Charge/Discharge Properties of Carbon Added $LiFeO_4$

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Abstract : Phospho-olivine $LiFePO_4$ cathode materials were prepared by hydrothermal reaction. Carbon black was added to enhance the electrical conductivity of $LiFePO_4$. The structural and morphological performance of $LiFePO_4$ and $LiFePO_4$-C powders were characterized by X-ray diffraction (XRD) and FE-SEM. $LiFePO_4$/SPE/Li and $LiFePO_4$-C/SPE/Li cells were characterized electrochemically by charge/discharge experiments. The results showed that the discharge capacity of $LiFePO_4$/SPE/Li cell was 103 mAh/g at the first cycle. The discharge capacity of $LiFePO_4$-C/SPE/Li cell with 5 wt% carbon black was the largest among $LiFePO_4$-C/SPE/Li cells, 126 mAh/g at the first cycle and 123 mAh/g after 30 cycles, respectively. It was demonstrated that cycling performance of $LiFePO_4$-C/SPE/Li cell with 5 wt% carbon black was better than that of $LiFePO_4$/SPE/Li cell.

Key Words : $LiFePO_4$, Hydrothermal, Carbon, Properties

1. Introduction

Recently, lithium secondary batteries have been widely used in devices such as electrical appliances due to high energy density, perfect cyclic performance and excellent capacity retention. The active cathode material, such as $LixCoO_2$ or LiMnO2 which provide high potentials and high capacities over 150mAh/g. However, such as $LixCoO_2$ was a high cost material and not compatible with environment [1]. Since the pioneering works of Padhi et al., mixes ortho- phosphates $LiMPO_4$(M=Co, Ni, Mn, Fe) isostructural to olivine haver been intensively studies as lithium insertion cathode materials for the next generation of lithium secondary batteries[2-3]. The choice of the cathode material has high capacity that can be retained for up to long cycles and also low cost and eco-friendly materials. Among $LiMPO_4$ series of materials, $LiFePO_4$is a low cost material and highly compatible to the environment. However, it is difficult to attain its full capacity(170mAh g^{-1}), because its electronic conductivity is very low and diffusion of Li+ ion in the olivine structure is low [4-5].

In this paper, phosphor-olivine $LiFePO_4$ was prepared by hydrothermal reactionand carbon nanotube added for enhance the electrical conductivity of $LiFePO_4$.

2. Experimental

$LiFePO_4$ was prepared with the starting materials of Lithium hydroxide monohydrote ($LiOH \cdot H_2O$, 99.95%), Iron(II) sulfate heptahydrote ($FeSO_4 \cdot 7H_2O$, 99.99+%), Phosphoric acid crystals (H_3PO_4, 99.999+%) and L-Ascorbic acid ($C_6H_8O_6$, 99+%) in a molar ratio for Li:Fe:P =3:1:1. Addition of ascorbic acid as a reducing agent to the precursor was useful in prohibiting the conversion of $Fe^{2+}$to Fe^{3+} during the hydrothermal reaction and generation of α-Fe_2O_3 during the annealing process. The mixed solution was heated at 150℃ for 3h. After being cooled to room temperature, the solution was filtered to separate the precipitate powder, and the power was washed with ultrapure water and were parched for the vacuum drying at 100℃ for 1h. The obtained powder was dried and the dried powders were further dried at 400℃ in nitrogen atmosphere for 1h. In order to improve low electron conduction of $LiFePO_4$, carbon black(several weight percent) was added. The crystalline phases were identified with X-ray diffraction (XRD, Dmax/1200, Rigaku). The X-ray diffraction pattern was collected by a step-scanning mode in the range of 10-80° with a step time of 5°/min. The powder morphologies of electrodes before and after cycling were examined with a Hitachi S-4700 FE-SEM which had an accelerating voltage of 15 kV.

A composite electrode was prepared by mixing $LiFePO_4$, Sp270 and polyvinylidene fluoride (PVDF) in a weight ratio of 70:25:5.This mixture was coated onto an Al-foil, cut into 2cm2 sections and heated at 110℃ for 24h under vacuum. A lithium foil was used as an anode. The $25PVDFLiClO_4EC_{10}PC_{10}$ as SPE prepared by mixing of $LiClO_4$ and propylene carbonate (PC), ethylene carbonate (EC) in a mole ratio of 1:10:10, and polyvinylidenefluoride-hexafluoro propylene (kynar2801) was added. The coin type cell was fabricated for the electrochemical tests in a potential range of 2.5-4.3 V at a constant current density of 0.1 mA/cm^2.

3. Results and discussion

XRD patterns of $LiFePO_4$-C powders are shown in Fig. 1. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure (space group Pmnb), which are the same as the theoretical value. No impurity is found in all the $LiFePO_4$-C powders.

FE-SEM of $LiFePO_4$ and LiFePO4 with carbon black 5wt% are shown in Fig. 2. As caon be seen from Fig. 2(a), the average particla size of $LiFePO_4$ is around 200nm. It is shown from Fig. 2(b) the $LiFePO_4$ with carbon black 5wt% is around 150nm. The

smaller particles, which shorten the lithium ions diffusion distance between the surfaces and center during lithium intercalation and de-intercalation, are expected to contribute the enhanced electrochemical performance of the carbon bleack added $LiFePO_4$.

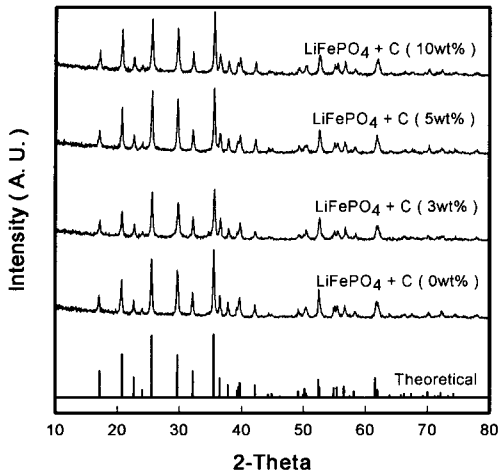

Fig. 1. XRD patterns of $LiFePO_4$ and $LiFePO_4$ with carbon black.

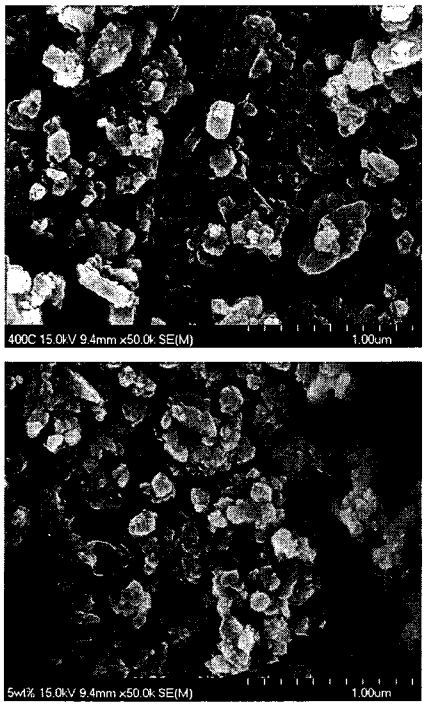

Fig. 2 FE-SEM images of (a) $LiFePO_4$ and (b) $LiFePO_4$ with carbon black 5wt%.

Cycling performance of $LiFePO_4$/SPE/Li and $LiFePO_4$-C(5wt%)/SPE/Li cells is shown in Fig. 3. As can be seen from Fig. 3, the discharge capacity of $LiFePO_4$/SPE/Li cell is 105 mAh/g at the first cycle. The initial discharge capacity of $LiFePO_4$ with 3 wt%, 5 wt% and 10 wt% carbon black is 126, 114 and 102 mAh/g, respectively. It is demonstrated that cycling performance of $LiFePO_4$-C/Li cell is better than that of $LiFePO_4$/Li cell and the discharge capacity is the largest when carbon content is 5 wt%.

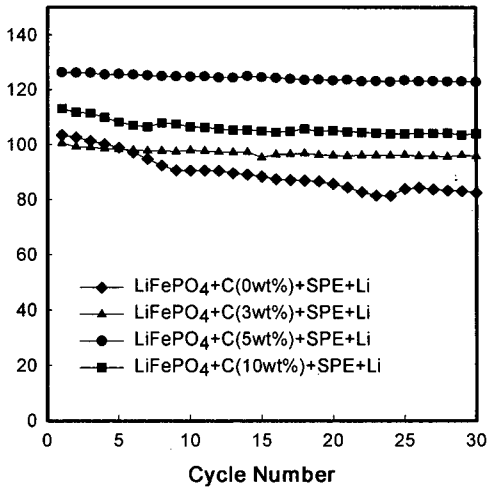

Fig.3. Cycling performance of $LiFePO_4$ added different amounts of carbon black.

4. Conclusions

Phospho-olivine $LiFePO_4$ cathode materials were prepared by hydrothermal reaction. Carbon black was added to enhance the electrical conductivity of $LiFePO_4$. The discharge capacity of $LiFePO_4$/SPE/Li cell is 105 mAh/g at the first cycle and with the carbon black 5wt% cell is the large among added other different amounts of carbon black, such as 3wt% and 10wt%. The discharge capacity of $LiFePO_4$-C(5wt%)/SPE/Li cell is 126 mAh/g at the first cycle and 123 mAh/g after 30 cycles, respectively. It is demonstrated that cycling performance of $LiFePO_4$-C/Li cell is better than that of $LiFePO_4$/Li cell and with 5wt% carbon black is best.

Acknowledgments

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