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Observation on Ferric Pyrophosphate and New Inquiry on Mechanisms of Capacity Degradation in Lithium Iron Phosphate Cathode Materials

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ABSTRACT

The hierarchical carbon-coated lithium iron phosphate ($LiFePO_4$) nano-grain microspheres are prepared by chemical co-precipitation method. The microstructure and cycling performance are compared for samples treated at 975 K and 1025 K. Transmission electron micrograph (TEM) analysis confirms the existence of ferric pyrophosphate phase of the general formula $Fe_4(P_2O_7)_3$. Reasons for the formation of the crystalline $Fe_4(P_2O_7)_3$ phase are intensively discussed. It is considered that a little amount of $Fe_4(P_2O_7)_3$ phase has no distinct detrimental effect on the cycling capacity of samples. Although there is a big decrease from 132 to 74.5 mAh/g in discharge capacity at a current rate of 1C for the sample treated at 975 K from 400 to 500 cycles. The capacities for the sample were observed to be recovered to its theoretical value in discharge at a current rate of 0.1C after 500 cycles. It is demonstrated that the degradation behavior for the sample treated at 975 K is attributed to the increase of diffusion resistance of the lithium ions into the bulk of $LiFePO_4$ electrode materials, which is not reported before in the literatures.

1. Introduction

Byoungwoo Kang [1] declared in *Nature* in 2009 that they created a glassy pyrophosphate coating on the surface of nanoscale $LiFePO_4$ and showed extremely high rate performance by this material for the first time. However, it is not clear why and how the $Fe_4(P_2O_7)_3$ phase formed.

It was declared in the literature [2–4] that iron traces are found on the surface of the anode and on the separator. Therefore, the degree of capacity degradation was thought to have a direct correlation with the iron content [3,5]. It was also believed that these iron residues are etched from the active $LiFePO_4$ particles by the acidic electrolyte solution. For example, it was indicated by Hui-Fen Jin et al. [3] that the presence of impurity phases such as $Fe_4(P_2O_7)_3$ lead to a higher rate of iron dissolution and faster capacity fade.

In this paper, however, a little amount of crystalline $Fe_4(P_2O_7)_3$ was proven to be existent in our samples. The reasons on its formation in our samples are intensively discussed. It showed hardly any deteriorative effect on the cycling capacity of the cathode. The degradation for discharge capacity was detected only after 400 cycles for the sample prepared at 975 K. More interestingly, the losing capacities of this sample can be recovered at the current rate of 0.1C. The capacity degradation behavior for this sample was investigated. It provides a new spotlight on mechanisms of capacity degradation in $LiFePO_4$ cathode materials.

2. Experimental

2.1. Preparation and characterization

The precursor powders of $LiFePO_4$ were prepared by chemical co-precipitation method using stoichiometric LiH_2PO_4 (Alfa, 97%), $FeSO_4 \cdot 7H_2O$(Alfa, 99%) and $LiOH \cdot H_2O$ (Alfa, 98%) as starting materials. The suspension was stirred at 0–4 °C for about 30 min and aged for about 2 h. The final precursor powder product was then filtered, washed with deionized water and ethanol, and dried at 100 °C in a vacuum oven for 2 h. To obtain $LiFePO_4$/C composites, the precursor powders were well mixed with glucose and treated at 975 K and 1025 K at Ar-4%H_2 atmosphere.

The crystal structure of the precursor powder and the $LiFePO_4$/C composites were investigated by X-ray diffraction (XRD) with Cu Kα radiation on a D8 ADVANCE XRD instrument. FTIR absorption spectra were recorded with a Fourier-transform interferometer

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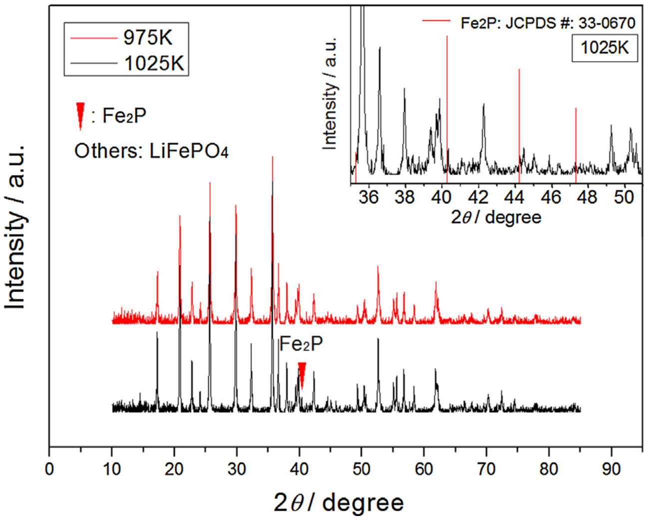

Fig. 1. The XRD patterns of the $LiFePO_4$/C microspheres sintered at 975 K and 1025 K. Insets: The magnification of XRD patterns with 2 theta from 35–51 °for the sample treated at 1025 K.

(Shimadzu FT-IR800) over a wavenumber range of 500–1300 cm^{-1} at a spectral resolution of 2 cm^{-1}. The morphology and dimension of the $LiFePO_4$ samples were characterized with a JSM-6700 scanning electron microscope (SEM) and Transmission Electron Microscopy (TEM). The microstructure of the sample was determined using high-resolution transmission electron microscopy (HRTEM) on a JEM-2100 apparatus with an acceleration voltage of 200 kV. Phase and structure of the material were monitored using selected area electron diffraction (SAED).

2.2. Electrochemical measurements

The working electrodes were prepared by 86 wt.% $LiFePO_4$/C composite material, 7 wt.% carbon black and 7 wt.% polyvinylidene fluoride (PVDF) binder. The working electrodes were pasted and pressed on an aluminum foil as the current collector. The cells were assembled in an argon-filled glove box using lithium metal as an anode, non-aqueous electrolyte (1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate) and Celgard 2325 as separator. For comparison of the cells, the addition amounts of electrolyte for both samples are equivalent and Li plates acted as anodes are totally the same. The loading density and the electrode area (footprint) for the cathodes are 3.36 mg/cm^2 and 1.13 cm^2, respectively. The cells were galvanostatically charged and discharged in the voltage range of 2.0–4.3 V at room temperature using Neware BTS Device. Eelectrochemical impedance spectroscopy (EIS) was performed from 100 kHz and 10 mHz using Chenhua CHI750.

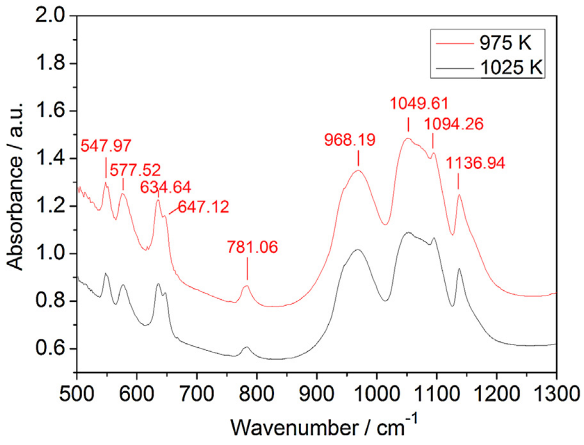

Fig. 3. The FTIR absorption spectra of samples sintered at 975 K and 1025 K over a wavenumber range of 400–1250 cm^{-1} at a spectral resolution of 2 cm^{-1}. The peaks distributed around 781 cm^{-1} in the energy gap can be attributed to the crystalline phase $Fe_4(P_2O_7)_3$.

3. Results and discussion

Fig. 1 shows the XRD pattern of the $LiFePO_4$/C composites treated at 975 K and 1025 K. Inset is the magnification of XRD pattern with 2 theta from 35–51° for the sample treated at 1025 K. The diffraction peaks can be well indexed to be $LiFePO_4$ with an orthorhombic olivine structure (JCPDS card No. 40-1499) for both samples. The diffraction peaks of $LiFePO_4$ are strong and narrow, indicating the high crystallinity of the $LiFePO_4$ sample. The Fe_2P conductive phase (JCPDS card No. 33-0670) appears at 1025 K as indicated in the inset of Fig. 1 due to a higher sintering temperature at a reducing atmosphere.

Fig. 2 displays the $LiFePO_4$ microspheres in the size of 1–2 micron by SEM, showing that they are hierarchically constructed with $LiFePO_4$ nano-grains, while these nano-grains are in size of about 20–100 nm in diameter and attached side by side in an ordered fashion.

Fig. 3 shows the FTIR absorption spectra of the $LiFePO_4$/C composites over a wavenumber range of 500–1300 cm^{-1} at a spectral resolution of 2 cm^{-1}. The FTIR probes the structure of $LiFePO_4$ at the molecular scale, accessing the vibration modes of the ions, primarily associated to the motion of iron and phosphate. Since the vibration characteristic of the P–O–P bridging of P_2O_7 unit is right between 700 and 900 cm^{-1}, FTIR is quite a sensitive tool to detect any pyrophosphate impurity. From FTIR absorption

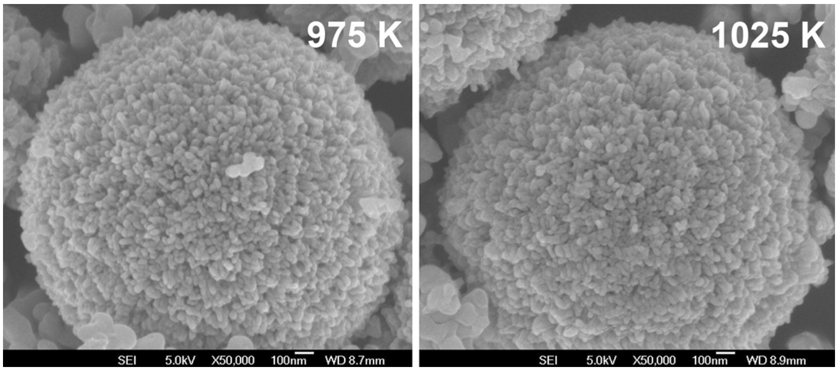

Fig. 2. The morphology of the $LiFePO_4$/C microspheres sintered at 975 K and 1025 K.