

## Synthesis and Electrochemical properties of LiFePO<sub>4</sub>/Carbon Composite Powder by Spray Pyrolysis

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Spherical LiFePO<sub>4</sub>/C cathode materials were successfully prepared by spray pyrolysis. Particle size, morphology and crystal phase of LiFePO<sub>4</sub>/C powders were characterized by XRD and SEM. XRD showed that olivine structure was formed by the calcination at 700 °C under Ar-H<sub>2</sub> atmosphere. They had spherical morphology with particle size of 1.5 μm. Electrochemical measurement revealed that the discharge capacity of LiFePO<sub>4</sub> was improved by the addition of carbon. The first discharge capacity of LiFePO<sub>4</sub>/C was about 141 mAh/g and 73 mAh/g at 0.1C and 5C respectively.

Key words: spray pyrolysis, LiFePO<sub>4</sub>, composite powder, cathode materials

### 1. INTRODUCTION

Lithium ion battery has been widely applied to portable type electronic equipment such as mobile phone, note PC, digital camera because of its high rechargeable capability compared with NiH battery. To date, LiCoO<sub>2</sub> [1, 2] has been commercially used as a cathode active material on high energy density lithium ion battery. Two types of lithium manganates have been noted as alternative cathode active materials because of low cost and high safety compared to LiCoO<sub>2</sub> and LiNiO<sub>2</sub>. LiMnO<sub>2</sub> [3-5] has been proposed as a cathode active material due to higher capacity rather than LiCoO<sub>2</sub>. There are two plateaus regions (3 V and 4 V) in charge and discharge curves because of the phase transition to LiMn<sub>2</sub>O<sub>4</sub> during Lithium insertion / extraction. Spinel type LiMn<sub>2</sub>O<sub>4</sub> [6-9] has been investigated for its possible use as an alternative cathode active material in rechargeable lithium batteries. The theoretical capacity of spinel LiMn<sub>2</sub>O<sub>4</sub> is much lower than those of layered structures such as LiCoO<sub>2</sub> and LiNiO<sub>2</sub>. Recently, it is noted that olivine type structure such as LiFePO<sub>4</sub> [10] is candidate for use as a cathode material because of low cost, relatively high theoretical capacity and stable cycle performance at high temperature. The electric conductivity of LiFePO<sub>4</sub> expires too low in order to use as cathode material.

Spray pyrolysis technique [11-13] is one of solution technique and has the following potential advantage: (1) as-prepared particles are spheres with a high surface area, (2) chemical homogeneity is enhanced relative to solid state reaction, (3) oxide powders can be directly prepared and take much shorter than that is required for solid state reaction and the sol-gel method. It is well-known that spray pyrolysis has been applied to preparation of submicrometer oxide precursor particles with narrow sized distribution.

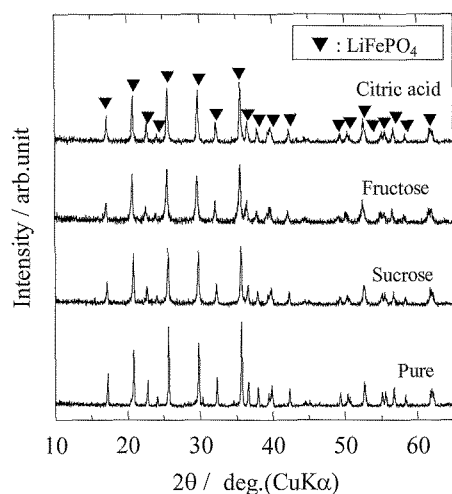
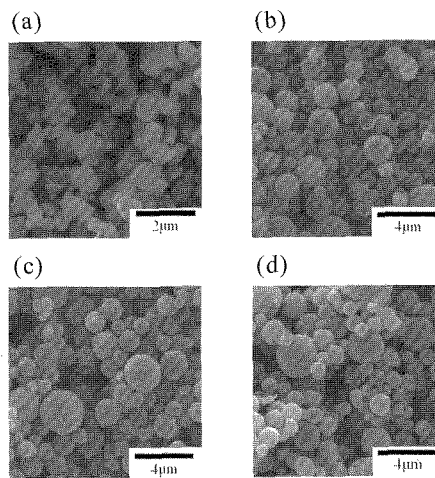
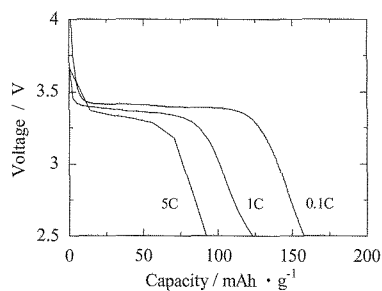
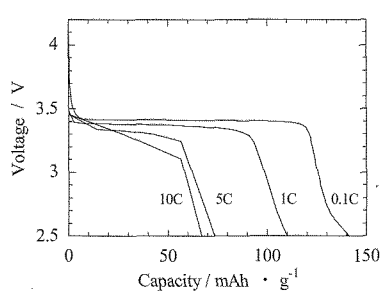
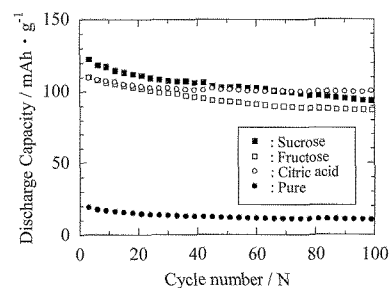
In this paper, carbon doped LiFePO<sub>4</sub> precursor particles were prepared by spray pyrolysis using saccharides and organic acid. Their particle characteristics and the influence of the addition of carbon to the electrochemical properties of LiFePO<sub>4</sub> were investigated.

### 2. EXPERIMENTAL PROCEDURE

LiNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> were used as starting materials. LiNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> were weighted out to attain the molar ratio of metal components (Li : Fe : P) of 1 : 1 : 1 and were dissolved in double distilled water to prepare aqueous solutions of 0.1 mol/dm<sup>3</sup>. Various types of saccharides or organic acid were added to aqueous solutions up to 100 wt%. The starting solution was misted at a frequency of 2.4 MHz by an ultrasonic nebulizer (HM-2412, Honda Electronics) and introduced into an electrical furnace (500 °C) by air as the carrier gas and pyrolysis was performed. The flow rate was 0.0835 dm<sup>3</sup>/s. As-prepared precursor powders were continuously collected using a cyclone. Furthermore, as-prepared precursor powders were calcined over 600 °C for 10 hr in furnace under an argon/hydrogen (5%) atmosphere.

Crystal phase of as-prepared powders and calcined powders was identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuKα radiation. Particle size and morphology were determined by scanning electron microscope (SEM, Hitachi, S-2300). The average particle size was determined by randomly sampling 200 particles from SEM photographs.

Electrochemical properties of LiFePO<sub>4</sub> were examined using CR2032 type coin cell. The cells consisted of the cathode materials, Li sheet (The Honjo Chemical Corporation) as the anode, a cellgard microporous membrane (Heist Japan, Co., Ltd.) as the separator. The electrolyte solution was 1 mol/dm<sup>3</sup> LiPF<sub>6</sub> in EC/DMC (1 : 1, Tomiyama Pure Chemical). The cathode materials were prepared using 80 wt% calcined powders, 10 wt% polyvinylidene fluoride as a binder and 10 wt% as acetylene black in 1-methyl-2-pyrrolidone. The slurry was then coated onto an aluminum foil. The coated aluminum foil was dried at 120 °C for 24 h in a vacuum oven. Lithium battery was built up in globe box under an argon atmosphere. The change of voltage during charge/discharge was measured with a potentiostat (Hosen, Battery cyler) between 2.5 V and 4.3 V.

Fig. 1 XRD patterns of  $\text{LiFePO}_4$ Fig. 2 SEM photographs of  $\text{LiFePO}_4$  (a) and carbon doped  $\text{LiFePO}_4$  powders derived from (b)fructose, (c)sucrose, (d)citric acid.Fig. 3 Discharge curves of carbon doped  $\text{LiFePO}_4$  derived from sucrose.Fig. 4 Discharge curves of carbon doped  $\text{LiFePO}_4$  derived from citric acid.Fig. 5 Cycle performance of  $\text{LiFePO}_4$  at 1C (25 °C)

### 3. RESULTS AND DISCUSSION

The crystal phase and crystallinity of calcined powders were identified by XRD. Figure 1 showed XRD patterns of carbon doped  $\text{LiFePO}_4$  and pure  $\text{LiFePO}_4$  powders. The crystallinity of as-prepared powders was very low. As-prepared powders were amorphous and crystallized by calcined at 700 °C for 10 hr under the atmosphere of argon/hydrogen (5%). XRD revealed that the crystal phases of calcined powders were resulted in olivine structure. The crystallinity of the pure  $\text{LiFePO}_4$  was higher than that of carbon doped  $\text{LiFePO}_4$ .

Figure 2 shows SEM photographs of carbon doped  $\text{LiFePO}_4$  powders obtained by calcined at 700 °C for 10 hr under the argon/hydrogen (5%) atmosphere. SEM showed carbon doped  $\text{LiFePO}_4$  powders had spherical morphology and non-aggregated. The average particle size and geometrical standard deviation was about 1.5  $\mu\text{m}$  and 1.2 - 1.3, respectively. On the other hand, the particle morphology of pure  $\text{LiFePO}_4$  powders was irregular shape.

By adding the carbon, the crystallization of  $\text{LiFePO}_4$  was suppressed and the spherical particle morphology was kept. Therefore, it is possible to consider that the particles growth is impeded by existence of the carbon

between particle formations.

Figure 3 shows discharge curves of carbon doped  $\text{LiFePO}_4$  derived from sucrose as a cathode for lithium secondary battery. The discharge curves of  $\text{LiFePO}_4$  were measured from 2.5 V to 4.3 V at rate of indicated. The discharge capacity of  $\text{LiFePO}_4$  derived from sucrose was 157 mAh/g at the rate of 0.1 C. The discharge capacity of carbon doped  $\text{LiFePO}_4$  decreased to 90 mAh/g with increasing discharge rate up to 5 C. Figure 4 shows discharge curves of carbon doped  $\text{LiFePO}_4$  derived from citric acid. The discharge capacity of  $\text{LiFePO}_4$  derived from citric acid was 141 mAh/g at the rate of 0.1 C. These are higher than that of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$ . The discharge capacity of carbon doped  $\text{LiFePO}_4$  decreased to 73 mAh/g with increasing discharge rate up to 5 C. The discharge capacity decreased to 70 mAh/g under the rate of 5 C.

The cycle performance for discharge of  $\text{LiFePO}_4$  was also examined. Figure 5 shows the relation between cycle number and discharge capacity at 25 °C. The discharge capacity gradually decreased with increasing cycle number. The discharge capacity of pure  $\text{LiFePO}_4$  was 20mAh/g because of low electric conductivity. The

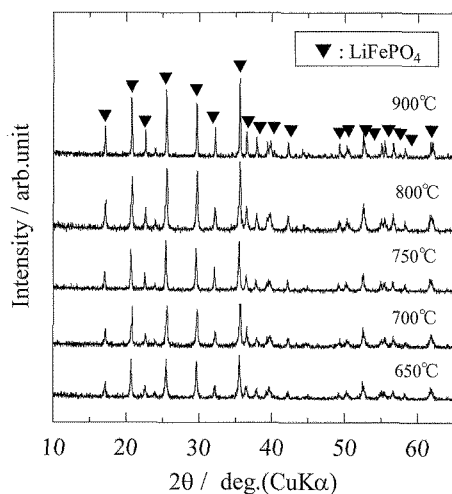


Fig. 6 XRD patterns of carbon doped LiFePO<sub>4</sub> powders (derived from citric acid) calcined at various temperatures.

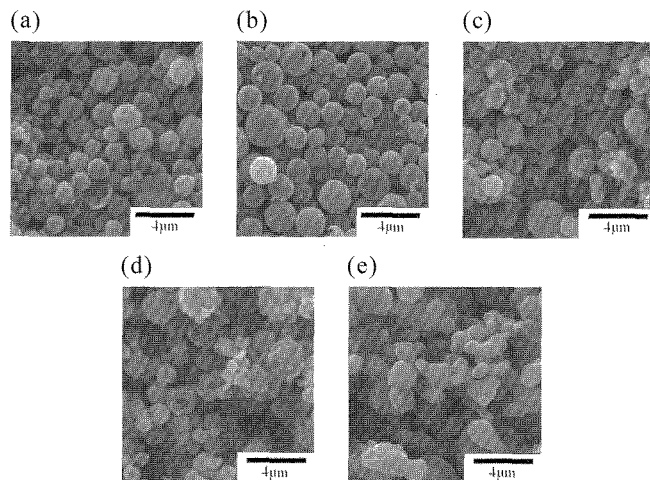


Fig. 7 SEM photographs of carbon doped LiFePO<sub>4</sub> powders (derived from citric acid) calcined at various temperatures. (a)650°C, (b)700°C, (c)750°C, (d)800°C and (e)900°C.

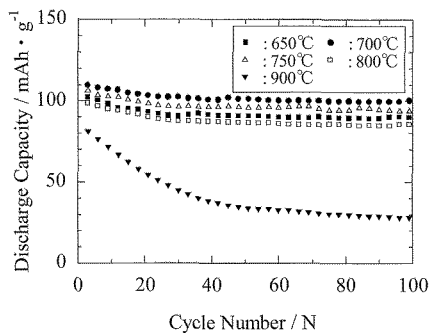


Fig. 8 Cycle performance of carbon doped LiFePO<sub>4</sub> powders calcined at various temperatures (at 1C, 25 °C).

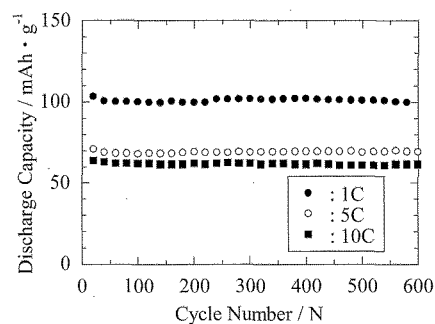


Fig. 9 Cycle and rate performance of carbon doped LiFePO<sub>4</sub> powders derived from citric acid and calcined at 700 °C (at 25 °C).

discharge capacity of carbon doped LiFePO<sub>4</sub> was drastically improved regardless of the type of the saccharides. It was found that the cycle performance of carbon doped LiFePO<sub>4</sub> was stable. The cycle performance of carbon doped LiFePO<sub>4</sub> derived from citric acid was most stable. It is worthy to note that the conductivity of the particles can be enhanced because of the existence of the carbon between particle formations [14]. The reason is that higher conductivity was provided because there is much quantity of carbon in the anode.

Figure 6 shows XRD patterns of carbon doped LiFePO<sub>4</sub> derived from citric acid. The carbon doped LiFePO<sub>4</sub> were calcined at 650 – 900 °C for 10 hr under the atmosphere of argon/hydrogen (5%). XRD revealed that the diffraction peak of all sample was agreement with olivine structure and other phase was not observed.

Figure 7 shows SEM photographs of carbon doped LiFePO<sub>4</sub> powders calcined at various temperatures. SEM showed carbon doped LiFePO<sub>4</sub> powders calcined under 800 °C had spherical morphology and

non-aggregated. On the other hand, when the carbon doped LiFePO<sub>4</sub> powders calcined at 900 °C, the carbon doped LiFePO<sub>4</sub> particles were melted, sintered and aggregated.

Figure 8 shows cycle performance of carbon doped LiFePO<sub>4</sub> powders calcined at various temperatures. After 50 cycles, the discharge capacity of carbon doped LiFePO<sub>4</sub> calcined at 900 °C was 30 mAh/g because the carbon doped LiFePO<sub>4</sub> particles were melted and sintered. On the other hand, the discharge capacity of carbon doped LiFePO<sub>4</sub> calcined under 800 °C was kept over 90 mAh/g after 100 cycles.

Figure 9 shows cycle and rate performance of carbon doped LiFePO<sub>4</sub> powders derived from citric acid and calcined at 700 °C. After 600 cycles, 92% of discharge capacity at first was maintained under the rate of 10C. It was found that the discharge capacity of carbon doped LiFePO<sub>4</sub> powders derived from citric acid offered stable cycle performance.

#### 4. CONCLUSION

Carbon doped LiFePO<sub>4</sub> precursor powders were successfully prepared by spray pyrolysis using aqueous solution with saccharides and citric acid. The crystallinity of as-prepared powders was low, but improved by calcined at more than 600 °C. The crystal phase of carbon doped LiFePO<sub>4</sub> was resulted in olivine structure. Carbon doped LiFePO<sub>4</sub> particles had spherical morphology with non-aggregated. The electrochemical properties of LiFePO<sub>4</sub> were improved by addition of carbon. The addition of citric acid led to most stable cycle life of LiFePO<sub>4</sub>. The discharge capacity of LiFePO<sub>4</sub>/carbon was 141 mAh/g at 0.1 C at 25 °C. 92% of discharge capacity at first was maintained after 600 cycles.

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