the particle size or coating electronically conductive agents [4–7]. In these approaches, adding conductive metallic additives including Ag [1,8], Au [9,10], Pd [11], and Cu [12] is one of effective ways to improve their electronic conductivity and therefore their electrochemical properties effectively. Croce and co-workers found that the kinetics of electrochemical reactions of LiFePO<sub>4</sub> materials can be effectively improved by adding Cu and Ag additives with high conductivity

[13]. The specific capacity of LiFePO<sub>4</sub> cathode materials can be increased from 110 mAhg<sup>-1</sup> to 140 mAhg<sup>-1</sup> at a rate of C/5, after adding metallic Cu or Ag particles of 0.1 μm in diameter. However, it was found that Cu can be easily oxidized with partial decomposition of the electrolytes and deposited onto lithium surface in the discharged process, which generates barrier layers hindering the release of Li ion from the electrodes and therefore lowers the capacity and cycling life of the cells constructed [12]. In contrast, Ag element is an excellent conductivity additive for its high conductivity of 6.3 × 10<sup>7</sup> S/m at room temperature, and has been therefore investigated extensively to improve the electrochemical performances of cathode materials, such as LiCoO<sub>2</sub> [14], LiMn<sub>2</sub>O<sub>4</sub> [15], especially LiFePO<sub>4</sub> [16]. Moreover, a little of electronic conductive Ag coating onto LiFePO<sub>4</sub> cathode materials can achieve better electrochemical performance but not sacrifice their energy density [16].

To date, some methodologies mainly based on wet chemical synthesis have been readily developed to prepare LiFePO<sub>4</sub>/Ag composites. Liu et al. prepared LiFePO<sub>4</sub>/C-Ag (2.1 wt%) powders by the reduction of AgClO<sub>4</sub> in deionized water to produce Ag nanoparticles and loading them onto the surfaces of LiFePO<sub>4</sub>/C, and LiFePO<sub>4</sub>/C-Ag electrode (136.6 mAhg<sup>-1</sup>) is 7.6% higher than that of uncoated LiFePO<sub>4</sub>/C electrode (126.9 mAhg<sup>-1</sup>) at 0.2 C [1]. Park et al. also fabricated LiFePO<sub>4</sub> coated with Ag of 1 wt% by the reduction of AgNO<sub>3</sub> in solution, and the electrochemical performances of

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LiFePO<sub>4</sub> can be improved from about 110 mAhg<sup>-1</sup> to 120 mAhg<sup>-1</sup> at 1C [17]. Wang et al. found that after modified with Ag using silver mirror reaction, the discharge capacities of LiFePO<sub>4</sub>/C are improved from 130.8 mAhg<sup>-1</sup> of LiFePO<sub>4</sub>/C to 149.8 mAhg<sup>-1</sup> of LiFePO<sub>4</sub>/C+Ag at 0.4 C [18]. In these methods, Ag additives are generally synthesized by performing the reduction of Ag<sup>+</sup> ions in aqueous solution, and there is no report in literature, to the best of our knowledge, concerned with LiFePO<sub>4</sub> cathode materials modified with Ag nanoparticles using solid-state reactions at ambient temperature so far.

Our group has developed a novel approach based on solid-state reactions at ambient temperature to synthesize noble metallic nanoparticles with well controlled structures [19,20]. Herein, we would like to report Ag@LiFePO<sub>4</sub> cathode materials produced by first mixing AgNO<sub>3</sub> with LiFePO<sub>4</sub> and then performing solid-state reactions between AgNO<sub>3</sub> and ascorbic acid directly at ambient temperature. It was found that Ag nanoparticles of *ca.* 10 nm can be closely attached onto the surfaces of LiFePO<sub>4</sub> particles with this environmental benign approach. The amount of Ag additives, which can be tuned conveniently by performing the solid-state reactions directly, dramatically affect the electrochemical performances of as-prepared materials. The coin cells assembled with the cathode materials show enhanced discharge specific capacities, excellent rate performances and high cycle stability.

## 2. Experimental

### 2.1. Materials

All of the chemicals of analytical grade were purchased from Shanghai Chemical Industrial Co. Ltd., Shanghai, China, and used without further purification. Ultrapure water (>18 MΩcm) was used for all solution preparation. The LiFePO<sub>4</sub> cathode materials with about 2 wt% carbon were from Deyu Chemical Co. of China.

### 2.2. Synthesis of LiFePO<sub>4</sub>/Ag composites

The Ag nanoparticles attached on the surfaces of LiFePO<sub>4</sub> particles were synthesized by performing solid-state reactions between AgNO<sub>3</sub> and ascorbic acid with an approach developed in our group [19,20]. Firstly, LiFePO<sub>4</sub> and AgNO<sub>3</sub> were ground in an agate mortar for 15 min to form a solid mixture, and the amount of AgNO<sub>3</sub> is 1, 2, 3, 4 and 5 wt% of LiFePO<sub>4</sub> (assigned as Ag@LFP1, Ag@LFP2, Ag@LFP3, Ag@LFP4 and Ag@LFP5), respectively. Secondly, ascorbic acid was added into the mortar with the mixture and ground together for 40 min to form a homogenous mixture. The molar ratio of AgNO<sub>3</sub> to ascorbic acid was 1:3 to have AgNO<sub>3</sub> fully reduced to form metallic Ag. Then the as-prepared solids were washed with a mixed solvent of deionized water and ethanol at volume ratio of 9:1 for 5 times and dried in vacuum at 60 °C for 12 h to obtain Ag@LiFePO<sub>4</sub> composites.

### 2.3. Characterization

Powder X-ray diffraction (XRD) analysis was performed on Bruker AXS D8 Advance diffractometer with Cu Kα radiation in order to identify the crystalline phases of the composites. The morphologies of the samples were observed with a field-emission scanning electron microscope (FESEM, JEOL, JSM-7001F) and a transmission electron microscopy (TEM, JEOL, JEM-2100F), respectively. The compositions of as-prepared materials were determined by energy dispersive spectroscopy (EDS).

## 2.4. Electrochemical measurements

The cathodes to assemble coin cells were fabricated by mixing 80 wt% active materials, 15 wt% acetylene black, and 5 wt% poly vinyl difluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The aluminum foils were adopted as current collectors. The detailed fabrication process of the working electrode was presented in Ref. [21]. The loading mass and capacity loading of the electrodes are important factors to influence the electrochemical performances of the active materials [22], therefore the mass loading is around 2.0 mg/cm<sup>2</sup>, and the capacity loading is from 0.35 to 0.5 mAh/cm<sup>2</sup>. Metallic lithium foils, polypropylene microporous films (Celgard 2300) and 1M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v) were used as counter electrodes, separators and electrolytes, respectively. Before being assembled, the electrodes with active materials were pressed under 10 MPa for 30s. Then, the composite cathodes were assembled into CR2016 coin-type cells in an Ar filled glove box.

The electrochemical characterizations of pristine LiFePO<sub>4</sub> and Ag@LiFePO<sub>4</sub> composites were carried out using a charge/discharge instrument (Chenhua, CHI660E) and electrochemical workstation (Xinwei, CT3008). The electronic conductivity was measured at room temperature using a 4-Point probes resistivity measurement system (Probes Tech, RTS-9) [23,24]. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 10 mHz with an applied amplitude of 5 mV using an electrochemical workstation (CHI660D, CH Instruments Inc., Shanghai, China) [21]. The parameters of the equivalent circuit are calculated and analyzed by computer simulations using the ZSimpWin software.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of LiFePO<sub>4</sub> and Ag@LiFePO<sub>4</sub> composites with different amount of silver additives. All the diffraction peaks in Fig. 1(a) can be indexed to LiFePO<sub>4</sub> with orthorhombic phase of olivine type structure (JCPDS: 40-1499) without any detectable impurity. After attaching Ag nanoparticles onto the surfaces of LiFePO<sub>4</sub> particles (Fig. 1(b)–(f)), there is no apparent change in the diffraction peaks corresponding to LiFePO<sub>4</sub> indicating the stability of its crystal structure. However, it is worth pointing out that the relative intensity of the diffraction peak

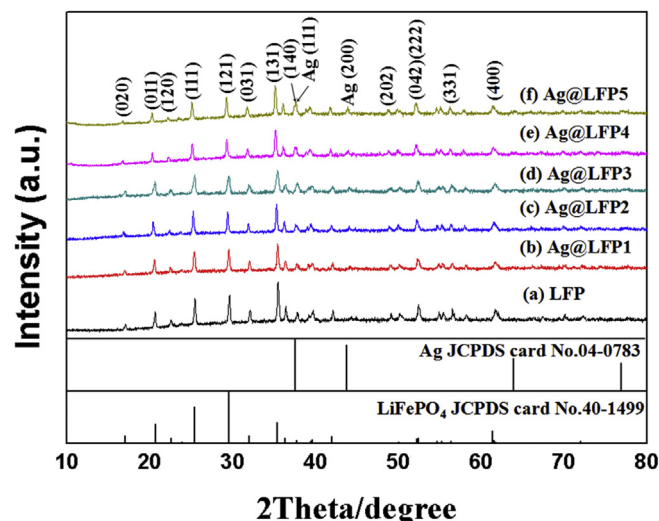


Fig. 1. XRD profiles of (a) pristine LiFePO<sub>4</sub> and (b–f) Ag@LiFePO<sub>4</sub> composites.

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