

Physical and electrochemical characterizations of LiFePO₄-incorporated Ag nanoparticles

Zhaolin Liu · Siok Wei Tay · Liang Hong · Jim Yang Lee

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Abstract Olivine-type LiFePO₄ composite materials for cathode material of the lithium-ion batteries were synthesized by using a sol-gel method and were coated by a chemical deposition of silver particles. As-obtained LiFePO₄/C-Ag (2.1 wt.%) composites were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), conductivity measurements, cyclic voltammetry, as well as galvanostatic measurements. The results revealed that the discharge capacity of the LiFePO₄/C-Ag electrode is 136.6 mAh/g, which is 7.6% higher than that of uncoated LiFePO₄/C electrode (126.9 mAh/g). The LiFePO₄/C coated by silver nanoparticles enhances the electrode conductivity and specific capacity at high discharge rates. The improved capacity at high discharge rates may be attributed to increased electrode conductivity and the synergistic effect on electron and Li⁺ transport after silver incorporation.

Keywords LiFePO₄ · Lithium-ion batteries · Rate performance · Ag · Coating

Introduction

Olivine-type LiFeO₄ was first studied by Padhi et al. [1] and has attracted extensive interest as a potential cathode

material for lithium-ion batteries because of its numerous appealing features, such as high theoretical specific capacity (170 mAh/g), good reversibility of cathode reactions, high thermal and chemical stability, low material cost, high safety and environmental benignity. In spite of these attractive features, the disadvantage of LiFePO₄ is its sluggish mass and charge transport, as confirmed by recent work on single crystals [2]. Consequently, its usability is limited because of the poor high-rate capability [3, 4].

Tremendous efforts have been made to overcome the electronic and ionic transport limitations by doping with foreign atoms, decreasing the particle size or coating electronically conductive agents (carbon, Au, RuO₂, conducting polymer, etc.) [5–11]. So far only the applied carbon-coating technique allows for high specific capacities. However, the rate performance enhancement of such electrode materials is still limited, as availability of the electronically conducting phase becomes insufficient at very high rates. Some metal oxides (Al₂O₃, ZrO₂, MgO and TiO₂) coatings have often been used to improve the performance of cathode materials [12–17]. RuO₂ has been used to coat electroactive materials by various researchers and also offers a high electronic conductivity and quick Li permeation [10, 18].

In this work, Ag nanoparticles were coated onto the surface of LiFePO₄/C via reduction of Ag⁺ solution, and the effects of the Ag coating on the electrode performance of the LiFePO₄-based cells were studied. The physicochemical properties and electrochemical behaviours of the LiFePO₄/C coated by Ag nanoparticles were also characterized.

Experimental

Carbon-containing (ca. 3 wt.%) LiFePO₄ was prepared via a poly(ethylene glycol) (PEG-400) assisted sol-gel route. Lithium acetate dehydrate, ferrous sulphate, phosphoric acid

Z. Liu (✉) · S. W. Tay · L. Hong
Institute of Materials Research and Engineering,
Agency for Science, Technology and Research (A*STAR),
3 Research Link,
Singapore 117602, Singapore
e-mail: zl-liu@imre.a-star.edu.sg

J. Y. Lee
Department of Chemical and Biomolecular Engineering,
National University of Singapore,
10 Kent Ridge Crescent,
Singapore 119260, Singapore

and citric acid with molar ratio 1:1:1 were dissolved in deionized water, and PEG-400 was added to the solution (the molar ration of PEG to LiFePO_4 was 0.5:1). The pH was maintained 9–9.5 by ammonia water, and the solutions were evaporated in the water bath at 80°C until gel appeared. After the gel was dried in an oven at 100°C for 12 h, the resulting powder was pressed into pellets. The pellets was initially heated at 350°C for 4 h and subsequently sintered at 700°C for 10 h in an argon atmosphere to get the powder of LiFePO_4/C .

For the reduction of Ag^+ to Ag and depositing them on the LiFePO_4/C powders, 0.2 g of LiFePO_4/C powder was suspended in 40 ml de-ionized water containing sodium citrate and sodium borohydride with vigorous stirring. A certain amount of silver perchlorate (7.7 mg of AgClO_4) were dissolved in 10 ml de-ionized water, and dropwise into above dispersion which was ultrasonically dispersed and ice-bathed for 1 h. Finally, the LiFePO_4/C -Ag powders were separated from the solution by centrifugation and dried at 60°C under vacuum.

The samples were examined by TEM on a JEOL JEM 2010. For microscopic examinations the samples were first ultrasonicated in acetone for 1 h and then deposited on 3 mm Cu grids covered with a continuous carbon film. The amount of carbon, Fe, P and Ag was determined by Oxford INCA Energy Dispersive X-ray (EDX) Spectrometer. The crystal structures of samples were characterized by X-ray diffraction (XRD) on a Bruker GADDS diffractometer using Cu $K\alpha$ radiation and a graphite monochromator. The specific surface areas were determined according to the Brunauer–Emmett–Teller (BET) method on NOVA 1000 Series, BET surface analyzer.

For preparing working electrodes, the samples of LiFePO_4/C or LiFePO_4/C -Ag were mixed with 10 wt.% of carbon black and 10 wt.% of poly(vinylidene difluoride) in 1-methyl-2-pyrrolidinone. The slurry was used to coat 20- μm thick aluminium discs of 13 mm diameter to a mass loading of $3 \text{ mg}/\text{cm}^2$ after drying (at 120°C) and compaction (at $2.0 \times 10^6 \text{ Pa}$). Each coated electrode was assembled in a 2,016 coin cell using a lithium counter electrode, a microporous polypropylene separator and an electrolyte of 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Cell assembly was carried out in an argon-filled glove box with less than 1 ppm each of oxygen and moisture. The cells were discharged and charged at 25°C on a Maccor 4000 battery test system. Cyclic voltammetry was conducted with an AUTOLAB potentiostat/galvanostat. The LiFePO_4/C or LiFePO_4/C -Ag pellets used for the electrical conductivity measurements were prepared by pressing the active powders with a pressure of 8 MPa, and then Ag paste was coated on both sides of the pellets of about 12 mm in diameter and 2 mm in thickness. The electrical conductivity was measured through linear polarization also under the AUTOLAB potentiostat/galvanostat.

Results and discussion

Figure 1a shows typical TEM image of the silver-coated LiFePO_4/C powder, showing a high dispersion of silver particles on the LiFePO_4/C surface. The particle size distributions of the silver were obtained by directly measuring the size of 100 randomly chosen particles in

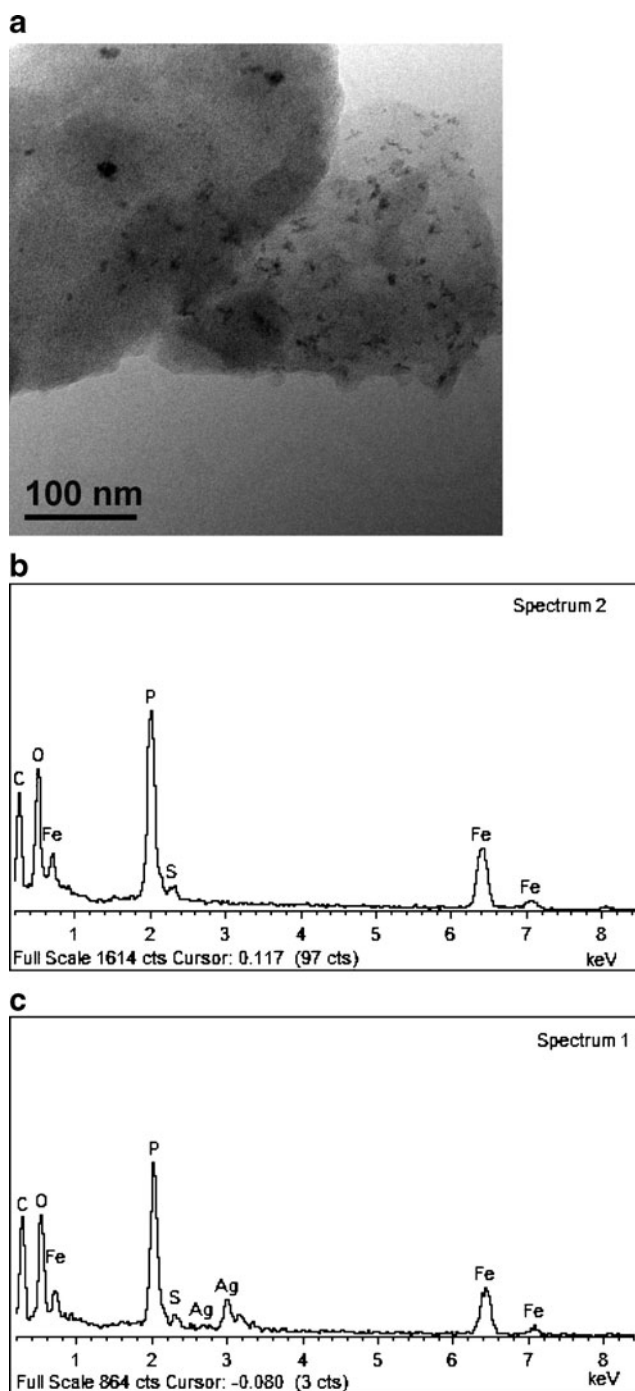


Fig. 1 a TEM image of the silver-coated LiFePO_4/C powder, b EDX spectrum of LiFePO_4/C powder and c EDX spectrum of LiFePO_4/C -Ag powder

the magnified TEM images. The average diameter of 6.1 nm was accompanied by narrow particle size distributions (2–12 nm). EDX spectra of the LiFePO_4/C and $\text{LiFePO}_4/\text{C-Ag}$ are shown in Fig. 1b, c. The Fe/P molar ratio is 1:1 in the LiFePO_4/C and there is 2.1 wt.% of Ag in the $\text{LiFePO}_4/\text{C-Ag}$, which corresponded well with the amounts of Fe, P and Ag used in the starting mixture. Fig. 2 shows a typical XRD pattern of carbon-containing LiFePO_4 before and after coating with nano-sized Ag. LiFePO_4 with an olivine structure was obtained by sol-gel method. The only difference observed for two samples is the change of the relative intensity of the reflection (410) and (401). A higher reflection (410) was seen from the XRD pattern of $\text{LiFePO}_4/\text{C-Ag}$, which can be attributed to the overlap of the reflection (111) of silver phase and the reflection (410) of olivine LiFePO_4 . The absence of any other signals for both LiFePO_4/C and $\text{LiFePO}_4/\text{C-Ag}$ indicates there are no unwanted impurity phases, such as Li_3PO_4 and Fe^{3+} related compounds. No evidence of diffraction peaks for crystalline carbon appeared in the diffraction patterns, which indicates that the carbon generated from poly(ethylene glycol) is amorphous carbon and its presence does not influence the structure of LiFePO_4 .

Figure 3 shows the typical charge/discharge profiles of carbon-containing LiFePO_4 before and after coating with nano-sized Ag at 5 C ($2 \text{ mA}/\text{cm}^2$). The discharge capacity of the $\text{LiFePO}_4/\text{C-Ag}$ electrode is 136.6 mAh/g, which is 7.6% higher than that of uncoated LiFePO_4/C electrode (126.9 mAh/g). After Ag coating, the polarization between the charge and discharge plateaux is reduced to 111 mV from 148 mV for the sample without Ag coating, indicating that the kinetics of the LiFePO_4 are improved after Ag coating. To examine the effectiveness of Ag coating in improving the rate capability of the electrode with respect to Li insertion/extraction, the comparison of the rate performance of carbon-containing LiFePO_4 before and after Ag coating were shown in Fig. 4. After Ag coating, specific

Fig. 2 X-ray diffraction profiles of LiFePO_4/C before and after coating with nano-sized Ag

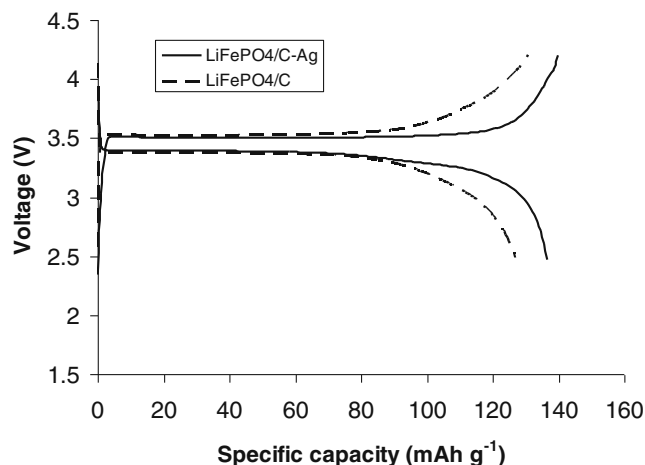
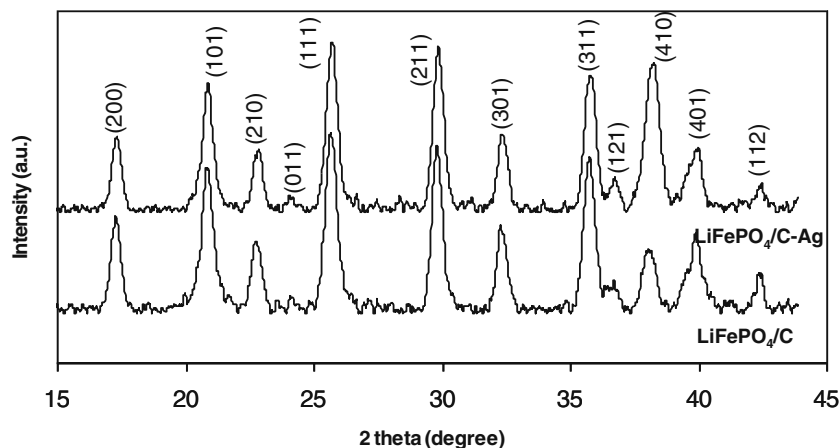


Fig. 3 The typical charge/discharge profiles of LiFePO_4/C before and after coating with nano-sized Ag at a 0.2 C rate ($2 \text{ mA}/\text{cm}^2$)

capacity of LiFePO_4/C in the hybrids increased at all discharge rates compared with the LiFePO_4/C without Ag coating. The relative increase in specific capacity is especially larger at higher rates. For instance, the specific capacity of the $\text{LiFePO}_4/\text{C-Ag}$ hybrid material at 20 C ($8 \text{ mA}/\text{cm}^2$) is as high as 50.8 mAh/g compared with 8.2 mAh/g of LiFePO_4/C without Ag coating. The results indicate that $\text{LiFePO}_4/\text{C-Ag}$ had a much better rate performance than that of LiFePO_4/C due to the lower polarization of $\text{LiFePO}_4/\text{C-Ag}$. We have made cycle testing at 0.2 C ($0.08 \text{ mA}/\text{cm}^2$) and 2 C ($0.8 \text{ mA}/\text{cm}^2$). The cycling performance of the $\text{LiFePO}_4/\text{C-Ag}$ electrode is obviously better than that of the uncoated LiFePO_4/C electrode. The $\text{LiFePO}_4/\text{C-Ag}$ and LiFePO_4/C electrodes have the capacity retention of 91% and 82% at 0.2 C ($0.08 \text{ mA}/\text{cm}^2$) after 100 cycles. The cell was charged at a rate of 2 C ($0.8 \text{ mA}/\text{cm}^2$), and the capacity retention of 96% for the $\text{LiFePO}_4/\text{C-Ag}$ and 90% for the LiFePO_4/C were obtained after 100 cycles. The excellent cycle

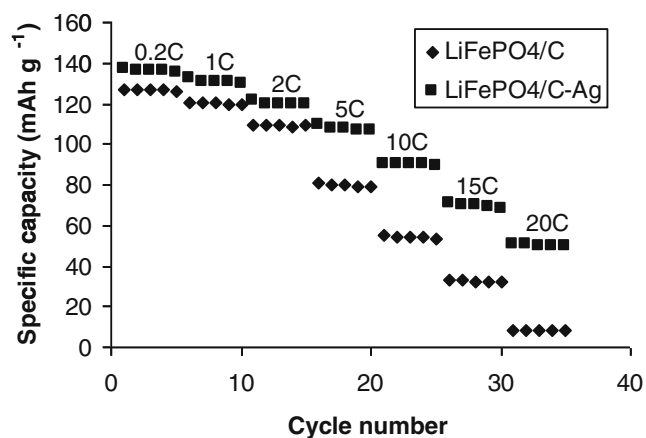


Fig. 4 The rate capabilities of LiFePO₄/C before and after coating with nano-sized Ag. The 0.2 C, 1 C, 2 C, 5 C, 10 C, 15 C and 20 C are 0.08 mA/cm², 0.4 mA/cm², 0.8 mA/cm², 2 mA/cm², 4 mA/cm², 6 mA/cm² and 8 mA/cm², respectively

performance delivered by the LiFePO₄/C-Ag electrode should be attributed to its high electronic conductivity.

To further understand the improved high rate performance, cyclic voltammograms measurements on carbon-containing LiFePO₄ before and after Ag coating were performed. The results of CV experiments on LiFePO₄/C and LiFePO₄/C-Ag are presented in Fig. 5, where anodic and cathodic peaks appear at ~3.6 and 3.3 V for both materials, respectively. The CV profile of LiFePO₄/C-Ag shows sharper shape of the oxidation-reduction peaks than the LiFePO₄/C does. The larger redox current for LiFePO₄/C-Ag results from its higher utilization because of its good electronic conductivity and lithium ion diffusivity, compared with the LiFePO₄/C. Generally, low electrical conductivity and Li ion diffusion in the material bulk are the main factors controlling the high-rate performances of LiFePO₄. Recently, effect of Ag additive on the perfor-

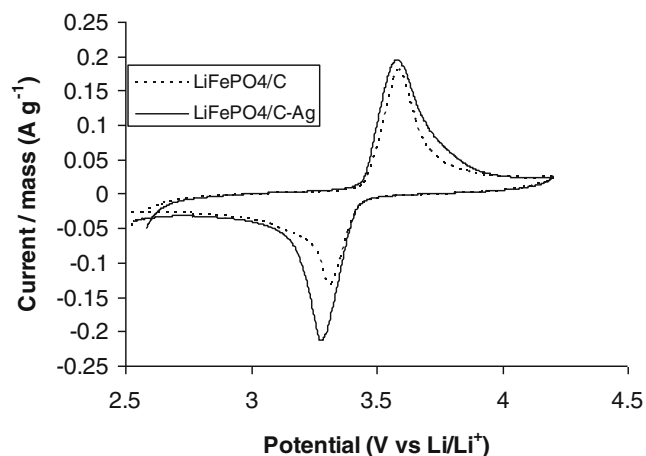


Fig. 5 Cyclic voltammograms of LiFePO₄/C before and after coating with nano-sized Ag at the scan rate of 0.05 mVs⁻¹

mance of LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials was reported [19, 20]. An additional oxidation peak at about 3.8 V was observable in the cyclic voltammogram and initial de-intercalation curve, which was probably attributed to the dissolution of silver. In our cyclic voltammetric measurement, no Ag oxidation/dissolution peak at a potential of about 3.85 V against Li/Li[±] was observed in Fig. 5, but the de-intercalation peak of LiFePO₄/C-Ag shows broader shape between 3.65 and 3.85 than the LiFePO₄/C does. This suggests silver oxidation peak may be overlaid in Li de-intercalation curve. In addition, it may be attributed to a lower silver content (2.1 wt.%) in LiFePO₄/C-Ag compared with those in the literatures 19 (5.7 wt.%) and 20 (6.6 wt.%). Further investigations and experiments will be carried out in order to determine the disposition of the Ag on LiFePO₄/C.

To clarify the origin of the improved rate capacity, cyclic voltammetry and linear polarization were performed to test the Li ion apparent diffusion constants and the electrical conductivity of two materials.

The Li ion apparent diffusion constant can be determined by Eq. 1 [21, 22].

$$i_p/m = 0.4463F(F/RT)^{1/2}C_{Li}^*v^{1/2}A_eD_{app}^{1/2} \quad (1)$$

where m is the mass of electrode, A_e is electrode area per unit mass, and D_{app} is the apparent diffusion constant of Li. C_{Li}^* is the initial concentration of Li in LiFePO₄, which is taken as the total amount of Li in a particle before delithiation. LiFePO₄ has a bulk density of 3.6 g/cm³ with a molar mass of 157.76 g/mol. This corresponds to a Li concentration of 0.0228 mol/cm³. Because LiFePO₄ has a one-dimensional path in the (010) direction, an effective area that corresponds to the (010) plane should be used for the calculation [20]. Therefore, the effective area of the (010) plane is taken as one-third the total BET surface area (A_{BET}).

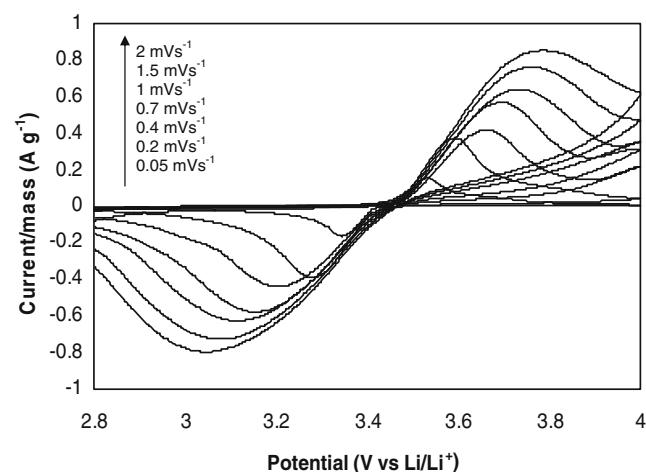


Fig. 6 Cyclic voltammograms of LiFePO₄/C with different scan rates

The CV profiles with different scan rates are presented in Fig. 6 for the LiFePO₄/C-Ag. Peak separation increases with increasing scan rate, and all CV profiles overlap regardless of scan rate at the beginning of charging and discharging. The slope values of a linear dependence between i_p/m and $v^{1/2}$ are 13.9 for the LiFePO₄/C and 34.3 for the LiFePO₄/C-Ag, respectively. The apparent diffusion constants of LiFePO₄/C and LiFePO₄/C-Ag calculated using Eq. 1 with the slope of the i_p/m vs $v^{1/2}$ plot are 1.83×10^{-15} and 1.10×10^{-14} cm²/s in 1 M LiPF₆ EC/DEC=50:50 at 25°C, respectively. The apparent diffusion constant of LiFePO₄/C-Ag is about one order of magnitude higher than that of the LiFePO₄/C. To further understand the improved high rate performance, electrical conductivity measurements on LiFePO₄/C before and after coating with Ag were performed. Electrical conductivity of the LiFePO₄/C with Ag coating was improved to 5.2×10^{-3} S/cm from 3.5×10^{-4} S/cm for the LiFePO₄/C without Ag coating. Therefore, improved high rate performance may be attributed to the increased conductivity of the LiFePO₄/C-Ag and the synergistic effect on electron and Li⁺ transport.

Conclusions

Olivine type LiFePO₄ was synthesized by using a sol-gel method and surface modification of the LiFePO₄ particles was successfully done using silver aqueous solution. Highly dispersed silver on the particles enhances the electrical conductivity and increases specific capacity at high discharge rates. This can be attributed to the increasing of conductivity after silver incorporation facilitates the Li⁺ ion diffusion. Surface treatment of LiFePO₄ powder by silver coating can be a promising method to preserve the capacity against high rates discharging.

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