Influence of carbon coating porosity on the electrochemical performance of LiFePO$_4$ cathode

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ABSTRACT

Electrochemical performance of LiFePO$_4$/C should be strongly dependent on the carbon coating structure for core-shell nanocomposites. In this work two types of LiFePO$_4$/C composites with the same carbon coating thickness were prepared using a sol–gel technique, enabling direct comparison of the influence of carbon coating porosity on the performance of LiFePO$_4$/C cathodes. It was found that the material with a distribution of dual mesopores delivers better electrochemical performance than the one with a narrow pore size distribution.

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1. Introduction

Lithium iron phosphate, which was first studied by Padhi et al. [1], is considered as a promising cathode material for new generation lithium-ion batteries due to its high theoretical capacity, relative low cost, good thermal stability and low environmental impact [2–5]. However, as most of olivine LiMPO$_4$ phosphates, intrinsic low ionic and electronic conductivities of LiFePO$_4$ restrict its high electrochemical activities and prevent its large-scale application in electric vehicles (EVs) and hybrid electric vehicles (HEVs). One of the challenging issues to achieve high power density using LiFePO$_4$ as electrode materials is to tackle its kinetic problems, sluggish mass and charge transport [6].

Porous LiFePO$_4$/C composites have been proved to be potentially attractive materials for high-rate cathodes [13–17,19,21,22]. The work of Gaberscek et al. [13,15,19], Munichandraiah et al. [16] and Cao et al. [22] indicate that a porous structure created inside the LiFePO$_4$/C composite offers improved kinetics and electrochemical performance of electrode material. Studies of Doherty et al. [17], Wu et al. [14] and He et al. [21] suggest that the incorporation of porous carbon matrix can bring considerable enhancement to electrode materials in terms of power and energy densities.

Carbon coating which can yield composite cathodes with better performance has been widely used for improving the electronic conductivities of poor electronically conductive electrode materials [7–13,22,23]. However, as for the influence of carbon coating porosity on the electrochemical performance of LiFePO$_4$/C, there are very few

reports addressing this issue until now. Probably because perfect surface coatings are often difficult to achieve and carbon coating introduced into LiFePO$_4$ is generally considered amorphous and porous. In the current work, a simple method was used to prepare LiFePO$_4$/C composites with nanosized particles, high specific area and fine carbon coating. The distribution of pores in the carbon coating layer was controlled by appropriate selection of synthesis parameters. And the carbon coating porosity on rate performance of LiFePO$_4$ composite cathodes was investigated.

2. Experimental

As a starting precursor, iron (III) citrate was dissolved at 60 °C in water. Then citric acid, with the citric acid to iron molar ratio of 1.2:1 (sample A) and 2:1 (sample B), was added under constant stirring until the ferric citrate was completely dissolved. Separately, an equimolar water solution of LiH$_2$PO$_4$ was prepared from lithium hydroxide (LiOH, AR) and ammonium dihydric phosphate (NH$_4$H$_2$PO$_4$, AR). Clear solutions were mixed together and magnetically stirred to get a transparent solution. The mixed solution was stirred until a pale green wet gel was formed. Wet gels of sample A and sample B were aged and dried separately with different method before sintered in an inert (pure nitrogen) atmosphere at 650 °C for 7 h to obtain LiFePO$_4$/C composites.

The specific area and porosity of LiFePO$_4$/C samples were examined by adsorption-desorption of N$_2$ using ASAP 2020 instrument. Carbon content in the samples was analyzed using Elementar (Vario ELIII). TEM and HRTEM were performed on a JEOL-2010 high-resolution transmission electron microscope at 200 kV.

The positive electrodes were prepared by pressing a mixture of the active materials, acetylene black, and binder (polyvinylidene fluoride,

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PVDF, dissolved in *N*-methyl-2-pyrrolidone, NMP) in a weight ratio of 80:15:5 on aluminum foil followed by a drying procedure in vacuum at 120 °C for 8 h. The Li metal was used as the counter and reference electrodes. 1 M LiPF$_6$ in a 1:1 mixture of ethylene carbonate/diethyl carbonate was used as electrolyte. Charge and discharge performance was tested on a multi-channel battery tester (Shenzhen Neware, BTS, China) at different current densities. CV and EIS were measured on an electrochemical workstation (CHI660C) with a three-electrode system.

3. Results and discussions

Morphology of the final products was characterized by transmission electron microscopy (TEM). Each primary crystallite is completely coated by a carbon layer to form core-shell LiFePO$_4$/C structure as shown in TEM images in Fig. 1. In addition, we can also show directly in Fig. 1(a) and Fig. 1(d) that the carbon film is deposited on the surface of each particle. As disclosed in the HRTEM images shown in Fig. 1(b) and Fig. 1(e), the carbon films of both samples are about 3 nm thick. As pointed out by Zhou et al. [4], surface carbon shell can effectively restrict the crystallite growth of LiFePO$_4$. Mean crystallite size of sample A and sample B estimated using Scherrer's formula is 56.4 and 27.7 nm, respectively.

In order to further investigate the pore structure of the nanocomposite, a nitrogen isothermal-adsorption technique was used. As shown in Fig. 1(c) and Fig. 1(f), adsorption/desorption isotherms of sample A and sample B both exhibit a hysteresis which is typical of a mesoporous structure. According to BET analysis, total specific surface areas of sample A and sample B are 88.6 and 135.2 m^2 g^{-1}, respectively. Shown in the inset of Fig. 1(c) and Fig. 1(f), the Barrett–Joyner–Halenda (BJH) pore-size distribution indicates that sample A has a dual pore-size distribution at 4 nm and 11 nm while sample B has a centered pore-size distribution at 4 nm. Since active particles in sample A and sample B are spherical and the average diameter of sample A is twice as much as that of sample B, mass fractions of carbon needed to cover sample B will be twice as many as

that of sample A, agreeing with the elemental analysis results which show that carbon content of sample A and sample B is 5.56% and 11.83%, respectively. According to BET analysis, total specific surface areas of sample A and sample B are 88.6 and 135.2 m^2 g^{-1}, respectively. If the specific surface area totally comes from the aggregated LiFePO$_4$ particles, then the calculated value in terms of diameter for sample A and sample B should be 29.5 m^2 g^{-1} and 59.8 m^2 g^{-1}, which are much smaller than the obtained results from BET analysis. So, the large specific surface area can be mostly attributed to the porous carbon phase in the composites. Additionally, Zhou et al. [4] reported the special BET surface of their synthesized core-shell LiFePO$_4$/carbon composite with an average particle size of 36 nm to be 50 m^2 g^{-1}. The difference may also be due to the contribution of porous carbon layer to the high specific area of LiFePO$_4$/C composites prepared in this work. And thus it is reasonable for us to assume that the BJH distribution of pore sizes shown in the inset of Fig. 1(c) and Fig. 1(f) mainly represents the pore size distribution in the coating layer.

Typical discharge curves of sample A and sample B are shown in Fig. 2(a) and Fig. 2(b). Excluding the mass of carbon in LiFePO$_4$/C composite, sample A and sample B delivered a specific capacity of 169 mAhg^{-1} and 161 mAhg^{-1} at 1 C, respectively, which are both close to the theoretical capacity (170 mAhg^{-1}) of LiFePO$_4$. Meanwhile, discharged at 10 C, sample A retained 74% of its full capacity when sample B retained 66% of its full capacity (based on the mass of LiFePO$_4$ in the composite). Comparison of the rate performance of sample A and sample B indicates that the specific capacity and material utilization was improved by the introduction of larger mesopores which act as a transport system for electrolyte and increase the accessibility of smaller pores [18]. Cycling stability of as-obtained samples with at different discharge current rates is presented in Fig. 2(c), from which we can see that both samples show good cycling stability at discharge rates of 1 C and 10 C.

The ac impedance of the two types of cathodes was measured before cycling. The impedance spectra are shown in Fig. 3(a). In the high frequency region, the intercepts with the real axis of the sample
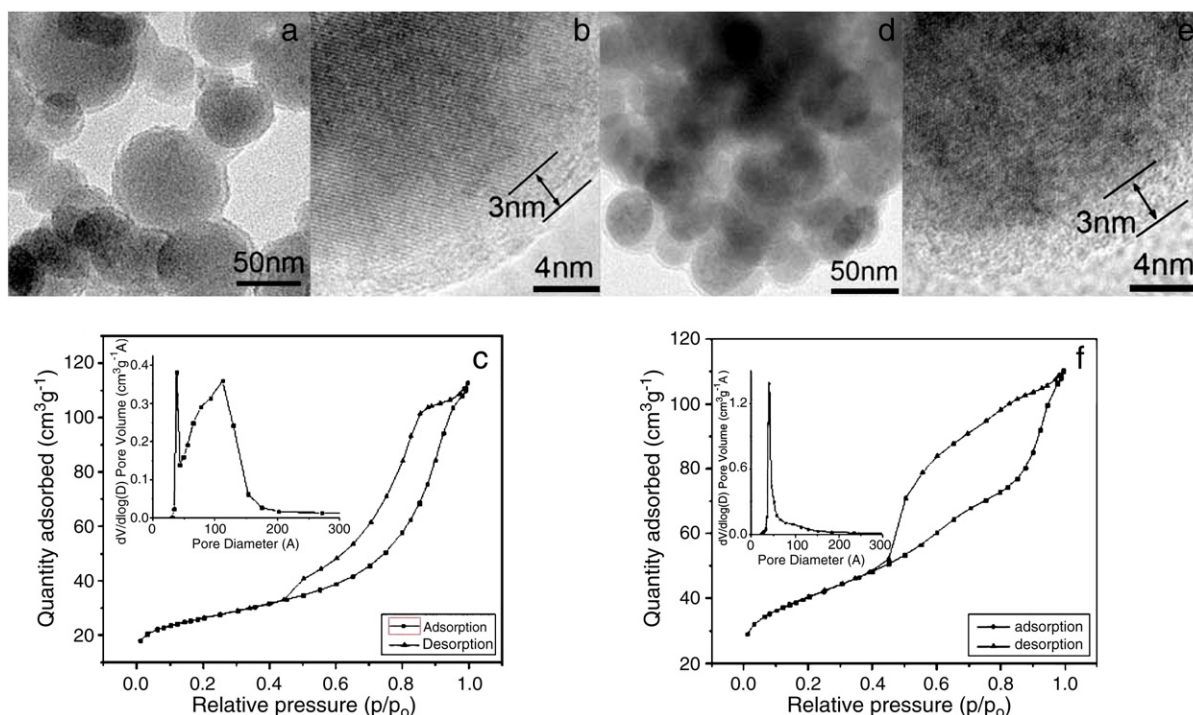
Fig. 1. Characterization of the as prepared LiFePO$_4$/C composites: (a) and (b) selected TEM image and HRTEM image of sample A; (d) and (e) selected TEM image and HRTEM image of sample B; (c) and (f) nitrogen adsorption and desorption isotherms of sample A and sample B. Inset: BJH distribution of pores obtained from desorption branch.