Facile synthesis of porous-carbon/LiFePO₄ nanocomposites

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Abstract Porous-carbon/LiFePO₄ nanocomposites were synthesized by a simple one-step sol–gel process without a pore-forming agent or ball-milling processes. These nanocomposites retained a specific capacity of 96 mAh g^{−1} even at a rate as high as 5 C (1 C = 170 mA g^{−1}). Smaller grain size and larger BET surface area induced by the increased carbon matrix do not insure the enhanced electrochemical properties. The optimum carbon content for the highest electrochemical properties is correlated well with the charge-transfer resistance and apparent Li⁺ diffusivity.

Keywords Li-ion batteries · LiFePO₄ · Nanocomposites · Porous carbon

Introduction

Olivine lithium iron phosphate has received extensive interest as a promising cathode material since the first report of Goodenough's group in 1997 (Padhi et al. 1997). LiFePO₄ has various appealing features such as high theoretical capacity (170 mAh g^{−1}), long cycle life, superior safety, environmental benignity, and low cost (Delacourt et al. 2005; Huang et al. 2001; Whittingham 2004; Yonemura et al. 2004). However, poor electronic conductivity and slow Li⁺ diffusion are critical drawbacks of LiFePO₄ for high-power lithium-ion batteries (Croce et al. 2002; Srinivasan and Newman 2004). A number of intensive researches have been done to overcome these limitations by improving the intrinsic properties of LiFePO₄ or developing nanostructures, including doping with foreign atoms, modifying surface of LiFePO₄ with electronic or ionic conductive layers, combining with metal nanoparticles, or reducing Li⁺ diffusion length by morphological control (Chung et al. 2002; Hsu et al. 2004; Huang et al. 2011; Kang and Ceder 2009; Kobayashi et al. 2009; Lou and Zhang 2011; Ravet et al. 2001; Wang et al. 2008; Wang et al. 2010; Zhu et al. 2011). These strategies have advanced the electrochemical performances considerably.

Recently, for the improvement in both the electronic conduction and Li⁺ diffusion, the morphology of LiFePO₄ mixed with porous 3D conducting networks has attracted much attention because of its ability to produce high-power and high-energy

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performance (Doherty et al. 2009; Dominko et al. 2006; Gaberscek et al. 2005; Hu et al. 2007; Oh et al. 2011; Shim et al. 2011; Wu et al. 2009; Zhao et al. 2011). Therefore, porous-carbon/LiFePO₄ nanocomposites can be considered as the ideal design for high-power and high-energy batteries. The combination of nanosized active materials and mesoporous carbon is advantageous for facile diffusion of Li⁺ due to the pores filled with electrolyte and also for the enhancement of electronic conduction through the carbon network (Dominko et al. 2006; Gaberscek et al. 2005; Hu et al. 2007; Wu et al. 2009).

Even though some groups (Wu et al. 2009; Zhao et al. 2011) have reported porous-carbon/LiFePO₄ nanocomposites, the synthesis processes require an additional pore-forming agent or high-energy ball-milling processes, and these extra procedures are the weaknesses for practical applications. In this study, we synthesized porous-carbon/LiFePO₄ nanocomposites by a simple one-step sol–gel method without any additional procedures from the fact that the porous carbon can be synthesized using citric acid with metal phosphate (Hsu et al. 2004; Liu et al. 2008). For further enhancement in performance, the content of the porous carbon was optimized, and we facilely and straightforwardly achieved comparable results without any complex processes compared to other researches dealing with porous-carbon/LiFePO₄ nanocomposites (Wu et al. 2009; Zhao et al. 2011). The origin of the optimum carbon content that yielded the highest electrochemical properties was identified by investigating the grain size, BET surface area, charge-transfer resistance, and apparent Li⁺ diffusivity consistently.

Experimental section

The porous-carbon/LiFePO₄ nanocomposites were synthesized by a one-step sol–gel process. Citric acid was used as the source for forming the carbon network which can also suppress the growth of LiFePO₄ nanoparticles. Ferrous oxalate dihydrate (0.1 mol), lithium nitrate (0.1 mol), citric acid (0.03–0.2 mol), and ammonium dihydrogen phosphate (0.1 mol) were dissolved in this order into 1 M nitric acid solution (90 ml) under stirring for 4 h (Hsu et al. 2004; Liu et al. 2008). After aging at 60 °C for 7 days, the dried powders were sintered at 700 °C for 2 h under Ar atmosphere.

Fig. 1 XRD patterns of the porous-carbon/LiFePO₄ nanocomposites with different carbon contents. The ideal peak positions and intensities for LiFePO₄ (JCPDS #40-1499) are marked at the bottom

The carbon/LiFePO₄ nanocomposites were characterized by x-ray diffraction (XRD: M18XHF-SRA, MAC Science), and the interfacial nanostructures were identified by high-resolution transmission electron microscopy (HRTEM: JEM-2010, JEOL). The carbon contents were measured using the CHNS analyzer (Flash EA 1112, Thermo Electron Corp.), and the nitrogen adsorption/desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface area and the pore size distribution of the porous-carbon/LiFePO₄ nanocomposites were calculated by the Brunauer-Emmett-Teller (BET) and the Barret-Joyner-Halenda (BJH) methods, respectively.

Electrochemical properties were tested using coin-type half cells (2016 type) with a Li counter electrode. The working electrode consisted of an active material, super P carbon black, and a polyvinylidene fluoride binder at a weight ratio of 8:1:1. The electrolyte was 1 M LiPF₆ in the ethylene carbonate/diethylene carbonate (1/1 vol%) (Cheil Industries Inc.). The cycling tests were performed on the coin cell using a WBCS 3000 battery cycle system (Won A Tech. Co.) in the range of 4.2–2.3 V at various current rates. Cyclic voltammetry (CV) measurements were carried out at

Table 1 Specific capacity, grain size, BET surface area, charge-transfer resistance, and apparent Li^+ diffusivity of the porous-carbon/ LiFePO_4 nanocomposites with different amounts of carbon

Carbon content (wt%)	Specific capacity (at 0.1 C) (mAh g^{-1})	Grain size (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Charge-transfer resistance ($\Omega \text{ g}$)	Apparent Li^+ diffusivity ($\text{cm}^2 \text{s}^{-1}$)
3.4	115	91 ± 18	38 ± 0.1	0.300	5.52×10^{-15}
8.7	130	80 ± 13	49 ± 0.3	0.176	8.52×10^{-15}
13.7	151	71 ± 14	84 ± 0.8	0.134	9.10×10^{-15}
15.3	138	65 ± 5	87 ± 0.9	0.194	4.64×10^{-15}

Fig. 2 TEM, HRTEM images, and SAED of the porous-carbon/ LiFePO_4 nanocomposites with different carbon contents: **a** 3.4 wt%, **b** 13.7 wt%, and **c** 15.3 wt%, respectively

Fig. 3 N_2 adsorption/desorption isotherms of the porous-carbon/ $LiFePO_4$ nanocomposites as a function of carbon content. The inset shows the pore-size distribution of the porous-carbon/ $LiFePO_4$ nanocomposites

the scan rate of 0.5 mV s^{-1} , and the apparent diffusivity of Li^+ was obtained from the peak currents in the CV measurements. Electrochemical impedance spectra were measured using a potentiostat (CHI 608C: CH Instrumental Inc.) in the frequency range from 1 mHz to 100 kHz at an AC amplitude of 5 mV.

Results and discussion

The XRD patterns of the carbon/ $LiFePO_4$ nanocomposites with different carbon contents show orthorhombic $LiFePO_4$ with the space group $Pmnb$ (62) (JCPDS #40-1499), and no impurity phases were detected, as shown in Fig. 1. To examine the effect of porous-carbon network on the grain size of $LiFePO_4$, Scherrer equation of Δk versus k (the scattering vector $k = (4\pi/\lambda)\sin\theta$) was used (Table 1). X-ray diffraction peak widths Δk (full width at half maximum) were fitted by double-peak Lorentzian function for $K\alpha_1$ and $K\alpha_2$ (Jung et al. 2008; Kim et al. 2000; Kim et al. 2005; Palomares et al. 2009; Son et al. 2007). The results

confirm that porous-carbon matrix prohibited the growth of $LiFePO_4$ nanoparticles, resulting in smaller grain size with increasing carbon content. The homogeneously distributed citrate was converted to the rigid carbon web surrounding $LiFePO_4$ nanoparticles during the heat treatment, thereby the carbon network suppressed the particle growth even at 700°C (Kim et al. 2005; Moon et al. 2006; Palomares et al. 2007; Palomares et al. 2009; Wang et al. 2008).

The TEM images of the carbon/ $LiFePO_4$ nanocomposites show that the $LiFePO_4$ nanoparticles are embedded in a porous-carbon matrix (Fig. 2). Because $LiFePO_4$ nanoparticles are rigidly interconnected, it was tricky to make submonolayer nanoparticle sample for SEM or TEM analysis. The HRTEM images of the carbon/ $LiFePO_4$ nanocomposites clearly indicate that the local thickness of the outer carbon layer increases from ~ 0.9 to ~ 2.2 nm with increasing carbon content. The thicknesses of carbon are comparable to the calculated values (~ 0.8 – ~ 2.6 nm) under the assumption of uniform core-shell structure. The lattice fringes demonstrate single-crystal $LiFePO_4$ nanoparticles. The selected area electron diffraction patterns (SAED) shown in Fig. 2a, b, c again confirm no impurity phases, consistent with the XRD results of Fig. 1.

To analyze the porosity of the porous-carbon/ $LiFePO_4$ nanocomposites, the nitrogen adsorption/desorption isotherms and the BJH distributions of pores were investigated, as shown in Fig. 3. The BET surface area of the carbon/ $LiFePO_4$ increases with increasing carbon content (Table 1). The obtained BET surface area is attributed to the porous-carbon matrix since the experimental BET surface area of ~ 25 -nm-sized $LiFePO_4$ nanoparticles is $\sim 7 \text{ m}^2 \text{ g}^{-1}$ (Hong et al. 2011), much smaller than that of the carbon/ $LiFePO_4$ with 13.7 wt% carbon ($\sim 84 \text{ m}^2 \text{ g}^{-1}$). Sufficient porosity of the carbon network can be obtained by carbonization of the homogeneously distributed citrate in the solution (Dominko et al. 2007). The evolving gases from organic decomposition penetrate through the xerogel, making pores in the electronic-conductive carbon matrix on the surface of $LiFePO_4$ nanoparticles (Dominko et al. 2007; Zhao et al. 2011). This porous-carbon network plays a critical role in both electronic and ionic conduction (Wu et al. 2009; Zhao et al. 2011). Considering both the thickness of carbon layer by TEM (Fig. 2) and the pore-size distribution (Fig. 3), a schematic illustration is shown in Fig. 4.

Fig. 4 Schematic illustration of the porous-carbon/LiFePO₄ nanocomposites

The carbon/LiFePO₄ with 13.7 wt% carbon shows the best cell performance (Fig. 5). The discharge capacity of the carbon/LiFePO₄ with 15.3 wt% carbon was diminished to 138 mAh g⁻¹ at 0.1 C rate (Table 1). The decreased specific discharge capacity with 15.3 wt% carbon may be caused by the thicker carbon layer prohibiting the electrochemical activity in LiFePO₄.

Regarding rate capabilities, the carbon/LiFePO₄ with 13.7 wt% carbon has the best reversible capacity of 96 mAh g⁻¹ at a rate as high as 5 C (Fig. 6). Recently, various morphologies of LiFePO₄/carbon were developed for the improved electrochemical performance, which include the core-shell of LiFePO₄/carbon, mesoporous LiFePO₄/carbon, or carbon-coated LiFePO₄ nanowire (Wang et al. 2008; Wang et al. 2010; Zhu et al. 2011). However, they have been

made with extra processes of using an additional process such as vacuum filtering, porous-carbon template, or electrospinning. Although these nanocomposites have high-quality electrochemical performances, the approaches to synthesize LiFePO₄/carbon nanocomposites were found to necessarily include additional costly procedures. For this reason, we believe that they have an obstacle for the practical applications. The synthesis method of our work is facile, straightforward, and quite inexpensive requiring only seven-day aging at 60 °C without any further steps. Furthermore, this rate capability of porous-carbon/LiFePO₄ is comparable to similar morphology of porous-carbon/LiFePO₄ nanocomposites with an additional pore-forming agent or high-energy ball-milling processes (~90 mAh g⁻¹ or ~100 mAh g⁻¹ at 5 C) (Wu et al. 2009; Zhao et al. 2011).

Fig. 5 Charge-discharge curves of the porous-carbon/LiFePO₄ nanocomposites with different carbon contents at various C rates (1 C = 170 mA g⁻¹)

Fig. 6 Rate capability of the porous-carbon/LiFePO₄ nanocomposites with different carbon contents at various C rates

The reasonable rate capability can be attributed to the morphology of the porous-carbon network which promotes both electron conduction and Li⁺ diffusion. Interestingly, an optimum carbon content exists for enhanced electrochemical performance although it is generally accepted that a smaller grain size and larger BET surface area result in better electrochemical properties. Our experiments exhibit the optimum carbon content for enhanced electrochemical

Fig. 7 Electrochemical impedance spectroscopy of the porous-carbon/LiFePO₄ nanocomposites with different carbon contents with an applied voltage of 3.4 V. The fitting lines were obtained using the equivalent circuit in the inset

Fig. 8 Cyclic voltammetry of the porous-carbon/LiFePO₄ nanocomposites measured between 4.2 and 2.3 V at a scan rate of 0.5 mV s⁻¹

performance. To identify the involved mechanisms, charge-transfer resistances (R_{ct}) were first analyzed by electrochemical impedance spectroscopy (EIS). The charge-transfer resistance of the carbon/LiFePO₄ with 13.7 wt% carbon obtained by fitting of the spectra based on the equivalent circuit (inset of Fig. 7) was found to be the lowest of all. When the carbon content is lower than 13.7 wt%, the porous-carbon network may not percolate all the LiFePO₄ nanoparticles, resulting in poor electron conduction, while too high carbon content can hinder Li⁺ diffusion through the carbon matrix, especially when high current densities are applied (Dokko et al. 2003; Dominko et al. 2005; Mohamedi et al. 2002; Moskon et al. 2006).

Fig. 9 Capacity, grain size, BET surface area, charge-transfer resistance, and apparent Li^+ diffusivity as a function of carbon content for the porous-carbon/ LiFePO_4 nanocomposites

In order to verify these arguments, the apparent diffusivity of Li^+ of the carbon/ LiFePO_4 for various carbon contents was examined by CV measurements between 4.2 and 2.3 V at a scan rate of 0.5 mV s^{-1} (Fig. 8). In the case of LiFePO_4 , the general laws of diffusion are not suitable for the description of Li motion inside the spinodal domain (Levi et al. 2008; Ramana et al. 2009). However, comparing the effect of carbon content on the apparent diffusivities is reasonable (Yu et al. 2007). The apparent Li^+ diffusivity can be calculated according to the diffusion formula $D = l^2/\tau$ where τ is the diffusion time constant (s), l is the diffusion length corresponding to the particle radius (cm), and D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$). The diffusion time constant τ can be obtained by the following relationship (Bard and Faulkner 1980; Yu et al. 2007; Levi and Aurbach 1999):

$$\tau = 0.119 \frac{F}{RT} \left(\frac{Q_m v^{-1/2}}{I_p} \right)^2, \quad (1)$$

where F is the Faraday constant, R is the gas constant, T is the absolute temperature, Q_m is the maximum intercalation charge (A s g^{-1}), v is the scan rate (V s^{-1}), and I_p is the peak current (A g^{-1}). The apparent diffusivity of Li^+ in the carbon/ LiFePO_4 nanocomposites with 13.7 wt% carbon content is the highest among the four cells, as given in Table 1. This confirms that too much carbon network blocks the diffusion of Li^+ across the electrolyte/ LiFePO_4 interfaces.

Figure 9 clearly shows the overall dependence of specific capacity, grain size, BET surface area, charge-transfer resistance, and apparent Li^+ diffusivity as a

function of carbon/ LiFePO_4 ratio. Smaller charge-transfer resistance and higher apparent Li^+ diffusivity can be achieved with the optimum carbon content.

Conclusions

Porous-carbon/ LiFePO_4 nanocomposites were synthesized by a simple one-step sol-gel method and the carbon/ LiFePO_4 had a specific capacity of 96 mAh g^{-1} even at a rate as high as 5 C. We confirmed that the optimum carbon content existed and resulted in minimum charge-transfer resistance and maximum apparent Li^+ diffusivity. Smaller grain size and larger BET surface area do not insure the highest electrochemical properties.

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