



Electrochemical Performance of Lithium Iron Phosphate by Adding Graphite Nanofiber for Lithium Ion Batteries

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Received March 6, 2012; Revised May 23, 2012; Accepted May 29, 2012

Olivine type LiFePO_4 cathode material was synthesized by solid-state reaction method including one-step heat treatment. To improve the electrochemical characteristics, graphite nanofiber (GNF) was added into LiFePO_4 cathode material. The structure and morphological performance of LiFePO_4 were investigated by X-ray diffraction (XRD); and a field emission-scanning electron microscope (FE-SEM). The synthesized LiFePO_4 has an olivine structure with no impurity, and the average particle size of LiFePO_4 is about 200~300 nm. With graphite nanofiber added, the discharge capacity increased from 113.43 mAh/g to 155.63 mAh/g at a current density of 0.1 mA/cm². The resistance was also significantly decreased by the added graphite nanofiber.

Keywords: LiFePO_4 , Solid-state, Graphite Nanofiber

1. INTRODUCTION

Lithium ion batteries are widely used in mobile phones, notebook computers, electronic equipment, electric vehicles and other applications. The cathode material plays a decisive role in determining the capacity and life time of the battery. Among cathode materials of lithium ion batteries, LiFePO_4 with olivine structure has attracted extensive attention due to a high theoretical specific capacity (~170 mAh/g), environmental friendliness, excellent thermal stability, and low cost. However, its weakness in diffusion limitation and poor electrical conductivity lead to poor electrochemical performance and makes it difficult to be used as a cathode material for commercial lithium ion batteries [1].

In recent years, many researchers have improved the electrochemical performance by coating with carbon [2-4] or preparing suitable procedures to minimize the particle size of the material [5-8], or doping supervalent metal ions to Li sites [9] or Fe sites [10, 11]. As an active additive, graphite nanofiber (GNF)

can be added to LiFePO_4 cathode material. As a carbon source, it can possibly improve the electrochemical characteristics of LiFePO_4 through increasing the electronic conductivity [12,13]. Furthermore, various synthesis methods have been developed to prepare LiFePO_4 materials. Among these methods, olivine-type LiFePO_4 can be synthesized by a solid-state reaction method. The solid-state reaction is widely adopted for synthesis of pure crystalline olivine phase LiFePO_4 [14].

In this study, LiFePO_4 cathode material was synthesized by solid-state reaction method followed by one-step heat treatment. To improve the electrochemical characteristics, graphite nanofiber (GNF) was added to the LiFePO_4 cathode material. The electrochemical characteristics of $\text{LiFePO}_4/\text{Li}$ cells were analyzed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge performance at 25 °C.

2. EXPERIMENTS

LiFePO_4 was prepared from starting materials of Li_2CO_3 (Aldrich, 99.0%), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99.0%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich, 99.999%). The starting materials were mixed in a molar ratio for Li/Fe/P=1:1:1 by ball-milling with N-methyl-2-pyrrolidone (NMP) solvent at 300 rpm for 24 h. After that, the obtained LiFePO_4 slurry was dried at 90 °C for 12 h in air. The prepared

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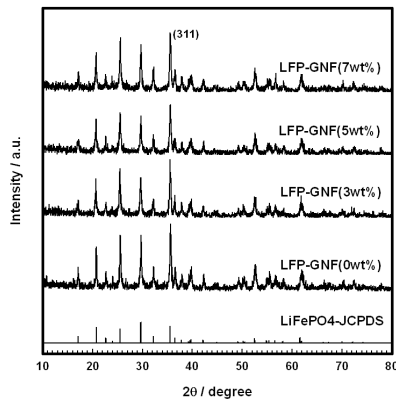


Fig. 1. XRD pattern for LiFePO_4 and LiFePO_4 -GNF.

Table 1. The unit cell parameters of LiFePO_4 and LiFePO_4 -GNF.

Specimen	a (nm)	b (nm)	c (nm)	V (nm^3)
LiFePO_4	0.6036	1.0313	0.4708	0.2931
LFPG(3 wt.%)	0.6007	1.0336	0.4690	0.2912
LFPG(5 wt.%)	0.5963	1.0329	0.4722	0.2908
LFPG(7 wt.%)	0.6010	1.0327	0.4696	0.2915

LiFePO_4 was pelletized then calcined at 650°C for 5 h in a nitrogen atmosphere, then ground and ball-milled with NMP at 300 rpm for 6 h. Lastly, it was dried at 90°C for 24 h in air and ground into powder.

In order to improve the low electronic conductivity of LiFePO_4 , 3 wt.%, 5 wt.%, and 7 wt.%, amounts of graphite nanofiber (GNF) (Diameter: ~ 300 nm, Length: ~ 30 μm , purity: 90%) were respectively added to different samples.

The cathode electrode was fabricated onto Al foil using a homogeneous slurry. The slurry was prepared with 70 wt.% of the synthesized LiFePO_4 (LFP) or LiFePO_4 -GNF (LFPG), 25 wt.% carbon black (SP-270), and 5 wt.% polyvinylidene di-fluoride (PVDF) binder, which was dissolved in NMP solvent. The slurry was spread onto the Al foil. After drying at 90°C and being roll pressed, the area of the coated cathode electrode was cut to 2×2 cm^2 . The electrodes were dried in a vacuum oven under a vacuum pressure of 760 Torr at 110°C for 24 h.

The LFP/Li cell and LFPG/Li cells were assembled in an argon filled glove box using lithium metal foil as the anode electrode. Polypropylene film (Celgard 2500) was used as the separator and a solution of 1M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) was used as the electrolyte.

The samples were charged and discharged over a voltage range of 2.5–4.0 V using a current density of 0.1 mA/cm^2 for both processes by WBCS-3000 8ch substation. Cyclic voltammetry (CV) measurements were performed using an IM6 instrument at a 0.1 mV/s scanning rate. AC impedance measurement was performed over the frequency range of 2 MHz to 10 mHz.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the LiFePO_4 and LiFePO_4 -GNF samples. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure with a space group of $Pnma$, which is almost the same as the one that is listed in the X-ray diffraction data file (JCPDS card). No impurities such as Fe_2O_3 , $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ or Li_3PO_4 were found in the LiFePO_4 or LiFePO_4 -GNF powders, as indicated by the lack of other peaks found in the main peaks of the LiFePO_4 . There was also no

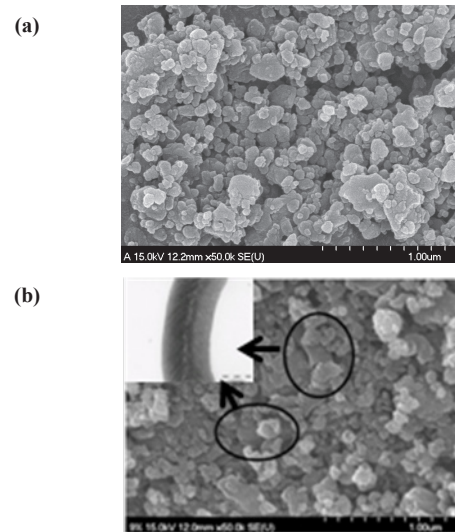


Fig. 2. FE-SEM image of LiFePO_4 (a) and LiFePO_4 -GNF (b).

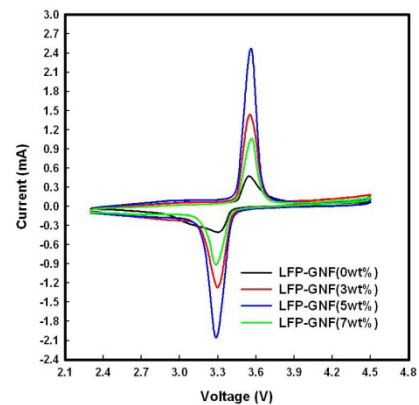


Fig. 3. 50th Cyclic voltammogram of LFP/Li cell and LFPG/Li cells at a scan rate of 0.1 mV/s .

evidence for crystalline carbon, nor were there any amorphous peaks present. This is undoubtedly due to the small amount of carbon present and the thinness of the layer on the LiFePO_4 and LiFePO_4 -GNF.

The unit cell parameters of the prepared samples are given in Table 1, which was calculated in the XRD analysis. The cell parameters for the LiFePO_4 sample are $a=0.6036$ nm, $b=1.0313$ nm, $c=0.4708$ nm, and the unit cell volume is $V=0.2931$ nm^3 . The unit cell parameters of LiFePO_4 -GNF(5 wt.%) are $a=0.5963$ nm, $b=1.0329$ nm, $c=0.4722$ nm, and $V=0.2908$ nm^3 . From Table 1, it can be seen that the lattice parameter changes slightly with added GNF. Meanwhile, we can clearly see from the phenomenon in Fig. 1 that the diffraction peaks (311) of the samples gradually shift right when GNF is added, which means the unit cell volume minimizes gradually according to the Prague equation. The volume contraction of the added samples might be due to the coexistence of lithium ion vacancies caused by added GNF [1].

FE-SEM was tested to confirm the particle size and image of LiFePO_4 and LiFePO_4 -GNF samples. Figure 2 show the FE-SEM images of LiFePO_4 and LiFePO_4 -GNF. The figure shows that the particle size of all the samples is about 200–300 nm. For LiFePO_4 , small particle size is important for enhancing the electrochemical properties [15]. In particles with a small diameter, the lithium ions may diffuse over smaller distances between the surfaces and center during lithium intercalation and de-intercalation. And as

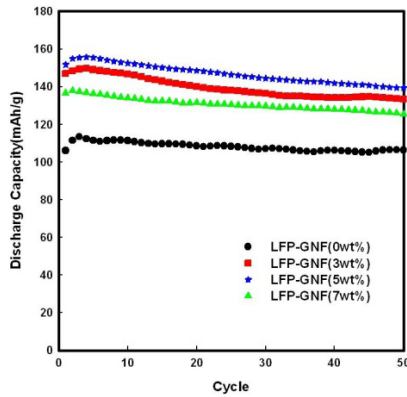


Fig. 4. Discharge capacity of the LFP/Li cell and LFPG/Li cells.

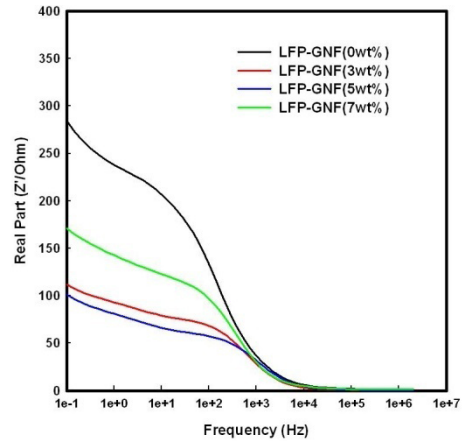


Fig. 6. Bode diagram of LFP/Li cell and LFPG/Li cells at 25 °C

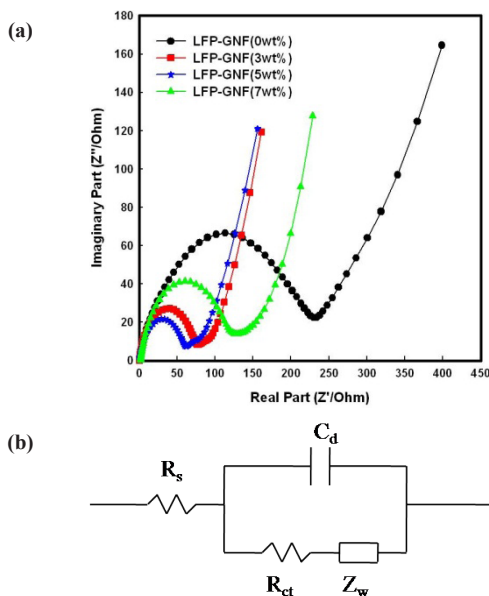


Fig. 5. 10th impedance spectra of LFP/Li cell and LFPG/Li cells at 25 °C (a) and Equivalent circuit of the impedance spectra (b).

shown in Fig. 2(b), the typical morphology of tubular graphite nanofiber was observed (the image of the graphite nanofiber is shown in the inset, which is on the left). It can be seen that the LiFePO₄ particles are homogeneously adhered to the surface of the graphite nanofiber. The bridging graphite nanofiber can form an effective conducting network. At the same time, a porous structure between LiFePO₄ and graphite nanofiber was formed by the random hybrid composite, which can facilitate the penetration of the electrolyte to the surface of active materials. As a result, LiFePO₄-GNF has a superior rate capability and higher reversible capacities in comparison with the LiFePO₄ [13].

Figure 3 shows cyclic voltammograms of the LFP/Li cell and LFPG/Li cells taken at a scan rate of 0.1 mV/s, between 2.3–4.5 V at the 50th cycle. As for CV, the voltage difference between the oxidation peak and reduction peak is an important parameter to evaluate the electrochemical reaction reversibility [16]. All of the cells' oxidation and reduction peaks appear at about 3.6 V and 3.3 V. The voltage difference between the oxidation and reduction peak is 0.3 V. Furthermore, the CV of the LFPG/Li cells shows more symmetry and a sharper shape of oxidation and reduction peaks, which indicates better electrochemical activity [17]. Particular, the intensity of the LFPG (5 wt.%) cell peak is highest. The well-defined peaks and smaller potential peak separation

indicate higher electrochemical reactivity and lower ohmic resistance for the LFPG(5 wt.%) /Li cell.

Figure 4 shows the discharge curves of the LFP/Li cell and LFPG/Li cells at a current density of 0.1 mA/cm². The initial discharge capacity of the LFP/Li cell is 106.03 mAh/g. The highest capacity, which appears in the 3rd cycle, is 113.43 mAh/g. After 50 cycles, the discharge capacity is retained 106.32 mAh/g. To improve the capacity of LiFePO₄, graphite nanofiber was added in amounts of 3 wt.%, 5 wt.%, 7 wt.% to LiFePO₄. The initial discharge capacity of LFPG(5 wt.%) /Li cell is 151.73 mAh/g. The highest capacity is achieved in the 4th cycle at 155.63 mAh/g. After 50 cycles, the discharge capacity is retained at 139.45 mAh/g. These results are the same as the FE-SEM and CV test results, which were analyzed above. In addition, compared to the LFP/Li cell, the discharge capacity of the LFPG(5 wt.%) /Li cell increased by 37.20%.

Figure 5(a) shows the impedance performance of the LFP/Li and LFPG/Li cells at 25 °C. The frequency range was from 2 MHz to 10 mHz, and amplitude was 5 mV. The AC impedance response of the cells consisted of a broad semicircle in the high-middle frequency region and a sloping line in the low frequency region. The impedance spectra can be interpreted on the basis of an equivalent circuit with ohmic resistance (Rs), charge-transfer resistance (Rct), capacitance of the double layer (Cd), and Warburg impedance (Zw), as indicated in Fig. 5(b). It has been recognized that the high-middle frequency semicircles might correspond to the charge-transfer impedance that resulted from the electrochemical reaction at the electrode and electrolyte interface. The sloping line in the low frequency region is attributed to the Warburg impedance, which is associated with lithium ion diffusion in the LiFePO₄ electrode. In the 10th cycle, the resistance of the LFP/Li cell is 280 Ω, and the resistance of the LFPG(5 wt.%) /Li cell is 100 Ω, which are shown in figure 3.6. It is obvious that the resistance decreased after adding the graphite nanofibers.

4. CONCLUSIONS

In this research, LiFePO₄ cathode material with olivine structure was synthesized by solid-state method followed by one-step heat treatment. To improve the electrochemical characteristics of LiFePO₄, graphite nanofiber was added, and the morphology properties were analyzed. During the lithium-ion intercalation and de-intercalation processes, the lithium-ion diffusion coefficient was boosted after adding GNF. Impedance results show that the conductivity was enhanced by the added GNF, because

the charge-transfer resistance was significantly reduced. Cyclic voltammetry results indicated that the electrode redox reaction reversibility was excellent due to adding GNF. The LFPG(5 wt.%) / Li cell exhibited superior high discharge capacity and cycling stability at 25°C. The results demonstrate that a feasible route of adding GNF by solid-state reaction has been offered.

ACKNOWLEDGMENTS

The following are results of a study on the “Human Resource Development Center for Economic Region Leading Industry” Project, supported by the Ministry of Education, Science & Technology (MEST) and the National Research Foundation of Korea (NRF).

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