Effect of Foreign Metal on Electrochemical Properties of C/LiMnPO₄ Powders Synthesized by Spray Pyrolysis

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Spherical C/LiMn_{1-x}M_xPO₄ (M=Mg, Zn X=0, 0.01, 0.05, 0.10) precursor powders were successfully prepared by ultrasonic spray pyrolysis. The C/LiMn_{1-x}M_xPO₄ were obtained by heating at 973 K for 3 hours under argon/hydrogen (5%) atmosphere. The crystal phases of all samples had an olivine structure with a Pmn2₁ space group and the impurity phase peak was not observed. The average particle size was approximately 0.7 μ m. The electrochemical properties of the C/LiMn_{1-x}M_xPO₄ cathode were estimated by the rechargeable capacity and cycle performance. Electrochemical measurement revealed that the discharge capacity was improved by doping foreign metal such as Mg and Zn ion. The first discharge capacity of C/LiMn_{1-x}Zn_xPO₄ (X = 0.1) cathode was approximately 60 mAh/g at 0.1 C. It was steady cycling characteristics.

Key words: Spray pyrolysis, LiMnPO₄, Olivine, Lithium ion battery, Powders

1. INTRODUCTION

Recently, lithium ion batteries are expected as an application for electric vehicles and hybrid electric vehicles. LiCoO₂ and LiMn₂O₄ have been studied as cathode materials for lithium ion batteries. LiCoO₂ has high capacity but it is very expensive and unstable under the high temperature. LiMn₂O₄ is low cost and high acceleration voltage. But, it is unstable cycle performance under the high temperature. On the other hand, LiMnPO₄ is low cost, relatively high theoretical capacity of 170mAh/g and stable cycle performance at high temperature. LiMnPO₄ has approximately 4 V rechargeable regions. However, the electric conductivity of LiMnPO₄ is too low to use as cathode material. [1-3] Therefore, C/LiMnPO₄ composites have been often prepared by coating conducting materials such as carbon [4-6], but the electrochemical property of C/LiMnPO₄ is not still improved. Spray pyrolysis is a versatile process that is used to synthesize homogeneous powders [7-9]. In this work, we tried to dope the foreign metal to C/LiMnPO₄ in order to raise the electric conductivity. Spherical C/LiMnM_xPO₄ (M = Mg, Zn) powders were prepared by ultrasonic spray pyrolysis using citric acid as a carbon source. The powders characteristics and the electrochemical properties of C/LiMnM_xPO₄ were investigated.

2. EXPERIMENT

LiNO₃, Mn(NO₃)₂·6H₂O, and H₃PO₄ were used as materials for LiMnPO₄. Mg(NO₃)₂·6H₂O and Zn(NO₃)₂·9H₂O were used as a foreign metal for C/LiMn_{1-x}M_xPO₄ (M = Mg, Zn). These reagents were dissolved in distilled water. The molar ratio of the element component (Li:Mn:M:P) was set to 1:1-X:X:1 (X = 0, 0.01, 0.05, 0.10) in the starting solution. The solution concentration was 0.1 mol/dm³. Citric acid was

added as a carbon source. Citric acid concentration was 0.5 mol/dm³. Starting solution was atomized at a frequency of 1.6 MHz by an ultrasonic nebulizer (HM-1630, Honda electronics). The atomized solution led to the electric furnace at a flow rate of 8 dm³ / min of air carrier gas. The temperature of electric furnace was in the range of 523 to 773 K. LiMnPO₄ and C/LiMn_{1-x}M_xPO₄ (M = Mg, Zn, X = 0, 0.01, 0.05, 0.10) precursor powders were continuously collected by cyclon. The precursor powders were calcined at 973 K for 3 hours in an electric furnace under argon/hydrogen (5%) atmosphere. The heating and cooling rates were 5 K / min. The crystal phases of the precursor powders and calcined powders were observed by powder X-ray diffraction (XRD, XRD-6100, Shimadzu) using CuK α radiation. The morphology and average particle size of LiMnPO₄ and C/LiMn_{1-x}M_xPO₄ were determined with a scanning electron microscope (SEM, JSM-6390, JEOL). The amount of the carbon content was measured by the differential thermogravimetric analysis (DTG, Shimadzu Corporation DTG-60). Reference substance of the measurement was used α -Al₂O₃ powders (Shimadzu Corporation). The sample has risen temperature from the room temperature to 1273K at a speed of 10K / min in the air atmosphere. The weight changes in exothermic reaction according to heating were measured. The specific surface area was measured by nitrogen gas adsorption (BELSORP-mini2, BEL JAPAN). The specific surface area was evaluated by the BET method. Organic matter of precursor powders and calcined powders were observed by Fourier transform infrared spectroscopy (FT-IR, NICOLETtISO10, Thermo Fisher Scientific) for attenuated total reflection technique. Electric conductivity was determined by LCRmeter. (LCRmeter, KC-537, KOKUYO). The cathode materials were prepared using 80 wt% calcined powders, 10 wt%

Fig. 1 XRD patterns powders obtained by calcining at 973 K for 3 hours. (a) LiMnPO₄ and C/LiMnPO₄, (b) C/LiMn_{1-x}Mg_xPO₄, and (c) C/LiMn_{1-x}Zn_xPO₄

polyvinylidene fluoride (PVdF) as a binder and 10 wt% as acetylene black (AB) in N-methyl-2-pyrrolidone (NMP). The slurry was coated on an aluminum foil and then dried at 373 K for 24 hours. Celgard (Heist, Celgard 2400) was used as a separator. A solution of 1 mol/dm³ LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC = 1:1, Tomiyama Pure Chemical) was used as the electrolyte. Lithium sheet (Honjo Chemical) was used as an anode. The electrochemical properties of LiMnPO₄ and C/LiMn_{1-x}M_xPO₄ cathode were examined using a CR2032-type coin cell. These coin cells were set up in globe box under argon atmosphere. The rechargeable capacity and cycle performance of the LiMnPO₄ and C/LiMn_{1-x}M_xPO₄ cathode were measured with a battery tester (Hosen, BTS2004) between 2.0 and 4.6 V at 0.01 C and 0.1 C.

3. RESULT AND DISCUSSION

3.1 Powder characteristics

The crystal phase and crystallinity of precursor powders, LiMnPO₄, and C/LiMn_{1-x}M_xPO₄ powders were identified by XRD. Figure 1 shows XRD patterns of LiMnPO₄ and C/LiMn_{1-x}M_xPO₄ powders obtained by calcining at 973 K for 3 hours and precursor powders. The crystal phases of calcining at 973 K for 3 hours

samples had an olivine structure with a Pmnb space group. The impurity phase peak was not observed. On the other hand, precursor powders were not uncrystallized. XRD patterns showed the crystallinity of LiMnPO₄ was higher than that of C/LiMnPO₄. Therefore, no evidence for diffraction peaks for crystalline carbon appeared in the diffraction patterns; this indicates that the carbon generated from ciyric acid was amorphous carbon and that the presence of carbon did not influence the crystal structure of LiMnPO₄. XRD patterns showed other phases were not observed regardless of amount of foreign metal.

Figure 2 shows the SEM photographs of LiMnPO₄ powders obtained by calcining at 973 K for 3 hours under argon/hydrogen (5%) atmosphere. The LiMnPO₄ powders had irregular particle morphology. In contrast, C/LiMnPO₄ powders had spherical particle morphology. The average particle size of LiMnPO₄ was approximately 0.8 μm, and that of C/LiMnPO₄ was approximately 0.7 μm. The average particle size of C/LiMnPO₄ was smaller than that of LiMnPO₄.

Figure 3 shows infrared absorption spectrum of precursor powders and C/LiMnPO₄ powders by FT-IR. C/LiMnPO₄ Precursor powders were observed the absorption spectrum of the H-O-H stretching was

Fig. 2 SEM photographs of (a) LiMnPO₄ and (b) C/LiMnPO₄

Fig.3 FT-IR absorbance spectra of C/LiMnPO₄ and precursor powders

Fig. 4 SEM photographs of $C/LiMn_{1-x}M_xPO_4$ powders (a) $M = Mg$, $X = 0.01$, (b) $M = Mg$, $X = 0.05$, (c) $M = Mg$, $X = 0.1$, (d) $M = Zn$, $X = 0.01$, (e) $M = Zn$, $X = 0.05$, and (f) $M = Zn$, $X = 0.1$.

observed the vicinity of 3500 cm^{-1} . The absorption spectrum that has roots in the nitrate was observed in the vicinity of 1400 cm^{-1} . It is found that the water of crystallization and the nitrate exist in $C/LiMnPO_4$ precursor powders. On the other hand, absorption spectrums were of these not observed at $C/LiMnPO_4$. $C/LiMnPO_4$ precursor powder and $C/LiMnPO_4$ was observed intense P–O stretching bands the vicinity of 1100 cm^{-1} . It is found that PO_4^{3-} exists in $C/LiMnPO_4$ precursor and $C/LiMnPO_4$.

Figure 4 shows the SEM photographs of $C/LiMn_{1-x}M_xPO_4$ powders obtained by calcining at 973 K for 3 hours under argon/hydrogen (5%) atmosphere. The $C/LiMn_{1-x}Zn_xPO_4$ powders had irregular particle morphology. In contrast, $C/LiMn_{1-x}Mg_xPO_4$ powders had spherical particle morphology. The average particle size of $C/LiMn_{1-x}M_xPO_4$ was from 0.7 to 0.8 μm . The average particle sizes of all samples were approximate.

The specific surface area of $LiMnPO_4$ and $C/LiMn_{1-x}M_xPO_4$ powders were observed by BET method. The specific surface area of $LiMnPO_4$ powders were $2.0\text{ m}^2/\text{g}$. On the other hand $C/LiMn_{1-x}M_xPO_4$ powders were approximately $30\text{ m}^2/\text{g}$. The specific surface was increased by carbon doping. $C/LiMnPO_4$ and $C/LiMn_{1-x}Mg_xPO_4$ powders were spherical morphology; $C/LiMn_{1-x}Zn_xPO_4$ powders had irregular morphology. But, the specific surface area of these were approximate.

As results of DTG, $LiMnPO_4$ was no weight loss and not identify exothermic or endothermic reaction. On the other hand, the weight loss of $C/LiMnPO_4$ and $C/LiMn_{1-x}M_xPO_4$ was 10 wt% and exothermic reaction by combustion of the carbon. The temperature was approximately 573 K from 873 K. The carbon content was assumed to 10 wt%. The addition of foreign metal did not influence the carbon content.

3.2 Electrochemical properties

Figure 5 showed the first charge and discharge capacities of $LiMnPO_4$ and $C/LiMn_{1-x}M_xPO_4$ ($M = Mg, Zn$, $X = 0, 0.10$) cathodes at a rate of 0.1 C. The first discharge capacity of $LiMnPO_4$ and $C/LiMnPO_4$ were 2 mAhg^{-1} and 16 mAhg^{-1} , respectively. The efficiency of rechargeable capacity of $LiMnPO_4$ and $C/LiMnPO_4$ cathodes were 85 %, 73%, respectively. The electrical conductivity of $LiMnPO_4$ was 10^{-9} S/cm . On the other hand that of $C/LiMnPO_4$ was 10^{-5} S/cm . The addition of carbon $LiMnPO_4$ led to the improvement of the electric conductivity of $LiMnPO_4$. However the discharge capacity of $C/LiMnPO_4$ is low. On the other hand, the electrical conductivity of $C/LiMn_{1-x}Mg_xPO_4$ and $C/LiMn_{1-x}Zn_xPO_4$ were approximately 10^{-4} S/cm . The doping foreign metal led to the improvement of the electric conductivity of $C/LiMnPO_4$. The first discharge capacity of $C/LiMn_{0.9}Mg_{0.1}PO_4$ was 45 mAhg^{-1} and the

Fig.5 First charge and discharge curves

Fig.6 Cycle performance of (a) C/LiMn_{1-x}Mg_xPO₄ and (b) C/LiMn_{1-x}Zn_xPO₄

efficiency of rechargeable capacity was 90%. The first discharge capacity of C/LiMn_{0.9}Zn_{0.1}PO₄ was 60 mAhg⁻¹ and the efficiency of rechargeable capacity was 84%. Figure 6 (a) showed the cycle performance of LiMnPO₄ and C/LiMnPO₄ at rate of 0.01 C and 0.1C by 298 K. The discharge capacity of LiMnPO₄ and C/LiMnPO₄ were 1 mAhg⁻¹ and 16 mAhg⁻¹ at 0.1 C, respectively. The discharge capacity of LiMnPO₄ and C/LiMnPO₄ were 2 mAhg⁻¹ and 45 mAhg⁻¹ at 0.01 C, respectively. Figure 6 (b) and (c) showed the cycle performance of C/LiMn_{1-x}M_xPO₄ (M = Mg, Zn, X = 0, 0.01, 0.05, 0.10) at a rate of 0.1C by 298 K. The discharge capacity of C/LiMn_{1-x}Mg_xPO₄ was increased, as the amount of Mg-dope was increased. After 100 cycles, 97% of the first discharge capacity was maintained at the rate of 0.1 C. The discharge capacity of C/LiMn_{1-x}Zn_xPO₄ was increased, as the amount of Zn-dope was increased. After 100 cycles, 97% of the first discharge capacity was maintained at the rate of 0.1 C. The discharge capacity of C/LiMn_{1-x}M_xPO₄ (M = Mg, Zn) powders derived from citric acid was found to result in stable cycle performance, and the results demonstrated improved electrical conductivity with carbon and metal material doping.

4. CONCLUSION

C/LiMn_{1-x}M_xPO₄ (M=Mg, Zn) precursor powders were successfully prepared by ultrasonic spray pyrolysis using aqueous solution with citric acid. XRD revealed that the diffraction peak of all sample were olivine structure. The discharge capacity of C/LiMnPO₄ led to the improvement of the Mg and Zn doped. The discharge capacity of C/LiMn_{1-x}Zn_xPO₄ was increasing Zn-doped volume. From electrochemical measurement, the discharge capacity of LiMn_{0.9}Zn_{0.1}PO₄ was 60 mAh/g at 0.1 C. After 100 cycles, 97% of the initial discharge capacity was maintained.

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