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Effects of Silver Nanowires on The Electrochemical Performance of $LiFePO_4$

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Abstract

Lithium iron phosphate ($LiFePO_4$) is a promising cathode material for lithium-ion batteries. However, an important drawback of this material is its poor conductivity. In this approach, a simple approach is firstly proposed to enhance the conductivity of $LiFePO_4$ cathodes by dispersing conductive Ag nanowires to these cathodes. $LiFePO_4$/Ag nanowires composite cathodes were characterized by X-ray diffraction (XRD) and field emission scanning electron microscope (FSEM), and their electrochemical performance were evaluated by charge/discharge tests. It is demonstrated that the capacity and rate capability of $LiFePO_4$/Ag nanowires composite cathodes can be improved considerably by the addition of Ag nanowires. Especially, discharge capacities are improved from ~110 mAh g^{-1} of $LiFePO_4$ cathodes to ~150 mAh g^{-1} for $LiFePO_4$/Ag nanowires composite cathodes at 0.2 C. Therefore, $LiFePO_4$/Ag nanowires cathodes can be used as an attractive positive electrode candidate for lithium-ion batteries.

Keywords: Nanostructures, Ag nanowires, $LiFePO_4$, conductivity, electrochemical performance

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1. Introduction

Lithium batteries have attracted extensive attention in recent years because of their wide applications in portable electronic devices such as mobile phones, laptop computers, and digital cameras [1, 2]. It is known that cathode materials ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and $LiFePO_4$) have significant influences on the electrochemical performance of the batteries [3]. Among these cathode materials, $LiCoO_2$ is the most famous positive cathode material for lithium-ion batteries because it has ease of preparation, high energy density, high operational voltage, and good cycleability [4]. However, it is associated with problems such as high cost, toxicity, and safety risks in large scale applications [5]. $LiNiO_2$ exhibits high discharge capacity and low cost in comparison with $LiCoO_2$, but it suffers of difficulty to be synthesized, poor cycling performance and poor thermal stability in its high oxidation state [6]. In addition, environmentally friendly and cost effective $LiMn_2O_4$ also has several drawbacks, e. g., the structural distortion occurs below the room temperature [7]. Compared with the above cathode materials, $LiFePO_4$ is regarded as a promising "green" cathode material for lithium-ion batteries owning to its large theoretical capacity (170 mAh g^{-1}), relatively low costs, environmental neutrality, thermal stability in the fully charged state and high charge/discharge capabilities. In spite of these advantages, a major limitation of this material is its poor electronic conductivity. Therefore, the preparation of $LiFePO_4$ cathode materials with good electronic conductivity has been and continues to be an area of active research.

In the past decade, enormous attempts have been made to improve the conductivity of $LiFePO_4$ cathode materials [8-16]. One of the significant approaches to enhance their conductivity is mixing them with conductive materials like carbon, metal and metal oxide. Investigations demonstrate that carbon materials are usually used to enhance the conductivity of $LiFePO_4$ [5, 17-22]. For example, Bhuvaneswari et al. have reported that $LiFePO_4$/carbon nano fiber (10 wt.%) delivers a higher specific capacity (~140 mAh g^{-1}) than $LiFePO_4$ with carbon black (25 wt.%) added after synthesis (~120 mAh g^{-1}) at a low rate of 0.1 C (note that the C rating refers to the charge or discharge rate of the battery in relation to its capacity.) [5]. Recently, conductive silver aslo has been incorporated to $LiFePO_4$ for improving their conductivity [23, 24]. For instance, Mi et al. have demonstrated that carbon and silver particles (5 wt.%) co-modification can improve the surface electronic conductivity of $LiFePO_4$. The reslut indicates that discharge capacities are improved from 153.4 mAh g^{-1} of $LiFePO_4$/C to 160.5 mAh g^{-1} for $LiFePO_4$/(Ag+C) cathodes prepared by the co-precipitation method at a low rate of 0.5 C [24]. However, there are no reports about the introduction of Ag nanowires into $LiFePO_4$ cathodes for improving their electrochemical performance.

In our previous work, we have sucessfully synthesized Ag nanowires with adjustable diameters by a simple solvothermal method [25]. In this paper, we describe a simple route to improve the electrochemical performance of $LiFePO_4$ cathodes by dispersing as-prepared Ag nanowires to these cathodes. It is found that $LiFePO_4$/Ag nanowires composite cathodes demonstrate an increased reversible capacity and good rate capability. We presume that the improved electrochemical performance of $LiFePO_4$ cathodes may be attributed to the addition of conductive Ag nanowires. The structure, morphology and electrochemical performance of $LiFePO_4$/Ag nanowires composite cathodes will be discussed in the following sections.

2. Experimental section

2.1 Materials

Silver nitrate ($AgNO_3$, 99.9%) was purchased from Hubei Xinyin Noble Metal Co. Ltd. Poly(N-vinylpyrrolidone) (PVP, Molecule Weight≈40000), ethylene glycol (EG) Na_2S, $FeSO_4$•$7H_2O$, H_3PO_4, $LiOH$•H_2O and ascorbic acid and were obtained from Sinopharm Chemical Reagent Co. Ltd. Lithium metal was purchased from China Energy Lithium Co., Ltd. Electrolyte solution were obtained from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.

2.2 Preparation of silver nanowires and $LiFePO_4$

The solvothermal method used in this study was similar to that reported previously [25]. Typically, a 10 mL ethylene glycol (EG) solution of Na_2S was stirred after the addition of 0.174 g Poly(vinyl Pyrrolidone) (PVP). This mixed solution was injected into 10 mL of EG solution of $AgNO_3$ (0.1 mol L^{-1}). Afterwards, the mixture was transferred into a 25 mL Teflon-lined autoclave, and then reacted at 160ºC for 2.5 h. When the reaction was finished, the autoclave was natural cooled to the room temperature. To remove most of EG and PVP, the products were washed with acetone and then with water by centrifugation at 6000 revolutions per minute (rpm) for 20 min. Finally, they were dispersed in deionized water for further characterization.

$LiFePO_4$ was prepared via the hydrothermal route from starting materials $FeSO_4$•$7H_2O$, H_3PO_4, $LiOH$•H_2O and ascorbic acid. Firslty, 0.025 mol $LiOH$•H_2O was dissolved in distilled water. H_3PO_4 and $FeSO_4$•$7H_2O$ powders were then added to LiOH solution in a molar ratio for Li:Fe:P = 3:1:1. After stirring for 10 min, this suspension (~40 mL) was transferred into a Teflon-lined autoclave, and reacted at 170°C for 24 h. The final product was washed by deionized water for several times, and finally dried at 70ºC overnight. The obtained material was further treated at 680ºC for 6 h under Ar atmosphere.

2.3 Measurements

The UV-visible absorption spectrum was taken at room temperature by a UV-Visible spectrophotometer (UV-2010). The morphologies are analyzed by FSEM (Sirion 200, FEI Company, Holland). The XRD patterns were taken on X'Pert PRO (PANalytical B.V., Holland) with Cu Kα radiation at 40 kV and 40 mA. The samples for the FSEM and XRD measurements were prepared on glass substrates, and dried under 80 °C before characterization.

For electrochemical testing, 0.695 mL of ethanol solution of Ag nanowires (0.05M) was firstly mixed with 0.0712 g $LiFePO_4$. Then $LiFePO_4$/Ag nanowires was blended with carbon black and polytetrafluoroethylene (PTFE) in a weight ratio of 75:20:5. The mixture was cut into pellets with a diameter of 12 mm (the cathodes). Afterwards, these cathodes were dried for 24 h at 120 °C in vacuum. The cells were assembled with the cathode as prepared, lithium metal as anode and Celgard 2300 film as separator in an argon-filled glove box. 1M $LiPF_6$ dissolved in ethylene carbonate (EC) and Dimethyl carbonate (DMC) (1:1, v/v) was used as the electrolyte solution. Charge-discharge tests was undertaken using Lixin battery cycler over a voltage of 2.5~4.2 V at 25°C (Lixin Instruments, China).

3. Results and discussion

3.1 The characterization

Fig. 1a shows the FSEM image of Ag nanowires synthesized with 0.15 mmol L^{-1} Na_2S at a fixed reaction time of 2.5 h. It can be seen that amounts of Ag nanowires can be obtained in the presence of Na_2S. In addition, it is interesting to note that the cross section of Ag nanowires synthesized in this method is polygonal. The side surface of this nanowire is smooth and the edges are indistinct. It is different from reported theory that the cross section of Ag nanowire is pentagonal [26]. Fig. 1b shows the UV–vis absorption spectra of the Ag nanowires. The surface plasmon resonance (SPR) peak at ~380 nm can be observed. Typically, there are two SPR peaks for silver nanowires, the maximal SPR peak (λmax, ~380 nm) corresponds to the transverse plasmon resonance of nanowires, and the weaker SPR peak (~350 nm) is attributable to the quadrupole resonance excitation of

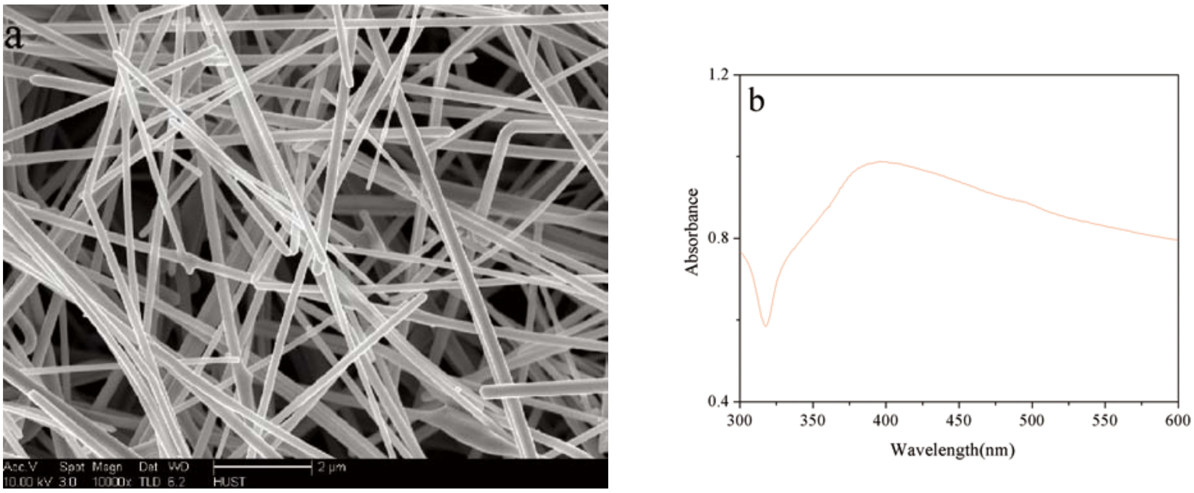

Fig. 1 (a) The FSEM image of Ag nanowires prepared with 0.15 mM Na_2S. (b) The UV–vis absorption spectra of the Ag nanowires.

nanowires [27]. In this method, the SPR peak at ~350 nm disappears. This is mainly because that the symmetry of the nanowires improves. It is consistent with the reported theory that the number of SPR peaks usually decreases with the increasing symmetry of nanowires [28].

In order to investigate the features of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes, these cathodes are analyzed with XRD, FSEM and energy-dispersive X-ray spectroscopy (EDX). Fig. 2 shows the XRD patterns of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes. In the absence of Ag nanowires, all the diffraction peaks can be indexed to the planes of $LiFePO_4$ (JCPDS File 83-2092). In the samples using Ag nanowires, the diffraction peaks mainly indicate the presence of $LiFePO_4$. In addition, the patterns in Fig. 2 also show the presence of silver nanowires that is confirmed due to the existence of 38.1° and 44.3° peaks, respectively (JCPDS File 04-0783). Fig. 3 gives the FSEM images of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes. As shown in Fig. 3a, the main products consist of $LiFePO_4$ and C particles. Compared with Fig. 3a, it is found that there are a few Ag nanowires onside the $LiFePO_4$/Ag nanowires composite cathodes (see Fig. 3b). It confirms that Ag nanowires have been added to $LiFePO_4$ cathodes. This phenomenon also indicates that a majority of these nanowires are dispersed inside these cathodes. In addition, it is worth noting that silver nanowires are well dispersed onside these cathodes. This is mainly because that silver nanowires

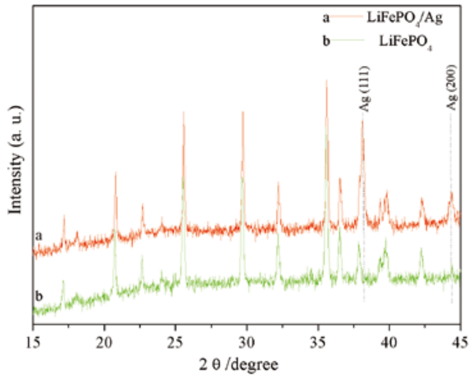

Fig. 2 XRD patterns of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes.

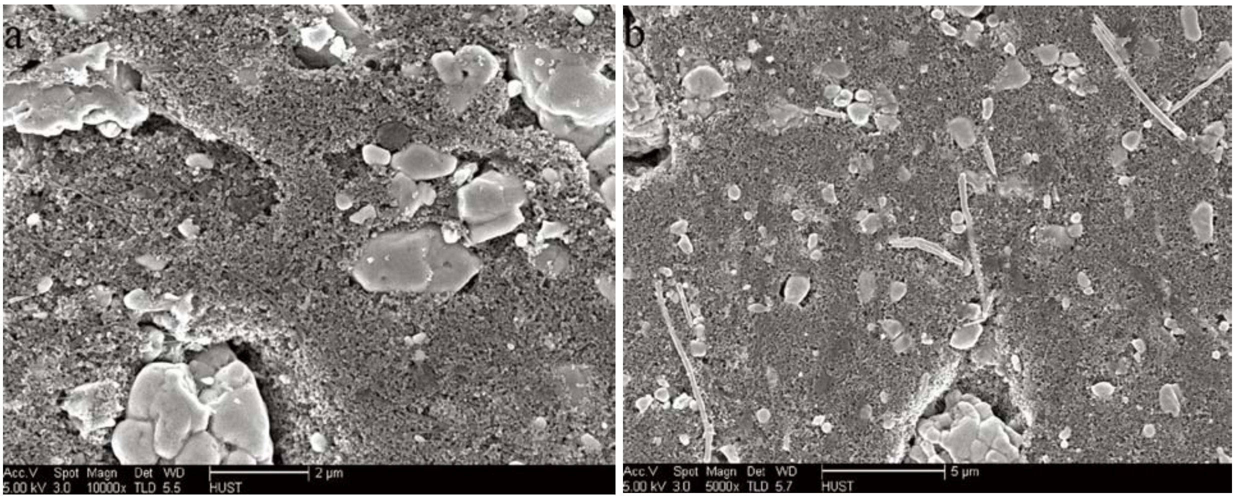

Fig. 3 FSEM images of $LiFePO_4$ (a) and $LiFePO_4$/Ag nanowires composite cathodes (b).

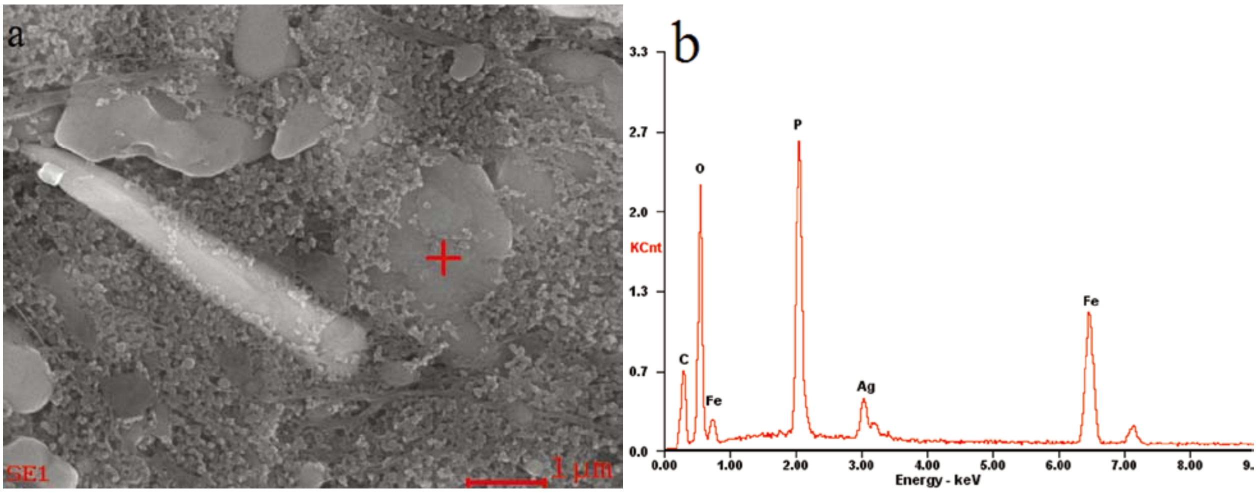

Fig. 4 The FSEM image of $LiFePO_4$/ Ag nanowires composite cathodes and the corresponding selected area EDX spectra indicated by the dot marked "+".

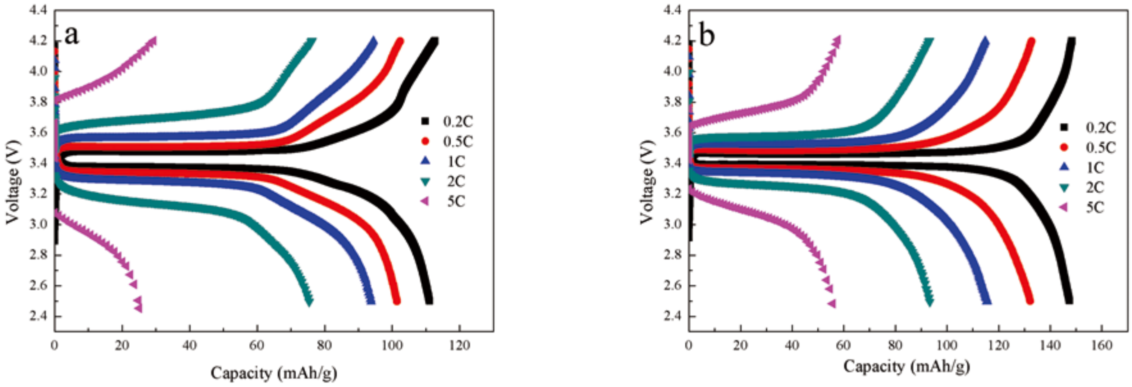

Fig. 5 Voltage profiles as a function of the specific capacity for the $LiFePO_4$ (a) and $LiFePO_4$/Ag nanowires cathodes

are firstly dispersed in ethanol before adding them to $LiFePO_4$ cathodes. By mixing the $LiFePO_4$ and the ethanol solution of silver nanowires, these nanowires may be well dispersed inside/onside $LiFePO_4$ cathodes. It is effective for them to improve the conductivity of $LiFePO_4$ cathodes because the aggregation of these nanowires can be avoided. Fig. 4 describes the FSEM image of $LiFePO_4$/ Ag nanowires composite cathodes and the corresponding selected area EDX spectra indicated by the dot marked "+". As Fig. 4a shows, there are no Ag nanowires onside these cathodes. Fig. 4b gives the EDX spectrum of the dot marked "+" shown in Fig. 4a. This result clearly conforms the existence of Ag nanowires inside these cathodes. As a result, it is possible that the conductivity of $LiFePO_4$ cathodes can be improved by the addition of conductive Ag nanowires. More details about how Ag nanowires influence the electrochemical performance of $LiFePO_4$ cathodes will be discussed later.

3.2 Electrochemical properties

Fig. 5 shows typical voltage profiles of the charge/ discharge process of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes at various rates. As shown in Fig. 5a, the discharge capacity of $LiFePO_4$ cathodes is ~110 mAh g^{-1} at a low rate of 0.2 C. In addition, it is worthy of note that the discharge capacity of these cathodes is less than 30 mAh g^{-1} at a high rate of 5 C. This phenomenon indicates that the poor conductivity of $LiFePO_4$ cathodes restricts them to get the excellent electrochemical performance. Compared with Fig. 5a, conductive Ag nanowires are added to $LiFePO_4$ cathodes for improving their conductivity. It is obvious that the specific capacity of the $LiFePO_4$/Ag nanowires composite cathodes is greatly enhanced at different rates (see Fig. 5b). At a low rate of 0.2 C, these cathodes deliver a higher specific capacity (~150 mAh g^{-1}) than the as-prepared $LiFePO_4$ cathodes (~110 mAh g^{-1}). Even the current was increased to a rate of 5 C, their discharge capacity can also reach ~60 mAh g^{-1}. Furthermore, it is interesting to note that the discharge curve of $LiFePO_4$/Ag nanowires composite cathodes is more flattened than that of $LiFePO_4$ cathodes. This result shows that more energy can be used effectively. The cyclability of $LiFePO_4$ and $LiFePO_4$/Ag nanowires cathodes recorded in continuous cycling at rates varying from 0.2 to 5 C at room temperature is shown in Fig.

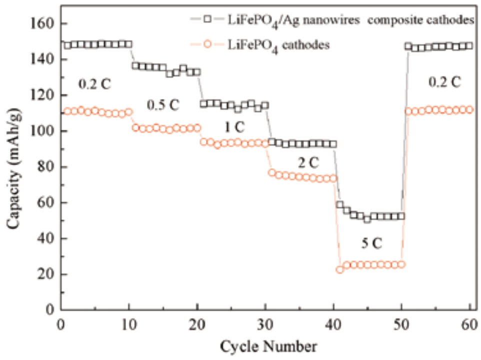

Fig. 6 Cycle performance of LiFePO$_4$ and LiFePO$_4$/Ag nanowires cathodes.

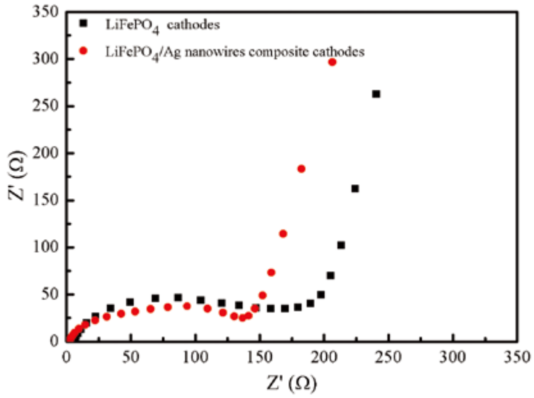

Fig. 7 Electrochemical impedance spectra of LiFePO$_4$ and LiFePO$_4$/Ag nanowires cathodes

6. It is found that discharge capacities of the LiFePO$_4$/Ag nanowires composite cathodes are higher than those of LiFePO$_4$ cathodes at various rates, and the capacity retention remains very good for all the rates. Based on the above results, the addition of Ag nanowires to LiFePO$_4$ cathodes does not affect the structure of LiFePO$_4$ cathodes. On the contrary, these nanowires improve its kinetics in terms of discharge capacity and rate capability. The improved electrochemical performance, e.g. discharge capability, rate capability and cyclability, can be ascribed to good kinetic conditions in the electrode material and Ag nanowires inside the cthodes serving as the electronic conducting network. In addition, the efficient contact between LiFePO$_4$ particles and Ag nanowires results in decreasing the contact resistance. Fig. 7 shows the Nyquist plots of LiFePO$_4$ and LiFePO$_4$/Ag nanowires cathodes. It is well known that depressed semicircle in the high frequency corresponds to the charge-transfer reaction at the electrolyte/electrode interface, and a linear Warburg part in the low frequency is associated with lithium ion diffusion in LiFePO$_4$ [2]. As can be seen from Fig. 7, the size of the depressed semicircle formed from the high frequency range of the data shows a good correlation with the capacity results in Fig. 5. Otherwise, the resistance is improved from ~181 Ω of LiFePO$_4$ cathodes to ~135 Ω for LiFePO$_4$/Ag nanowires composite cathodes. This indicates that the resistance can be improved by the addition of Ag nanowires. Finally, it is obvious that the electrochemical performance of LiFePO$_4$ cathodes can be improved considerably by the addition of Ag nanowires.

4. Conclusion

A novel route for the synthesis of LiFePO$_4$/Ag nanowires composite cathodes with high electrochemical performance has been investigated. It is found that Ag nanowires do not affect the structure of LiFePO$_4$ cathodes but improve its kinetics in terms of discharge capacity and rate capability. Discharge capacities are improved from ~110 mAh g^{-1} of LiFePO$_4$ cathodes to ~150 mAh g^{-1} for LiFePO$_4$/Ag nanowires composite cathodes at 0.2 C, and the good rate capability can aslo be obtained. Finally, we believe that this approach can be applied to improve the conductivity of the electrodes.

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