The Effect of Carbon Doping on Electrochemical Properties of LiFePO4/C Powders Prepared by Spray Pyrolysis
The Effect of Carbon Doping on Electrochemical Properties of LiFePO$_4$/C Powders Prepared by Spray Pyrolysis

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Abstract. Spherical LiFePO$_4$/C precursor powders were successfully prepared by spray pyrolysis. Various types of organic compounds such as glycolic acid, malic acid, citric acid, fructose and sucrose were used as carbon sources. X-ray diffraction analysis revealed that the olivine phase was obtained by calcining over 600 °C under an argon (95%)/hydrogen (5%) atmosphere. The particles exhibited a spherical morphology with approximately 1.5 µm. LiFePO$_4$/C cathode derived from sucrose exhibited higher rechargeable capacity and cycle stability. The rechargeable capacity of LiFePO$_4$/C cathode was approximately 154 mAh/g at 1 C. 90% of initial discharge capacity was maintained after 100 cycles.

Introduction

Recently, olivine-type LiMPO$_4$ (M = Fe, Mn, Ni, and Co) has attracted extensive attention due to a relatively high theoretical capacity (170 mAh/g) [1]. LiFePO$_4$ is the most attractive because of its rare-metal free composition, its long plateau during charge and discharge, its good cycle stability at high temperatures. However, the rechargeable capacity was low at high rates because electrical conductivity of LiFePO$_4$ is very low. Therefore, conductive materials such as carbon and metals were added to LiFePO$_4$ in order to enhance its electrical conductivity [2-4]. Spray pyrolysis [5] is a versatile process that is used to synthesize oxide and metal fine powders. The advantages of spray pyrolysis are that it allows to control of the particle size, particle size distribution, and particle morphology. In addition, fine powders with a homogeneous composition can be easily synthesized, because the starting solution components are kept in a mist. In this study, LiFePO$_4$/C powders were prepared by spray pyrolysis using various types of organic compounds. The powder characteristics of them and the Effect of carbon doping on electrochemical properties of LiFePO$_4$/C were investigated.

Experimental procedure

Spray pyrolysis process [6] was used to prepare LiFePO$_4$/C powders. LiNO$_3$, Fe(NO$_3$)$_3$・9H$_2$O and H$_3$PO$_4$ was used as starting materials. These compounds were dissolved in water at room temperature. The molar ratio of the metal component (Li : Fe : P) was set to 1 : 1 : 1 in the starting solution. The concentration of the solution was 0.25 mol/dm$^3$. Various types of organic compounds such as glycolic acid, malic acid, citric acid, fructose and sucrose were used as carbon sources. The molar ratio of LiFePO$_4$ : C was set to 1 : 12 in the starting solution. The starting solution was mixed using an ultrasonic nebulizer at a frequency of 1.6 MHz. Air was used as the carrier gas during the preparation of LiFePO$_4$/C powders. The generated mist were carried to an electric furnace by air carrier gas with a flow rate of 8 dm$^3$/min and then pyrolyzed at 500 °C. LiFePO$_4$/C precursor powders were continuously collected using cyclone. Furthermore, the precursor powders were calcined over 600 °C in electric furnace under an argon (95%)/hydrogen (5%) atmosphere. The heating and cooling rates were 5 °C/min and 4 °C/min, respectively.

The crystal phase of LiFePO$_4$/C powders and the calcined powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuKα radiation. The chemical composition of LiFePO$_4$/C powders was determined by inductively coupled plasma atomic emission spectroscopy.
(ICP-AES, SII NanoTechnology, SPS-7800). The particle size, morphology and microstructure of 
LiFePO₄/C powders were determined by using a scanning electron microscope (SEM, JEOL, 
JSM-6390). In the SEM images, 200 particles were randomly sampled to determine the average 
particle size of LiFePO₄/C powders. The thermal behavior of carbon sources was observed using a 
thermo gravimetric-differential thermal analysis equipment (TG-DTA, Shimadzu, DTG-60). The 
carbon content of the LiFePO₄/C particles was determined by TG-DTA. Cathodes were prepared 
using 75 mass% LiFePO₄/C powders, 15 mass% acetylene black and 10 mass% fluorine resin. A 
metal lithium sheet (Honjo chemical) was used as an anode. The celgard (Heist, celgard 2400) was 
used as a separator. 1mol/dm³ LiPF₆ in ethylene carbonate / 1,2-dimethoxyethane (EC : DEC = 1 : 1, 
Tomiyama pure chemical) was used as the electrolyte. 2032 coin type cell was built up in globe box 
under an argon atmosphere. The rechargeable capacity and cycle stability of cathodes were measured 
with a battery tester (Hosen, BTS2004) at between 2.5V and 4.3V.

Results and discussion

The crystal phase and crystallinity of LiFePO₄/C powders were observed by using the XRD. Figure 1 
shows the XRD patterns of LiFePO₄/C powders prepared by spray pyrolysis of an aqueous solution 
with the indicated organic compound. These powders were calcined at 750 °C for 3 hrs. From these 
patterns, it was observed that the diffraction patterns of LiFePO₄/C powders were good agreement 
with olivine phase (space group: Pnma), and other phases were not observed. The crystallinity of 
LiFePO₄/C powders obtained from glycolic acid was similar to that of LiFePO₄ powders. On the other 
hand, the crystallinity of the LiFePO₄/C powders obtained from saccharides was relative low. 
Chemical analysis revealed that the metal component (Li : Fe : P) ratio of the calcined powders was 
agreement with the starting solution component. The diffraction patterns of carbon were not observed 
by XRD. This suggested that the carbon contained in LiFePO₄/C powders is amorphous and that the 
presence of carbon does not influence the formation of LiFePO₄. TG-DTA analysis showed that the 
carbon contents of LiFePO₄/C powders obtained from glycolic acid, malic acid, citric acid, fructose 
and sucrose were 0.5 mass%, 2 mass%, 1.5 mass%, 16 mass% and 18 mass%, respectively. The 
thermal behavior of carbon sources was observed using TG-DTA. The thermal decomposition 
temperature of organic acid was from 150 to 470 °C. On the other hand, the thermal decomposition 
temperature of saccharides was from 200 to 650 °C. Therefore, the carbon contents of LiFePO₄/C 
powders obtained from saccharides was rich compared with that of LiFePO₄/C powders obtained 
organic acid. Figure 2 shows the SEM images of LiFePO₄ and LiFePO₄/C powders obtained from
various types of organic compounds. LiFePO$_4$ particles and LiFePO$_4$/C particles obtained from glycolic acid exhibited an irregular morphology. When the other carbon sources were used, the particles exhibited a spherical morphology with a hollow microstructure and nonaggregated regardless of the types of carbon sources used. This resulted in the drastic decomposition of organic acid in the step of pyrolysis. The average size of LiFePO$_4$ and LiFePO$_4$/C powders was approximately 1.2 µm.

The electrochemical properties of LiFePO$_4$/C as cathode for lithium battery were examined. Figure 3 shows rechargeable curves of LiFePO$_4$/C cathodes obtained from various types of organic compounds at 1 C. A long plateau was observed at approximately 3.5V in each rechargeable curve. The charge and discharge capacities were 154 mAh/g for the LiFePO$_4$/C cathode obtained from sucrose, approximately 158 mAh/g and 148 mAh/g for the LiFePO$_4$/C cathode obtained from fructose, 123 mAh/g for the LiFePO$_4$/C cathode obtained from malic acid, 73 mAh/g for the LiFePO$_4$/C cathode obtained from citric acid, 23 mAh/g for the LiFePO$_4$/C cathode obtained from glycolic acid, and 4 mAh/g for the LiFePO$_4$ cathode, respectively. The rechargeable efficiency was very high regardless of the type of organic compounds. The rechargeable capacity of the LiFePO$_4$/C cathode obtained from sucrose was higher than that obtained from other organic compounds. It is considered that the difference in carbon contents is related to the difference in rechargeable capacities. Figure 4 shows the relation between cycle number and discharge capacity of LiFePO$_4$/C cathodes obtained from various types of organic compounds at 1 C. The discharge capacity decreased with increasing discharge rate.
The discharge capacity of the LiFePO$_4$/C cathodes after 100 cycles at 1 C was approximately 90% of the initial discharge capacity regardless of the type of organic compounds. It was found that the LiFePO$_4$/C cathodes exhibited excellent cycle stability.

Figure 5 shows rechargeable curves of LiFePO$_4$/C cathodes obtained from sucrose at 1 C. LiFePO$_4$/C cathodes obtained from sucrose were calcined from 600 °C to 800 °C in electric furnace under an argon (95%)/hydrogen (5%) atmosphere for 3hrs. When LiFePO$_4$/C cathode was calcined at 750 °C, LiFePO$_4$/C cathode exhibited the best rechargeable capacity and rechargeable efficiency. Figure 6 shows the relation between cycle number and discharge capacity of LiFePO$_4$/C cathodes obtained from sucrose at 1 C. After 50 cycles, approximately 90% of initial discharge capacity was maintained regardless of the calcination temperature. Figure 7 shows the relation between cycle number and discharge capacity of LiFePO$_4$/C cathodes obtained from sucrose and calcined at various time at 1 C. LiFePO$_4$/C cathodes were calcined at 750 °C. When LiFePO$_4$/C cathode was calcined for 1 hr, the discharge capacity of the LiFePO$_4$/C cathode after 100 cycles was approximately 95% of the initial discharge capacity. On the other hand, the discharge capacity of the LiFePO$_4$/C cathodes calcined for other time after 100 cycles was approximately 90% of the initial discharge capacity. However, the discharge capacity of these cathodes was high compared with the discharge capacity of LiFePO$_4$/C cathode calcined for 1 hr.

**Conclusion**

LiFePO$_4$/C powders were prepared by spray pyrolysis using an aqueous solution of organic compounds. XRD revealed that the diffraction peaks of all samples were agreement with olivine phase. LiFePO$_4$/C powders were a spherical morphology with 1.2 µm and nonaggregation. The calcined powders have uniform chemical composition. The electrochemical properties of LiFePO$_4$ were improved by addition of carbon. The addition of sucrose led to highest discharge capacity of LiFePO$_4$/C. The discharge capacity of LiFePO$_4$/C was 154 mAh/g at 1 C. The rechargeable capacity changed by changing the calcination temperature and the calcination time, but the stability of cycle performance was maintained. The electrochemical measurement revealed that LiFePO$_4$/C cathodes obtained from sucrose had the higher rechargeable capacity and stable cycle performance.

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