PREPARATION AND SILVER MODIFICATION OF LiFePO_4/C FOR LI-ION BATTERIES ¹

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ABSTRACT

LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ samples were prepared by sol-gel method. Samples were characterized by XRD, SEM, EIS and electrochemical discharge and charge tests. Silver modification does not affect the olivine structure of LiFePO_4 but enhances its electrochemical performance in terms of discharge capacity and rate capacity. Discharge capacities are improved from 130.8 mAhg^{-1} of LiFePO_4/C to 149.8 mAhg^{-1} of $\text{LiFePO}_4/\text{C}+\text{Ag}$ cathodes. EIS measurements show that Silver modification slightly decreases the charge transfer resistance of LiFePO_4/C , and lithium ion diffusion coefficient is enhanced from 2.89×10^{-14} to $8.17 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

Key words: Li-ion battery; LiFePO_4/C ; Silver modification; EIS; Li-ion diffusion coefficient

INTRODUCTION

Since the pioneering work of Goodenough and co-workers ¹, the phosphor-olivine LiFePO_4 has been recognized as a potential positive electrode material for use in lithium ion batteries. Although LiFePO_4 possesses a number of advantages (high capacity, high stability during lithium extraction/insertion, environmental friendliness, etc) ², its main drawback is poor electrochemical performance due to its sluggish charge/discharge kinetics. In order to increase the charge capacity and improve the conductivity, many attempts have been performed, using approaches such as decreasing active particle size ³⁻⁵, carbon coating ⁶⁻⁹, ion doping ¹⁰⁻¹² and surface modification ¹³⁻¹⁵ etc. Surface modifications are of great importance in developing electrode materials ¹⁵. In the present paper we investigate the role of silver modification in improving the performance of LiFePO_4 . Wherein we took silver mirror reaction to coat each particle with a thin silver coating. Particles are prepared via a sol-gel route using Fe(III) citrate as chelating agent. The impacts of silver coating on the electrochemical properties of LiFePO_4 -based cathodes are systematically studied.

EXPERIMENT

LiFePO_4/C composites were prepared by a sol-gel method with subsequent firing of xerogel in argon (purity $\geq 99.99\%$) atmosphere. First, Fe(III) citrate (Sigma, Technical Grade) was dissolved at 70°C in deionized water. Second, equimolar aqueous solution of LiH_2PO_4 was prepared from $\text{NH}_4\text{H}_2\text{PO}_4$ (GR, sinopharm) and Li_2CO_3 (99.84%, self-made). The solutions were mixed together and the obtained transparent sol was dried at 70°C for at least 20h after grinding with mortar and pestle for 10min, the obtained material was fired in argon atmosphere at 700°C for 18h the heating rate being $10\text{K}/\text{min}$.

The surface modification was performed by silver mirror reaction ¹³⁻¹⁴. The LiFePO_4/C powders were suspended in the AgNO_3 solution with stirring, and solution of glucose was added to reduce Ag^+ ions. A solution of AgNO_3 by a weight ratio of 6(Ag):94(LiFePO_4/C) was added. After stirring, the suspended powders were separated by filtration. The obtained $\text{LiFePO}_4/\text{Ag}+\text{C}$ powders were dried in argon atmosphere at 500°C for 2h. The completion of the Ag^+ reduction was checked by adding 5M HCl to the filtrate.

The powders were characterized by SEM and X-ray diffraction. The SEM observation was performed on a JEOL scanning electrode microscope (JSM-5610LV), the X-ray diffraction was carried out by using a PANalytical X'Pert PRO diffractometer with Cu K α radiation.

Electrodes were made by dispersing appropriate 85wt.% active materials, 8wt.% carbon black and 7wt.% polyvinylidene fluoride (PVDF) binder in 1-Methyl-2-pyrrolidone solvent to form a slurry. The slurry was then spread uniformly on to an electrode slice and dried in the vacuum oven at 65°C for at least 12h. The cells were assembled in an argon filled glove-box (MBraun, Unilab, USA). The electrolyte was 1M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The cells were galvanostatically charged and discharged in the voltage range of 2.5-4.3V versus Li/Li^+ counter electrode.

EIS was measured on an IM6ex electrochemical workstation (ZAHNER

electric, Germany) at 3.4V, the amplitude of the AC voltage was 5mv over the frequency range 10^{-2} to 10^6 Hz

RESULTS AND DISCUSSION

The X-ray diffraction profiles of LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ are shown in Fig.1. Ag diffraction patterns are detected and numbered in the X-ray diffraction profile of $\text{LiFePO}_4/\text{C}+\text{Ag}$. The LiFePO_4/C is pure single phase indexed with the orthorhombic Pnmb space group. The lattice parameters of LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ are calculated separately by MDI Jade 5.0. The results are $a = 6.005(5) \text{ \AA}$, $b = 10.32(11) \text{ \AA}$, $c = 4.687(5) \text{ \AA}$, $V = 290.6(5) \text{ \AA}^3$ (LiFePO_4/C) and $a = 6.01(11) \text{ \AA}$, $b = 10.32(18) \text{ \AA}$, $c = 4.689(9) \text{ \AA}$, $V = 291.1(3) \text{ \AA}^3$ ($\text{LiFePO}_4/\text{C}+\text{Ag}$).

Fig.1.- X-ray diffraction patterns of Lithium iron phosphates

Fig.2 shows the SEM photos of prepared LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$. After sintering at 700°C for 18h, well crystallized powders are obtained with an average crystal size of 1-5 μm . LiFePO_4/C particles have smooth surface, whereas a lot of flocculi cover the surface of $\text{LiFePO}_4/\text{C}+\text{Ag}$ particles, which may well be the elementary silver produced by silver mirror reaction.

Fig.2.- SEM micrographs of various samples: (a) LiFePO₄/C; (b) LiFePO₄/C+Ag.

The electrochemical performance of LiFePO₄/C and LiFePO₄/C+Ag is displayed in Fig.3. The reversible capacity of silver modified LiFePO₄/C is 149.8mAhg⁻¹ at a current density of 60mA g⁻¹, as opposed to 126.0mAhg⁻¹ for LiFePO₄/C at the same current density. The introduction of silver obviously enhances the electrochemical properties of the active material.

Fig.3.- Discharge/charge curves of LiFePO₄/C and LiFePO₄/C+Ag in the third cycle at 60mA g⁻¹ (0.4C, 1C=150mAhg⁻¹) at room temperature.

In Fig.4, the impedance spectra are combinations of a depressed semicircle at high frequencies and a straight line at low frequencies. In the high frequency region, the intercepts with real impedance axis of LiFePO₄/C and LiFePO₄/C+Ag composite are 115Ω and 110Ω respectively. This value is believed to be the total electric resistance of the electrode materials, electrolyte resistance and electrode leads. The minor decrease of the total electric resistance may be attributed to the silver modification to LiFePO₄/C. In the low frequency region, faraday reaction is the main effect. The slope of impedance of the LiFePO₄/C+Ag composite is higher than that of LiFePO₄/C, indicating that silver is able to enhance the electrochemical activity of LiFePO₄¹⁶.

The lithium ion diffusion coefficients (*D*) of LiFePO₄/C and LiFePO₄/C+Ag are calculated according to the following equation¹⁷:

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

Where *R* is the gas constant, *T* is the absolute temperature, *n* is the number of electrons per molecule during oxidation, *F* is the Faraday Constant, *C* is the concentration of lithium ion, and *σ* is the Warburg factor which has relationship with *Z_{lm}*:

$$Z_{lm} = -\sigma \omega^{-1/2} \quad (2)$$

Fig.5 shows the relationship between $-Z_{lm}$ and square root of frequency in the low frequency region for LiFePO₄/C and LiFePO₄/C+Ag. The diffusion coefficients of lithium ion are calculated based on equation (1) and (2). The calculated diffusion coefficients for LiFePO₄/C and LiFePO₄/C+Ag are 2.89×10^{-14} and $8.17 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ respectively. The lithium ion diffusion coefficient increases markedly by the silver modification.

Fig.4.- EIS spectra of fresh LiFePO₄/C and LiFePO₄/C+Ag composite electrodes in two-electrode configuration in 1MLiPF₆/EC-DMC (1:1 volume ratio) at room temperature in the frequency range from 0.01 to 1M Hz.

Fig.5.- The relationship between $-Z_{im}$ and square root of frequency in low frequency region for LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$.

The cycle life of the LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ samples is shown in Fig.6. It is found that discharge capacities of $\text{LiFePO}_4/\text{C}+\text{Ag}$ are higher than that of LiFePO_4/C . The highest discharge capacity is 130.8mAhg^{-1} at the first circle for the latter and 149.8mAhg^{-1} at the third circle for the former. Table 1 presents the statistics of the cycling properties of LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ cathodes at various discharging rates. At the discharging rates of 0.4C and 1.0C , better electrochemical performance can be achieved by silver modification.

(A)

(B)

Fig.6.- Specific capacity vs cycle number for LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ at room temperature. (A) Charge-discharge current density: 60mAhg^{-1} ; (B) Charge-discharge current density: 150mAhg^{-1} .

Table1.- Statistics of the cycling properties of LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ cathodes at different discharging rates.

Property	Capacity (mAhg^{-1})		Fading rate per cycle	
	0.4C	1.0C	0.4C (%)	1.0C (%)
LiFePO_4/C	130.8	110.6	0.51	0.03
$\text{LiFePO}_4/\text{C}+\text{Ag}$	149.8	123.6	0.03	—

CONCLUSION

LiFePO_4/C and $\text{LiFePO}_4/\text{C}+\text{Ag}$ were prepared by a sol-gel process. Silver modification improves its electrochemical performance in terms of discharge capacity and rate capability. Discharge capacities are improved from 130.8mAhg^{-1} of LiFePO_4/C to 149.8mAhg^{-1} of $\text{LiFePO}_4/\text{C}+\text{Ag}$ cathodes. EIS measurements show that the Ag modification slightly decreases the charge transfer resistance of LiFePO_4/C , and enhances its lithium ion diffusion rate.

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REFERENCES

1. A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* **144**, 1188, (1997).
2. J. Kim, G. Cheruvally, J. Choi et al. *J. Power Sources*. **166**, 211, (2007).
3. S.T. Myung, S. Komaba, N. Hirotsaki et al. *Electrochim. Acta*. **49**, 4213, (2004).
4. H. Liu, J. Xie, K. wang. *J. Alloys Compd.* **459**, 521, (2008).
5. J. Lee, A.S. Teja. *Mater. Lett.* **60**, 2105, (2006).
6. R. Dominko, M. Gaberscek, M. Bele et al. *J. Eur. Ceram. Soc.* **27**, 909, (2007).
7. R. Dominko, M. Gaberscek, M. Bele et al. *J. Power Sources* **119-121**, 770, (2003).
8. H. C. Shin, W.I. Cho, H. Jang. *Electrochim. Acta* **52**, 1472, (2006).
9. C. Lai, Q. Xu, H. Ge et al. *Solid State Ionics* **179**, 1736 (2008).
10. M.R. Roberts, G. Vitins, J.R. Owen *J. Power Sources*. **179**, 754, (2008).
11. X.Q. Qu, G.C. Liang, J.S. Liang et al. *Chin. Chem. Lett.* **19**, 345, (2008).
12. D. Shanmukaraj, G.X. Wang, R. Murugan et al. *Mater. Sci. Eng., B* **149**, 93, (2008).
13. K.S. Park, J. T. Son, H.T. Chung et al. *Solid State Commun.* **129**, 311, (2004).
14. C. H. Mi, Y. X. Cao, X.G. Zhang et al. *Powder Technol.* **181**, 301, (2008).
15. L.J. Fu, H. Liu, C. Li et al. *Solid State Sci.* **8**, 113, (2006).
16. X.L. Li, F.K. Kang, X.D. Bai et al. *Electrochem. Commun.* **9**, 663, (2007).
17. F.Gao, Z.Y. Tang. *Electrochim. Acta* **53**, 5071, (2008).