

Short communication

Kinetic study on LiFePO_4/C nanocomposites synthesized by solid state technique

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Abstract

Well-crystallized, homogeneous nanocomposites of lithium iron(II) phosphate and carbon was synthesized by solid state reaction, and the obtained particles are spherical. Measurement of both CV and EIS shows that the lithium ion diffusion coefficient in the nanocomposites is affected by the incorporated carbon, and markedly increases with the carbon content. Meanwhile, the kinetics of lithium intercalation and de-intercalation is greatly ameliorated. These data provide strong evidence of the potential use of this kind of nanocomposite cathode in lithium ion battery.

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1. Introduction

Since the work on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in phospho-olivines was first reported in 1997 [1–3], LiFePO_4 has been intensively studied as a promising cathode material [4–16]. The LiFePO_4 material demonstrates reversible lithium insertion at around 3.4 V versus Li with a theoretical capacity of 170 mAh g^{-1} [2,4,5], long cycle life due to small volume change (6.8%). Furthermore, it is also environmentally benign and inexpensive.

Its main disadvantages are that its electronic conductivity is low and rate capability poor. As a result, only 60% of the capacity could be obtained for the original LiFePO_4 in the early work, and its capacity decreases remarkably at larger current density. High utilization and improvement of rate capability have been achieved, for example, by admixing with carbon [5–8], adding 1 wt% Ag or Cu [9,10], and doping with heteroatoms [8]. However, so far there is no systematic report to investigate the reason from the point of view of kinetics.

In this paper, we first synthesized spherical nanocomposites of LiFePO_4 with carbon, and then investigated dependence of

kinetics and lithium ion diffusion coefficient on the carbon content by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

Nanocomposites of LiFePO_4 with carbon were prepared by a solid state route. Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and acetylene black (0, 5, 10, 20 wt%) were mixed in ratio of $\text{Li}:\text{Fe}:\text{PO}_4 = 1:1:1$ in a planet mixer (QM-BP) for 24 h. The mixtures were sintered in a tube furnace at 750°C for 15 h in an inert atmosphere.

Powder samples were identified using a powder X-ray diffractometer with monochromatized $\text{Cu K}\alpha$ radiation. Morphological observation was done by SEM (Philips XL 300) and TEM (JEOL JEM 2011).

The cathodes were prepared by mixing active material: PVDF: carbon black at a ratio of 90:5:5 (w/w/w). The mixture was coated on an aluminum foil and cut to pieces, then coin-type model cells were assembled in the glove box using lithium foil as the counter and reference electrode, Celgard 2400 as the separator, and LIB315 (Guotai Huarong Chemical Plant) as the electrolyte.

The model cells were used to measure the CV and EIS behavior at room temperature. The CV was carried out at a voltage

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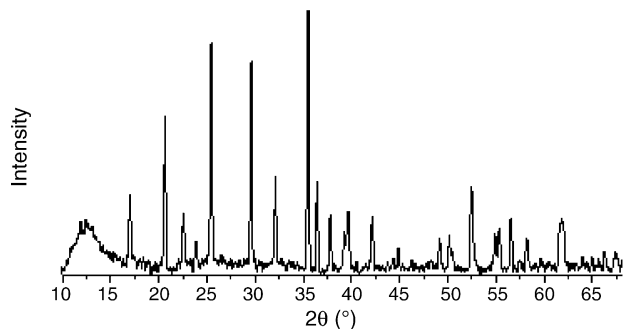


Fig. 1. XRD profile of the LiFePO₄/C nanocomposites containing 5% carbon.

range of 2.1–4.5 V, and the EIS frequency range was 10 mHz to 100 kHz with the vibration of 10 mV.

3. Results and discussion

The X-ray diffraction pattern of one typical LiFePO₄ composite containing 5% carbon obtained from solid state reaction is shown in Fig. 1. It confirms that the product is a single phase with an ordered olivine structure indexed to the orthorhombic P_{nmb} space group. The peaks at low degree ($<15^\circ$) and the fluctuation around the baseline were due to the existence of amorphous carbon in the sample.

Lithium intercalation/de-intercalation is a movement between the phase boundary of two phases during the charge/discharge and the characteristics of the material surface play an important part [1]. Fig. 2 is the SEM micrograph of the synthesized LiFePO₄/C nanocomposites containing 5% carbon. The LiFePO₄/C powder was homogeneous and the particles size was within nanometer range. Its TEM micrograph is shown in Fig. 3, suggesting that the particle size was around 100 nm and the product particles were spherical. This has not been reported yet, and the particle size is within nanometer range and smaller than that reported by others [14,15]. The unique morphology and size are due to the admixing of carbon in the starting material, which protects LiFePO₄ from oxidation

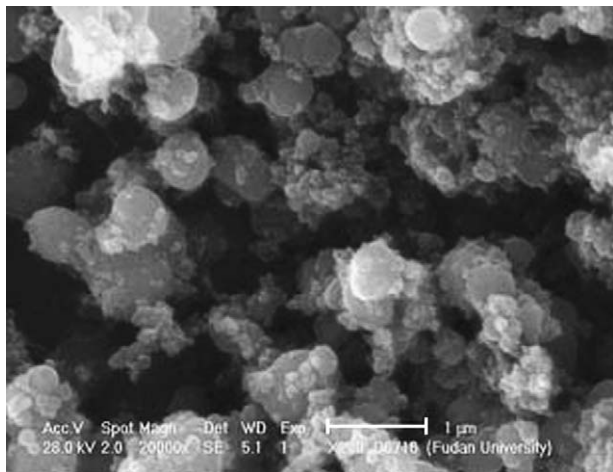


Fig. 2. SEM photograph of LiFePO₄/C containing 5% carbon synthesized from the solid state reaction.

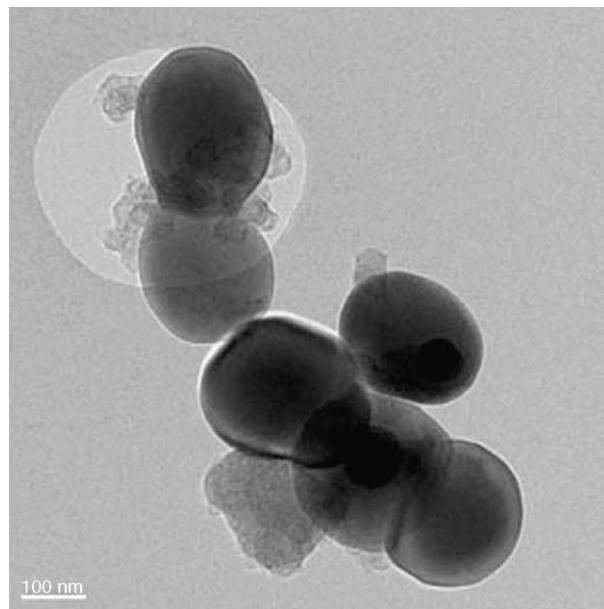
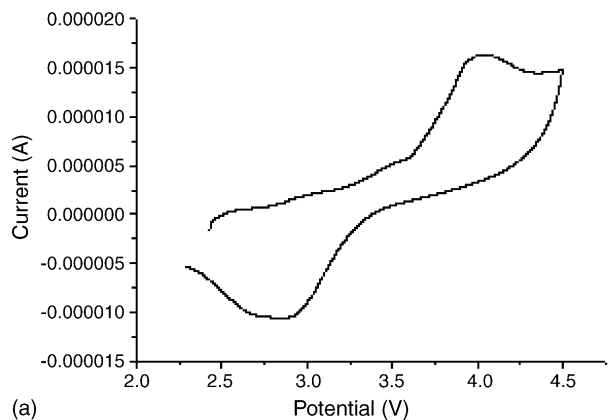
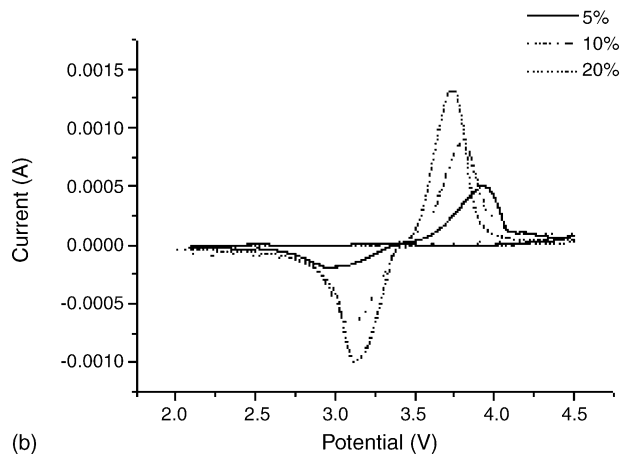


Fig. 3. TEM photograph for the LiFePO₄/C particles containing 5% carbon.



(a)



(b)

Fig. 4. CV profile of (a) the untreated LiFePO₄ at 0.1 mV s^{-1} and (b) the nanocomposites incorporating different content of carbon at the scan rate of 0.1 mV s^{-1} .

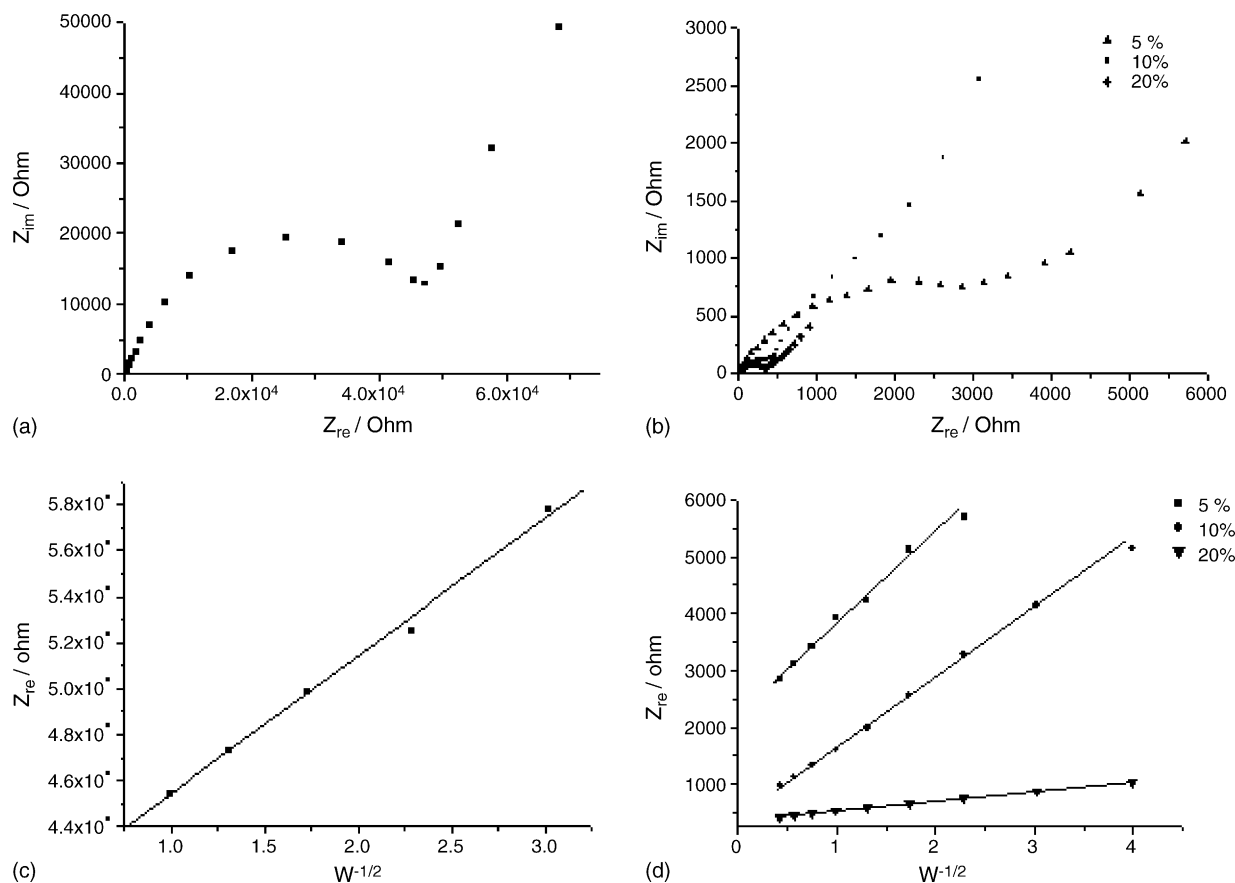


Fig. 5. (a) The Nyquist plot of untreated LiFePO₄, (b) the impedance spectroscopy of the LiFePO₄/C nanocomposites, (c) the relationship between Z_{re} and $\omega^{1/2}$ at low-frequency region of untreated LiFePO₄, and (d) the relationship between Z_{re} and $\omega^{1/2}$ at low-frequency region of the LiFePO₄/C nanocomposites.

and agglomeration. We believe that the unique morphology will improve surface characteristics of the cathode nanocomposite, and make it possible to achieve better electrochemical performance.

CV was used to evaluate the electrochemical performance of the prepared nanocomposites. Fig. 4 is the CV profiles of original and nanocomposites LiFePO₄ samples. It is shown from the Fig. 4a that the anodic/cathodic peaks of untreated LiFePO₄ are located at 4.08 V/2.88 V at the scan rate of 0.1 mV s⁻¹ and the I_p of the redox peaks is at the around of 10⁻⁵ A. The big separation between redox peaks (ΔV) of 1.20 V indicates that the electrochemical behavior is controlled by the diffusion step. From Fig. 4b, it can be seen that the I_p of nanocomposites materials increases with the content of carbon apparently. When the content of carbon is 5, 10, and 20 wt%, their I_p evidently increases to 4.95×10^{-4} , 8.69×10^{-4} , and 1.32×10^{-3} A, respectively. Meanwhile, the ΔV between redox peaks was reduced to 0.97, 0.70, and 0.64 V, respectively. Both I_p and ΔV data confirm that kinetics of lithium intercalation and de-intercalation is greatly ameliorated by the incorporation of carbon. This amelioration will improve the rate capability of the nanocomposites cathode and make its application possible.

Electrochemical impedance spectroscopy (EIS) is an important method to evaluate the diffusion coefficient of lithium ion and was used to investigate the influence of carbon content on the lithium ions transfer in the LiFePO₄ nanocomposites. Fig. 5a

shows the Nyquist plot of untreated LiFePO₄. The radius of the semicircle at high-frequency region on the real axis is the charge transfer resistance (R_{ct}) approximately. Compared with untreated sample, the obtained data for nanocomposites investigated by EIS technology are shown in Fig. 5b. All plots exhibit a semicircle in the high-frequency region, which is attributed to the charge transfer process. The semicircles' diameters decrease as the carbon content increases, this tendency means that the resistance of charge transfer, R_{ct} , decreases with the carbon content [15].

The lithium ion diffusion coefficient is calculated according to the following equation:

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 s^2} \quad (1)$$

where the meanings of n is the number of electrons per molecule during oxidization, A the surface area of the cathode, D the diffusion coefficient of lithium ion, R the gas constant, T the absolute temperature, F the Faraday constant, C the concentration of lithium ion, and σ is the Warburg factor which has relationship with Z_{re} :

$$Z_{re} = R_D + R_L + \sigma\omega^{1/2} \quad (2)$$

Fig. 5c shows the relationship between Z_{re} and square root of frequency ($\omega^{1/2}$) in the low-frequency region. The diffusion coefficient of lithium ion is calculated based on Eqs. (1) and

(2) [17]. The diffusion coefficient of the untreated LiFePO_4 is $9.98 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, which is comparable with the reported [16]. Fig. 5d shows the Z_{re} and σ relationship of the nanocomposites, and the calculated diffusion coefficients of lithium ion in the nanocomposites containing 5, 10, and 20 wt% carbon are 1.01×10^{-13} , 9.20×10^{-13} , and $4.89 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively. The diffusion coefficient of lithium ion increases markedly after admixing with carbon. In the meanwhile, it increases greatly with the content of carbon. It is consistent with the above data from CV. The improvement in kinetics of lithium ion during intercalation and de-intercalation is apparently from the admixed carbon.

4. Conclusion

The nanocomposites of LiFePO_4 and C are synthesized by solid state reaction. The product is well-crystallized and the particles are spherical. This unique morphology is reported for the first time. Measurement by CV and EIS shows that the kinetics of lithium intercalation and de-intercalation is ameliorated and the diffusion coefficient of lithium ion is greatly improved after incorporating of carbon. These results clearly expound the favourable effects of the admixed carbon, and the nanocomposites of LiFePO_4 with carbon are of great potential use as cathode material for lithium ion battery.

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References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
- [2] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1609.
- [3] Y.P. Wu, X.B. Dai, J.Q. Ma, Y.J. Chen, Lithium Ion Batteries: Practice and Application, Chemical Industry Press, Beijing, 2004.
- [4] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
- [5] N. Ravet, Y. Chouninard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97–98 (2001) 503.
- [6] H. Huang, S.-C. Yin, L.F. Nazar, Electrochem. Solid State Lett. 4 (2001) A170.
- [7] Z. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184.
- [8] S.Y. Chung, J. Bloking, Y.M. Chiang, Nat. Mater. 1 (2002) 123.
- [9] F. Croce, A.D. Epifanio, J. Hassoun, A. Deptula, T. Olczac, B. Scrosati, Electrochem. Solid State Lett. 5 (2002) A47.
- [10] K.S. Park, J.T. Son, H.T. Chung, S.J. Kim, C.H. Lee, K.T. Kang, H.G. Kim, Solid State Commun. 129 (2004) 311.
- [11] Y. Chen, M. Ueno, N. Iltchev, S. Okada, J. Yamaki, Proceedings of 2001 IAMS International Seminar on Li Batteries, vol. A-10, Kasuga, Japan, 26–27 November, 2001, p. 67.
- [12] H.S. Kim, B.W. Cho, W.I. Cho, J. Power Sources 132 (2004) 235.
- [13] S. Franger, F.L. Cras, C. Bourbon, H. Rouault, J. Power Sources 119–121 (2003) 252.
- [14] T.H. Cho, H.T. Chung, J. Power Sources 133 (2004) 272.
- [15] D. Zane, M. Carewska, S. Scaccia, F. Cardellini, P.P. Prosini, Electrochim. Acta 49 (2004) 4259.
- [16] P.P. Prosini, M. Lisi, D. Zane, M. Pasquali, Solid State Ionics 148 (2002) 45.
- [17] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980, p. 213.