Research Article

Mass Production of LiFePO_4/C Powders by Large Type Spray Pyrolysis Apparatus and Its Application to Cathode for Lithium Ion Battery

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Spherical LiFePO_4/C powders were successfully produced at a rate of 100 g/h using a large type spray pyrolysis apparatus. Organic compounds such as citric acid and sucrose were used as carbon sources. Scanning electron microscopy observation showed that they had a spherical morphology with nonaggregation. X-ray diffraction analysis revealed that the olivine phase was obtained by heating at 600°C under argon (95%)/hydrogen (5%) atmosphere. The chemical composition of LiFePO_4/C powders was in good agreement with that of the starting solution. Electrochemical measurement revealed that the use of citric acid was most effective in ensuring a high rechargeable capacity and cycle stability. The rechargeable capacity of the LiFePO_4/C cathode obtained using citric acid was 155 mAh/g at a discharge rate of 1 C. Because of the good discharge capacity of the LiFePO_4/C cathode, it exhibited excellent cycle stability after 100 cycles at each discharge rate. Moreover, this high cycle stability of the LiFePO_4/C cathode was maintained even at 50°C .

1. Introduction

Recently, olivine-type LiFePO_4 has been considered as a suitable cathode material for lithium-ion batteries used in EVs (electric vehicles), HEVs (hybrid electric vehicles), and power supplies used for load leveling in wind power generation and solar power generation. [1, 2]. Olivine-type LiFePO_4 exhibits a relatively high theoretical capacity of 170 mAh/g and a stable cycle performance at high temperatures. However, in the past, the low electrical conductivity of LiFePO_4 prevented its application as a cathode material for the lithium-ion battery. Therefore, conductive materials such as carbon and metals were added to LiFePO_4 in order to enhance its electrical conductivity [3–6]. Yang et al. reported the electrochemical properties of LiFePO_4/C cathode materials prepared by spray pyrolysis [7]. The advantages of spray pyrolysis [8, 9] are as follows: (1) spherical and homogeneous oxide powders can be directly prepared, and the synthesis time is much shorter than that required for a solid-state reaction and the sol-gel method and (2) carbon or metal ions are directly doped to the particles in one step. We have synthesized various types

of lithium oxide powders such as LiNiO_2 , LiMn_2O_4 , and $\text{LiNi}_{1/3}\text{Mn}_{2/3}\text{O}_4$ for the development of the lithium-ion battery by spray pyrolysis [10–12]. We found that by using the materials prepared by spray pyrolysis as cathode materials for the lithium-ion battery, the rechargeable capacity and cycle life of the battery were improved. It has been found clear that a LiFePO_4/C cathode produced by spray pyrolysis, where organic compounds were used as carbon sources, has improved rechargeable capacity and cycle performance at high-rate charging and elevated temperatures.

However, using spray pyrolysis, it is difficult to uniformly pyrolyze a large amount of mist within a short time in an electrical furnace where the scale-up was done. In spray pyrolysis, the difference between the pyrolysis temperatures inside and outside the electrical furnace increases with increasing dimensions of the electrical furnace, leading to a fluctuation in the properties of the resulting powders. In this study, we attempted to prepare LiFePO_4/C powders by using a large type spray pyrolysis apparatus and then characterized the particles of the prepared LiFePO_4/C powders. Furthermore, we examined the electrochemical properties of LiFePO_4/C as a cathode for the lithium-ion battery.

FIGURE 1: Schematic diagram of spray pyrolysis apparatus.

2. Experimental Procedure

LiNO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and H_3PO_4 were used as starting reagents. They were weighted out to attain a molar ratio of $\text{Li}:\text{Fe}:\text{P} = 1:1:1$ and then dissolved in double distilled water to prepare 1 mol/dm^3 of aqueous solutions. Various types of organic compounds such as sucrose, fructose, white sugar, and citric acid were used as carbon sources. The contents of organic compound were 10 wt%. Figure 1 shows the schematic diagram of the spray pyrolysis apparatus. It consisted of a two-fluid nozzle, electric furnace, and bag filter. The starting solution was introduced into the two-fluid nozzle using a roller pump. The mist of the aqueous solution was generated in the two-fluid nozzle with $0.16 \text{ dm}^3/\text{s}$ of air carrier gas. The pyrolysis temperature was 500°C . As-prepared LiFePO_4/C powders were produced at 100 g/hr and collected in the bag filter.

As-prepared LiFePO_4/C powders were heat treated at 700°C for 2 hours in the electric furnace under argon (95%)/hydrogen (5%) atmosphere. The average particle size, morphology, and microstructure of the LiFePO_4/C powders were determined using a scanning electron microscope (SEM, Hitachi, S-2400). The crystal phase of the LiFePO_4/C powders was identified using powder X-ray diffraction (XRD, Shimadzu, XRD-6100). Specific surface area of the powders was measured by the BET method using nitrogen adsorption (Shimadzu, Tristar-3000), and their chemical composition was determined by inductively coupled plasma analysis (ICP, SII, SPS-3000). The particle density of LiFePO_4/C powders was determined by a pycnometer (Shimadzu, AccupycII 1340). The carbon content of the LiFePO_4/C particles was determined by thermogravimetry (TG, Shimadzu, DTG-60).

The cathode was prepared using 80 wt% LiFePO_4/C powders, 10 wt% acetylene black, and 10 wt% fluorine resin. A metal lithium sheet (Honjo chemical) was used as the anode. The polypropylene sheet (Heist, celgard 2400) was used as a separator. Further, 1 mol/dm^3 LiPF_6 in

FIGURE 2: SEM photographs of LiFePO_4/C powders obtained from sucrose and citric acid.

ethylene carbonate/1,2-dimethoxyethane ($\text{EC}:\text{DME} = 1:1$, Tomiyama pure chemical) was used as the electrolyte. A coin cell (2032 type, $20.0 \text{ mm}\phi \times 3.2 \text{ mm}$) was built in a globe box under argon atmosphere. The rechargeable capacity and cycle stability of the LiFePO_4/C cathode were measured using a battery tester (Hosen, BTS2004) between 2.5 V and 4.3 V.

3. Results and Discussion

Figure 2 shows SEM photographs of as-prepared LiFePO_4/C powders produced at 100 g/hr by spray pyrolysis of an aqueous solution of sucrose and citric acid. The yield of the as-prepared LiFePO_4/C powders was 95% regardless of the types of carbon sources. The as-prepared C/LiFePO_4 particles had a spherical morphology with a smooth surface and nonaggregation regardless of the types of carbon sources used. Figure 2 also shows these hollow particles. This resulted in the drastic decomposition of organic acid in the step of pyrolysis. The average particle size of as-prepared LiFePO_4/C powders obtained from sucrose and citric acid was approximately 1.02 and $1.2 \mu\text{m}$, respectively. Figure 3 shows the particle size distribution of LiFePO_4/C powders obtained from sucrose and citric acid. The particle size of these powders ranged from $0.2 \mu\text{m}$ to $3 \mu\text{m}$. It was found that these powders had a broad size distribution because of the broad size distribution of the mist generated by the two-fluid nozzle. The specific surface area of the LiFePO_4/C powders was approximately $10 \text{ m}^2/\text{g}$ regardless of the types of carbon sources used; this suggested that the particle microstructure of LiFePO_4/C powders was porous. The powder densities of the LiFePO_4/C powders

FIGURE 3: Particle size distribution of LiFePO_4/C powders obtained from sucrose and citric acid.

obtained from sucrose and citric acid were 3.5 kg/m^3 and 3.2 kg/m^3 , respectively. It is considered that the hollow or porous microstructure led to a reduced particle density of the LiFePO_4/C powders. Figure 4 shows XRD patterns of the LiFePO_4/C powders prepared by spray pyrolysis of an aqueous solution with the indicated organic compound. The LiFePO_4/C powders were crystallized to the olivine phase by heat treatment under argon (95%)/hydrogen (5%) atmosphere. XRD revealed that the diffraction patterns of the LiFePO_4/C powders were in good agreement with the olivine structure (space group: Pnma), and that other phases were not observed. From the XRD patterns, it appeared that the crystallinity of the LiFePO_4/C powders obtained from white sugar was relative low. The chemical composition of the LiFePO_4/C powders was in good agreement with that chemical composition of the starting solution determined by inductively coupled plasma analysis. Therefore, no evidence of the diffraction peaks for carbon was found in the diffraction pattern; this indicates that the carbon contained in the organic compounds is amorphous and that the presence of carbon does not influence the formation of LiFePO_4 .

FIGURE 4: XRD patterns of LiFePO_4/C powders calcined at 700°C for 2 hours under argon (95%)/hydrogen (5%) atmosphere.

FIGURE 5: Rechargeable curves of LiFePO_4/C cathode at 1 C.

The electrochemical properties of LiFePO_4/C as cathode for lithium ion battery were examined. Figure 5 shows the rechargeable curves of LiFePO_4/C cathodes at 1 C. A long plateau was observed at approximately 3.5 V in each rechargeable curve. The charge and discharge capacities were 165 mAh/g and 155 mAh/g for the LiFePO_4/C cathode obtained from citric acid, approximately 158 mAh/g and 148 mAh/g for the LiFePO_4/C cathode obtained from sucrose, 145 mAh/g and 138 mAh/g for the LiFePO_4/C cathode obtained from fructose, and 130 mAh/g and 122 mAh/g for the LiFePO_4/C cathode obtained from white sugar, respectively. The rechargeable efficiency was 93% for the LiFePO_4/C cathode obtained from citric acid and greater than 90% for the LiFePO_4/C cathodes obtained from other organic compounds. The rechargeable capacity of the LiFePO_4/C cathode obtained from citric acid was higher than that obtained from sucrose. TG analysis showed that the concentrations of residual organic species in as-prepared

FIGURE 6: Relation between cycle number and discharge capacity of LiFePO₄/C cathode at indicated discharge rate.

FIGURE 7: Relation between cycle number and discharge capacity of LiFePO₄/C cathode at 50°C.

LiFePO₄/C powders obtained from citric acid and sucrose were approximately 20 wt% and 18 wt%, respectively. The carbon contents of LiFePO₄/C powders obtained from citric acid and sucrose were 14 wt% and 10 wt%, respectively, after calcination at 700°C for 2 hours. It is considered that this difference in carbon contents is related to the difference in rechargeable capacities. This suggests that sucrose may be easier to decompose than citric acid.

Figure 6 shows the relation between the cycle number and the discharge capacity of the LiFePO₄/C cathode obtained from citric acid at the indicated discharge rate. A rechargeable test was carried out for up to 100 cycles at each discharge rate. The discharge capacity decreased with increasing discharge rate. The discharge capacity was 60 mAh/g at 20 C. The discharge capacity of the LiFePO₄/C cathode after 100 cycles at 1 C was 96% of the initial discharge capacity. The same tendency of cycle stability was also observed in the cycle data from 3 C to 20 C. The retention of discharge capacity was greater than 90%. It was found that the LiFePO₄/C cathode exhibited excellent cycle stability at each discharge rate.

Figure 7 shows the relation between the cycle number and the discharge capacity of the LiFePO₄/C cathode obtained from citric acid at 50°C. The rechargeable test of the coin cell was performed at 1 C for up to 100 cycles while being heated on a plate maintained at temperatures from 48°C to 52°C. The LiFePO₄/C cathode obtained from citric acid exhibited a discharge capacity of 150 mAh/g and a stable cycle life. This suggests that the electrical conductivity of the LiFePO₄/C cathode might be enhanced at 50°C. It has been previously reported that LiFePO₄/C cathodes have excellent rechargeable capacities and cycle stabilities because of improved electrical conductivities at elevated temperatures [7]. The discharge capacity of the LiFePO₄/C cathode was 96% of its initial discharge capacity after 100 cycles at 50°C. Moreover, the LiFePO₄/C cathode had high cycle stability at elevated temperatures.

4. Conclusion

LiFePO₄/C powders were prepared by spray pyrolysis using an aqueous solution of organic acid. The produced LiFePO₄/C powders were spherical and had a particle size of approximately 1 μm with broad size distribution and nonaggregation. XRD analysis revealed that the crystal phase of the LiFePO₄/C powders was in good agreement with the olivine phase. The addition of citric acid as a carbon source significantly improved the rechargeable properties of the LiFePO₄ cathode. Electrochemical measurement revealed that the rechargeable capacity of the LiFePO₄/C cathode obtained from citric acid was 155 mAh/g at 1 C and that its rechargeable efficiency was 93%. Among all the organic compounds used as carbon sources, the addition of citric acid led to the highest rechargeable capacity for the LiFePO₄/C cathode. The discharge capacity of the LiFePO₄/C cathode decreased with increasing discharge rate. High cycle stability can be inferred from the fact that the final discharge capacity of the LiFePO₄/C cathode was greater than 90% of its initial value at each discharge rate after 100 cycles. Moreover, the high cycle stability of the LiFePO₄/C cathode was maintained at 50°C.

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