High rate performance of LiFePO$_4$ cathode materials co-doped with C and Ti^{4+} by microwave synthesis

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Abstract. Nanostructured LiFePO$_4$ powder with a narrow particle size (ca. 100 nm) for high rate lithium-ion battery cathode application was obtained by microwave heating and using citric acid as carbon source. The microstructures and morphologies of the synthesized materials were investigated by X-ray diffraction and scanning electron microscope while the electrochemical performances were evaluated by galvanostatic charge–discharge. The carbon coating and Ti^{4+} could improve the conductivity both between the LiFePO$_4$ particles and the intrinsic electronic conductivity. The LiFePO$_4$ doped with 5% C and 1% Ti^{4+} resulted in a specific capacity of 114·95 mAh·g^{-1} and 102·4 mAh·g^{-1} at discharge rates of 0·3C and 1C, respectively, and the cycle performance is very good.

Keywords. LiFePO$_4$; co-doping; microwave heating; high rate discharge.

1. Introduction

Lithium iron phosphate (LiFePO$_4$) has been identified as an interesting cathode material for lithium-ion batteries since it was first proposed by Padhi *et al* (1997). This material has many advantages of low cost, non-toxicity and thermal stability in the fully charged state. In addition, LiFePO$_4$ has a large theoretical capacity of 170 mAh/g and good cycle stability (Andersson 2001; MacNeil 2002; Takahashi 2002). However, it is difficult to utilize the full theoretical capacity at useful rates due to the low intrinsic electronic conductivity (10^{-8} to 10^{-10} S/cm) of LiFePO$_4$. In order to overcome this drawback, conductive agent coating is used to enhance the electronic conductivity. Carbon coating is a common method to overcome the limited rate capacity because the dispersed carbon provides pathways for electron transference, resulting in improvement of the conductivity and electrochemical properties (Huang 2001; Spong 2005; Zaghib 2005). For example, Yamada (2001) has shown that the control of particle size through control of the synthesis temperatures with addition of carbon is pivotal for assuring the high performance of the LiFePO$_4$ cathode material. On the other hand, small metal particles such as Cu, Ag (Park 2004), and conductive polymers are also used as coating materials. Chung *et al* (2002, 2003) reported that the electronic conductivity of LiFePO$_4$ could be enhanced by a factor of about 10^8 (10^{-2} S cm^{-1}) by doping supervalent cations delivering specific capacity of ~140 mAh g^{-1} at 0·1C rate. Nevertheless, the high rate capacity needs further enhancement to fulfil ever-increasing demand for batteries applying to current and future portable electronic devices and electrical vehicles.

In a word, co-doped LiFePO$_4$ with carbon and metallic ion is a promising way to reinforce the electronic conductivity of LiFePO$_4$. It could improve the conductivity both between the LiFePO$_4$ particles and the intrinsic electronic conductivity. This method has attracted attention of only a few researchers. Here, we report firstly enhancing high rate performance of the LiFePO$_4$ electrode by doping C and Ti^{4+} simultaneously using citric acid as carbon source via microwave synthesis.

2. Experimental

Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O and NH$_4$H$_2$PO$_4$ were used as starting materials for LiFePO$_4$. Stoichiometric amounts of Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O and NH$_4$H$_2$PO$_4$ were dissolved in ethanol with different amounts of citric acid as carbon sources and TiO$_2$ (the composition of the samples is given in table 1), followed by ball-milling for 7 h and drying. The obtained mixture was pressed into pellets and then put inside a quartz crucible that was filled with active carbon. The quartz crucible was put in the middle of a domestic microwave oven and microwaves were irradiated at 90 W for 35 min. During treatment, carbon generated heat through the direct absorption of microwave energy and made a reductive atmosphere together with sucrose decomposition. After microwave irradiation, LiFePO$_4$/(C + Ti^{4+}) was obtained.

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Table 1.   Compositions of the samples.

| A_1	A_2	A_3	A_4	B	C
3% C + 1% Ti^{4+}	3% C + 2% Ti^{4+}	5% C + 1% Ti^{4+}	5% C + 2% Ti^{4+}	5% C	1% Ti^{4+}

The electrode was prepared by using 80% of LiFe PO$_4$/C + Ti^{4+} active material, 10% acetylene black and 10% polyvinylidene difluoride (PVDF) as binder. After being dissolved in *n*-methyl pyrrolidinone (NMP) solvent, the obtained slurry was then cast on the Al current collector and dried for 12 h in an oven at 100°C. The resulting electrode film was subsequently pressed and punched into a circular disc. The electrode films were preserved in an argon-filled glove box. The coin cell was fabricated using the lithium metal as a counter electrode. The electrolyte used consisted of a 1 M solution of LiPF$_6$ in a mixture 1 : 1 by volume of ethylene carbonate (EC) and diethyl carbonate (DEC). The separator (Celgard 2400) was soaked in an electrolyte for 24 h prior to use. 2430 coin-type cell assemblies were performed in the argon-filled glove box by keeping both oxygen and moisture levels < 1 ppm. The cells were charged and discharged galvanostatically between 2·5 and 4·2 V (vs Li/Li$^+$) at room temperature by means of a Neware battery tester. The rest time between charging and discharging was 1 min.

The structure of the powders was examined by X-ray diffraction analysis and JADE5 software. The morphology and the particle size of the powders were observed by transmission electron microscope and scanning electron microscope.

3.   Results and discussion

3.1   *X-ray diffraction analysis*

The X-ray diffraction spectrum of the LiFePO$_4$/(C + Ti^{4+}) material is shown in figure 1, and the standard pattern is also given for comparison. During the synthesis process, electronic conductive carbon was formed from the decomposition of the citric acid, but no peak corresponding to carbon is visible in the X-ray diffraction pattern of LiFePO$_4$/(C + Ti^{4+}). It can be concluded that the presence of carbon is in a disordered or amorphous state. Also there are no obvious impurity peaks of Ti^{4+} and other unexpected impurity phases such as Fe^{3+}. It is shown from figure 1 that the X-ray diffraction pattern of the sample is in good agreement with standard LiFePO$_4$ with an olive structure of *Pnma* space group. Hence, LiFePO$_4$/(C + Ti^{4+}) composites have been obtained by microwave synthesis within a short time. The relative small radius ion tends to occupy the *M*1 (Li) site in olivines, especially at low doping levels, based on Chung' theory (Chung 2002; Guo 2005; Xie 2006). It is, therefore, believed that Ti ions occupy the *M*1 sites because
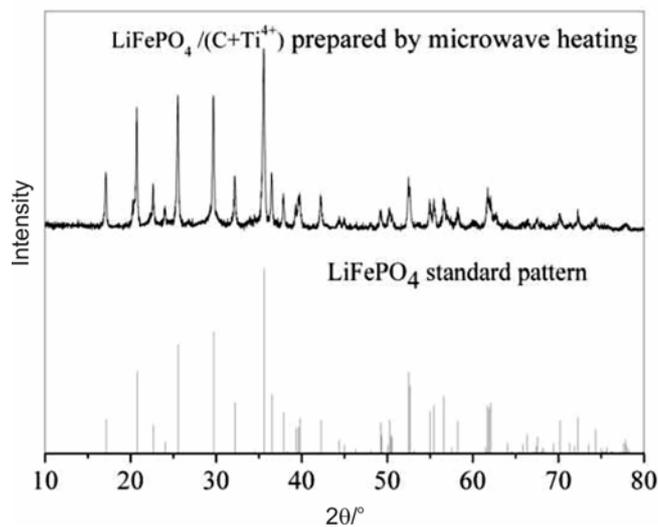
Figure 1.   XRD pattern of the sample.

the Ti^{4+} ion has an ionic radius smaller than that of Li$^+$, which is also indirectly proved by X-ray diffraction patterns. Ti^{4+} occupation of *M*1 sites will create a cation-deficient compound, Li$_{1-x-y}$Ti$_y$FePO$_4$, with a certain *M*1 vacancy concentration, *y*, for charge compensation. It will definitely enhance the electronic conductivity of the materials.

3.2   *Morphology*

Scanning electron microscopic and transmission electron microscopic pictures of the synthesized composites are given in figure 2. Scanning electron microscope indicates that the particle distribution is uniform and there is almost no coagulation. Two distinctive morphologies, viz. spherical particles and cotton-like particles, are observed in the transmission electron microscope image. These particles are identified as LiFePO$_4$ and amorphous carbon, respectively. Almost all the particles of LiFePO$_4$ are connected by amorphous carbon, and the grain size has an average diameter of about 100 nm. This is in agreement with the crystallite size (*D*) calculated from the Scherrer equation

$$\beta\cos(\theta) = k\lambda/D,$$

where β is the full-width-at-half-maximum (FWHM) of the X-ray diffraction peak and *k* a constant (0·9).

3.3   *Electrochemical properties*

The initial discharge curves of series *A* at 0·1C rate are given in figure 3. It clearly shows the initial discharge

capacity order of series A is $A_3 > A_1 > A_4 > A_2$. A_3 delivers the highest capacity of $138 \cdot 52$ mAh·g^{-1}, for A_1 and A_2 samples carbon content is too low to form an effective conductive network to connect the LiFePO₄ particles, and for A_2 and A_4, the higher Ti^{4+} content could lead to capacity loss due to its inertia for Li$^+$ storage. So 5% C and 1% Ti^{4+} is a proper content to enhance the electrochemi-
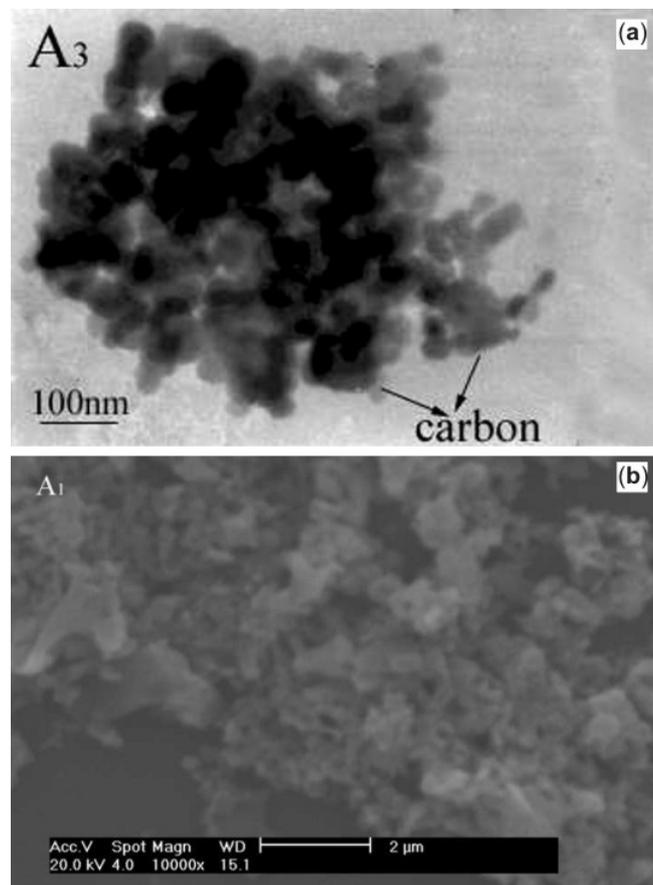
cal properties. Figure 4 shows the initial discharge curves of samples A_3, B and C. It validates further improvement

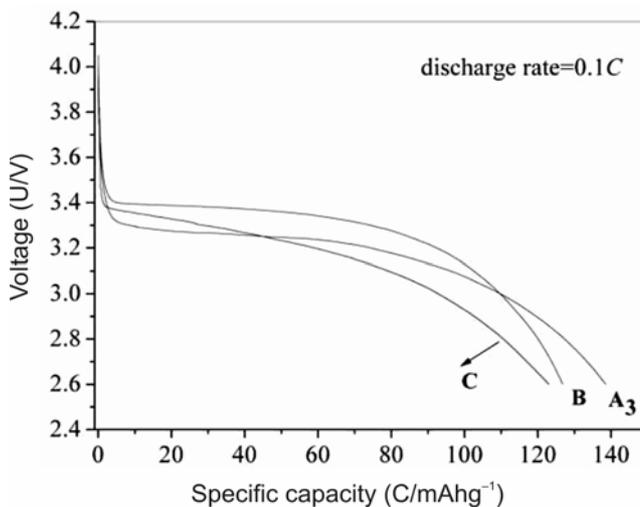**Figure 2.** (**a**) TEM photograph of A_3 sample and (**b**) SEM photograph of A_1 sample.

Figure 4. Initial discharge curves of samples A_3, B and C at $0 \cdot 1$C rate.
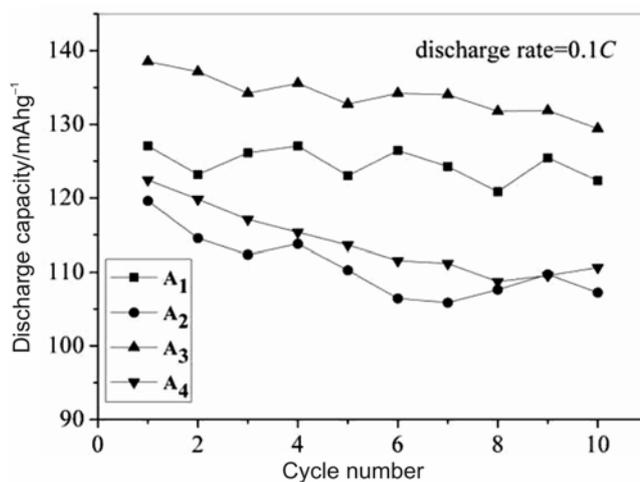
Figure 5. Cycle performance curves of series A.

Figure 3. Initial discharge curves of A series.
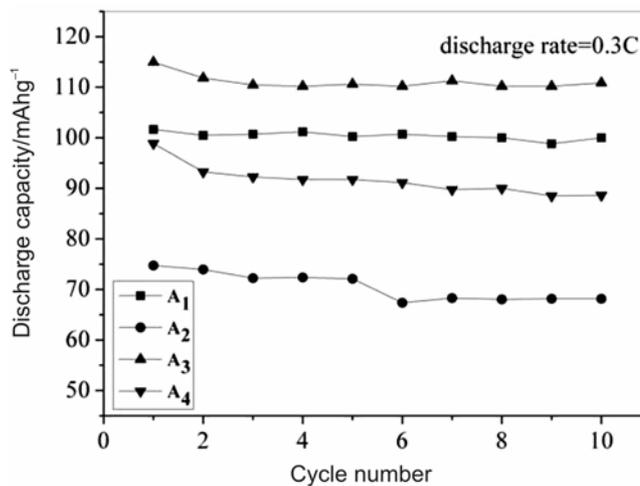

Figure 6. Cycle performance curves of A series at $0 \cdot 3$C rate.

of the electrochemical properties by doping C and Ti^{4+} at the same time due to the small particle size (ca. 100 nm) together with the cation-deficiency created by the Ti^{4+} occupation.

Cycle performance curves of series A at 0·1C rate are shown in figure 5. The capacity loss ratio is 3·69% after 10 cycles of sample A_3, it presents the best cycle performance of all the samples. However, it is not so good as the cycle performance of sample A_3 at 0·3C rate, which can be seen from figure 6. The initial discharge capacity at 0·3C and 1C rates are 114·95 mAh·g^{-1} and 102·4 mAh·g^{-1}, respectively, as is shown in figure 7. Polarization happens during the course of charging and discharging, due to the poor lithium ion diffusion at the high-rate discharge.

Figures 6 and 8 are the cycle performance curves of A series at 0·3C and 1C rates, respectively. The capacity loss ratio after 10 cycles discharging at 0·3C rate is 3·54% compared to that of 3·69% corresponding to 0·1C rate. No obvious capacity decrease is observed and stable
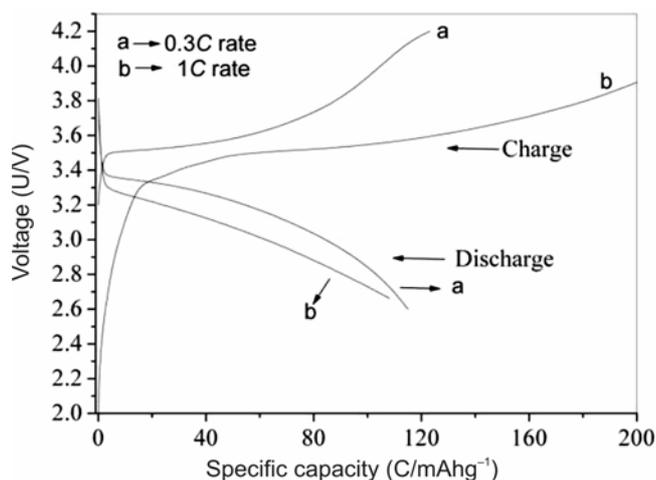

Figure 7. Initial charge and discharge curves of sample A_3.
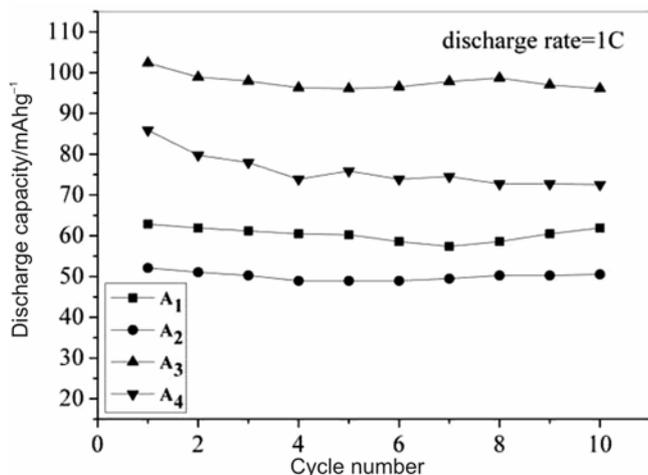

Figure 8. Cycle performance curves of A series at 1C rate.

cycle life is present at discharge currents of both 0·3C and 1C for sample A_3. The good cycle behaviour is mainly attributed to the nanometric particle size and the enhancement of the electronic conductivity by the lattice doping together with uniform carbon coating. The carbon coating here possesses a triplex functionality: it serves as an electronic wire supplying electrons to the whole surface area of active material. Also, it is permeable for Li^+ ions through the carbon coating direction; last but not least, it minimizes the size and agglomeration of the phosphate particles. In addition, a proper amount of Ti^{4+} doping creates some cation-deficiency to further enhance the electronic conductivity. Based on the above reasons, the cycle performance is reinforced significantly.

4. Conclusions

High rate performance of LiFePO$_4$ cathode powders were synthesized by microwave heating with a domestic microwave oven for a short time. Nanostructured LiFePO$_4$ doped with 5% C and 1% Ti^{4+} delivered a specific capacity of 114·95 mAh·g^{-1} and 102·4 mAh·g^{-1} at discharge rates of 0·3C and 1C, respectively, which is a significantly better rate performance compared to the phosphate obtained by single doping of either of them. Besides, the cycle performance being very good, no obvious capacity decrease is observed and stable cycle life is present at discharge currents of both 0·3C and 1C. These results show that the rate performance of LiFePO$_4$ cathode can be enhanced by changing the particle size of LiFePO$_4$ particles and co-doped with proper amount of metal ion and electric carbon.

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