

Online available since 2011/Jul/04 at www.scientific.net
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doi:10.4028/www.scientific.net/KEM.485.115

Synthesis and Electrochemical Properties of C/LiMnPO₄ Cathode Materials by Complex Polymerized Method

Atsushi Fujita, Fuminari Isobe, Takayuki Kodera, and Takashi Ogihara

Graduate School of Engineering, Materials Science and Engineering, University of Fukui, 3-9-1
Bunkyo, Fukui-shi, Fukui, Japan

ogihara@matse.u-fukui.ac.jp

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Keywords: LiMnPO₄, Olivine, Lithium ion battery, Complex polymerized method

Abstract C/LiMnPO₄ materials were synthesized by the complex polymerized method. An orthorhombic olivine type structure was obtained by calcination at temperatures over 973 K under an argon/hydrogen (5%) atmosphere. Differential thermogravimetric analysis showed that the carbon content of C/LiMnPO₄ was about 65 wt%. The initial discharge capacity of C/LiMnPO₄ calcined at 973 K was 135 mAh/g at 0.1 C and 60 mAh/g at 1 C.

Introduction

Lithium ion batteries are expected to be used in electric vehicles and hybrid electric vehicles. LiCoO₂ and LiMn₂O₄ have been studied for their use as cathode materials in lithium ion batteries. LiCoO₂ has high capacity, but it is very expensive and unstable under high temperatures. LiMn₂O₄ is cheap and has a high operating voltage. But it has an unstable cycle performance under high temperatures. On the other hand, LiMnPO₄ is cheap and has a relatively high theoretical capacity of 170 mAh/g and stable cycle performance at high temperatures. Batteries made from LiMnPO₄ cathode are rechargeable approximately 4 V. However, it has very poor electrical conductivity and lower capacity at higher charging/discharging rate [1–3].

Therefore, composites of LiMnPO₄ with conducting materials such as carbon have been prepared [4–6]. It is expected that the complex polymerized method can be used to prepare cathode powders with carbon sources at lower temperature, similar to the conventional sol-gel method. Powder preparation using the complex polymerized method involves the formation of polybasic acid chelates through a reaction between a carboxylic acid and an organic compound with a hydroxyl group. When these chelates are heated in polyhydroxyl alcohol, esterification occurs, leading to the formation of a polymeric species with a uniform distribution of cations. The polymeric species retains homogeneity on the molecular scale and calcines at low temperatures to yield an oxide with a precisely controlled chemical composition [7–8]. The carboxylic acid and the organic compound utilized in the esterification are also used as carbon sources. In this paper, the synthesis and electrochemical properties of C/LiMnPO₄ cathode materials by the complex polymerized method are described.

Experimental procedure

LiNO₃, Mn(NO₃)₂·6H₂O, and NH₄H₂PO₄ were used as the starting materials. They were weighed in molar ratio of Li:Mn:P = 1:1:1 and dissolved in a citric acid (anhydrous, C₆H₈O₇) solution. Furthermore, ethylene glycol (C₂H₆O₂) was added to the starting solution. The concentrations of starting materials were 0.1 mol/dm³ each. The concentrations of citric acid and ethylene glycol were 1.5 mol/dm³ each. After mixing with a magnetic stirrer, the solution was heated at 413 K for 24 h to remove water and to accelerate the esterification between citric acid and ethylene glycol. The solution was condensed by heating at 573 K, yielding tar-like precursors. The precursors were milled for 12 h by ball mill with zirconia balls. The precursor powders were calcined at 973 K or 1073 K for 3 h in an electric furnace under an argon/hydrogen (5%) atmosphere. The heating and cooling rates were 5 K/min.

The carbon content was measured by differential thermal analysis/thermal gravimetry (DTA-TG, Shimadzu Corporation DTG-60). The crystal phases of the precursor powders and the obtained powders were observed by powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation (XRD-6100, Shimadzu). The chemical compositions of the obtained powders were determined by inductively coupled plasma atomic emission spectroscopy (SII, SPS-7800). The morphologies of obtained powders were observed with a scanning electron microscope (SEM, JSM-6390, JEOL). The specific surface areas (SSA) of the obtained powders were measured by the BET method using nitrogen gas adsorption (BELSORP-mini, Bel Japan). The organic species in the obtained powders were observed by Fourier transform infrared spectroscopy (FT-IR, NICOLETiSO10, Thermo Fisher Scientific).

A C/LiMnPO_4 cathode was prepared using 80 wt% calcined powders, 10 wt% polyvinylidene fluoride as a binder, and 10 wt% acetylene black as an electric conducting agent in *N*-methyl-2-pyrrolidione. These materials were mixed using an agate mortar, creating a slurry of C/LiMnPO_4 cathode material. The slurry was coated on aluminum foil and then dried at 373 K for 24 h. A polypropylene sheet was used as a separator. A solution of $1 \text{ mol/dm}^3 \text{ LiPF}_6$ in ethylene carbonate/diethyl carbonate (1:1) was used as the electrolyte. A lithium sheet was used as an anode. The electrochemical properties of C/LiMnPO_4 cathodes were examined using CR2032-type coin cells. These coin cells were set up in a glove box under an argon atmosphere. The rechargeable capacity and cycle performance of the C/LiMnPO_4 cathodes were measured with a battery tester (Hosen, BTS2004) between 2.0 and 4.6 V at 0.1 C and 1 C.

Results and discussion

To estimate the carbon content in the obtained powders by the complex polymerized method, DTA-TG analysis was carried out. The exothermic peak with a weight loss of 65 wt% was observed in the DTA-TG curve. It was found there was a large amount of carbon in the obtained powders. The crystal phase and crystallinity of the precursor and calcined powders were identified by XRD. Figure 1 shows XRD patterns of the precursor and calcined powders obtained at the temperatures indicated. The precursor powders were not crystallized, while the calcined LiMnPO_4 powders had high crystallinity. The diffraction patterns were in agreement with an orthorhombic olivine structure. The impurity phase peak was not observed. No evidence for diffraction peaks of crystalline carbon appeared in the diffraction patterns; this indicates that the carbon generated from ethylene glycol and citric acid was amorphous and that the presence of carbon did not influence the crystal structure of LiMnPO_4 . Molar ratios of the powders calcined at 973 K and 1073 K were determined by ICP to be

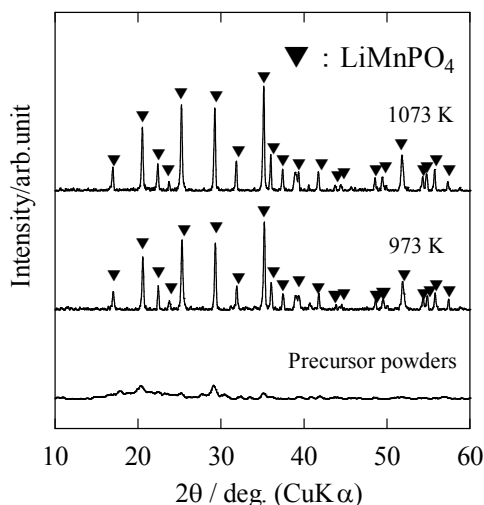


Fig.1 XRD patterns of precursor powders and C/LiMnPO_4 powders

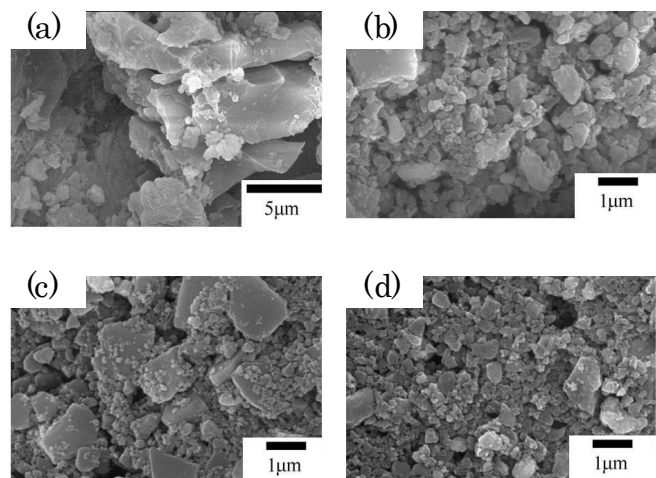


Fig.2 SEM photographs of LiMnPO_4 powders, (a) precursor powders, (b) precursor powders after ball milling, (c) calcined at 973 K, and (d) calcined at 1073 K

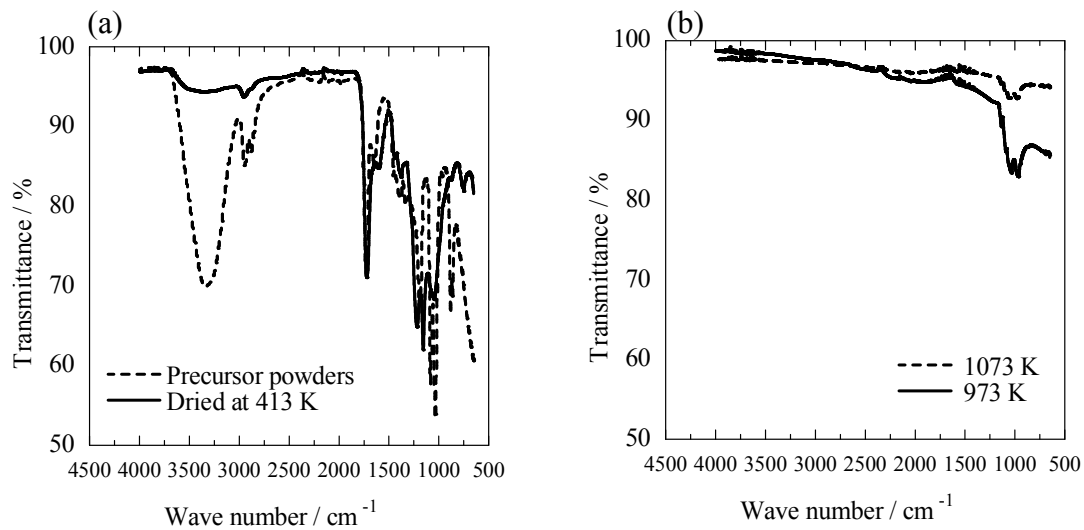


Fig.3 FT-IR spectra of LiMnPO_4 , (a) precursor powders and (b) calcined powders

$\text{Li:Mn:P} = 1:1.02:0.98$ and $1:0.99:0.98$, respectively. These results were in good agreement with the molar ratio of the starting solution (1:1:1). It was found that homogeneous LiMnPO_4 could be obtained by the complex polymerized method. The influence of particle morphology during calcination was examined by SEM observation. Figure 2 shows SEM photographs of the precursor powders and C/LiMnPO_4 powders calcined at 973 K for 3 h under an argon/hydrogen (5%) atmosphere. The precursor powders had large particles about 5 μm in size and bulk-type morphology. After the ball milling, their morphology changed to flake particles approximately 1 μm in size. After calcination at 973 K, the precursor powders were sintered to form both a plate-like morphology of more than 1 μm in size and an irregular morphology of less than 1 μm in size. Fine particles with irregular morphology were observed after calcination at 1073 K. The SSA of the precursor powders determined by the BET method was 20.1 m^2/g . After ball milling, the SSA of the precursor powders increased to 301 m^2/g . This suggested that the precursor powders were milled by ball mill. On the other hand, the SSA of C/LiMnPO_4 powders calcined at 973 K and 1073 K decreased to 195 m^2/g and 212 m^2/g , respectively, due to sintering. Figure 3 shows the IR spectra of both the precursor and C/LiMnPO_4 powders. The absorption peak of the ester bond was observed at 1750 cm^{-1} in the precursor powders. This result suggested that esterification occurred during the formation of the precursor powders. The absorption peak attributed to the N-O bond in nitrates was also observed at 1400 cm^{-1} . The absorption spectra of precursor powders dried at 413 K became sharper than those of the non-dried precursor powders, and the hydrogen bond peak was observed at 3250 cm^{-1} . On the other hand, the peaks disappeared upon calcination. The absorption peak of the P-O bands (PO_4^{3-})

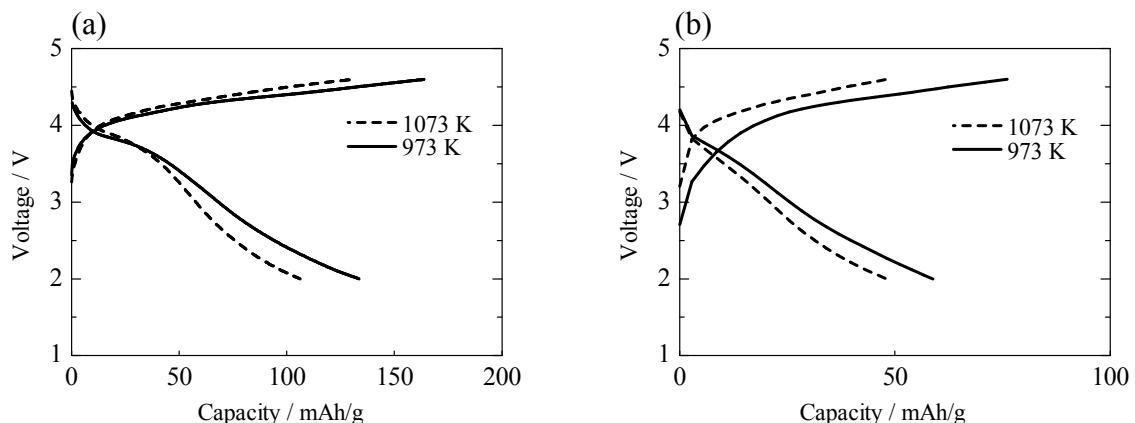


Fig.4 First charge and discharge capacities of C/LiMnPO_4 cathode, (a) at 0.1 C and (b) at 1 C

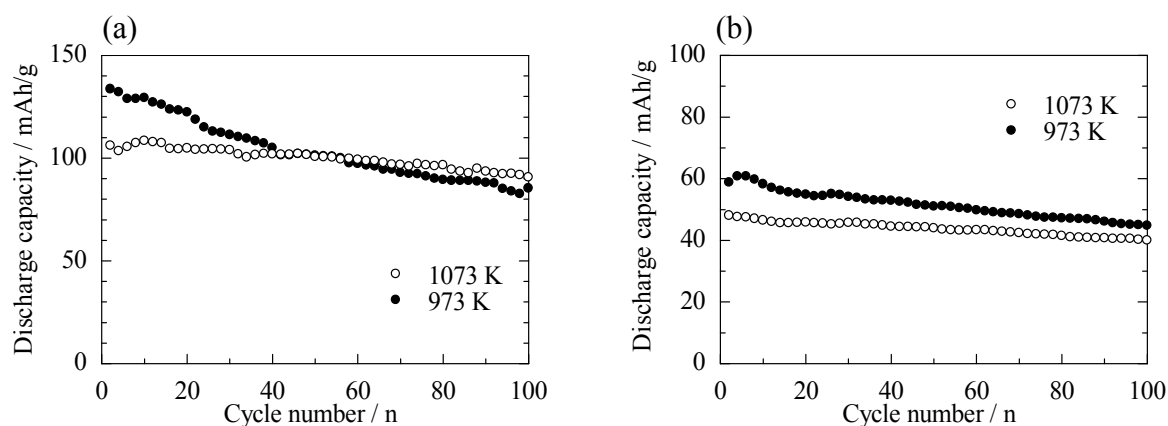


Fig.5 Cycle performance of C/LiMnPO₄ cathode, (a) at 0.1 C and (b) at 1 C

were observed in all C/LiMnPO₄ powders at 1100 cm⁻¹. Figure 4 shows the first charge and discharge curves of C/LiMnPO₄ cathodes at 0.1 C and 1 C. The typical long plateaus of the olivine structure were not observed in these curves. At 0.1 C, the first discharge capacity of C/LiMnPO₄ cathodes calcined 973 K and 1073 K was 135 mAh/g and 105 mAh/g, respectively. At 1 C, the first discharge of C/LiMnPO₄ cathodes calcined 973 K and 1073 K were 60 mAh/g and 50 mAh/g, respectively. It was not observed the redox peak in cyclic voltammogram of C/LiMnPO₄ cathodes. These results suggested that the Li⁺ ion was difficult to intercalate/deintercalate in the LiMnPO₄ structure. Figures 5a and 5b show the cycle performance of C/LiMnPO₄ cathodes at 0.1 C and 1 C, respectively. After 100 cycles at 0.1 C, the discharge capacities of C/LiMnPO₄ cathodes calcined 973 K and 1073 K were 85.6 mAh/g and 90.4 mAh/g, respectively; thus, the discharge capacities reduced to 64.0% and 85.1%, respectively, of the first discharge capacities at 0.1 C. After 100 cycles at 1 C, the discharge capacities of C/LiMnPO₄ cathodes calcined at 973 K and 1073 K was 44.8 mAh/g and 40 mAh/g, respectively; thus, the discharge capacities reduced to 74.7% and 80%, respectively, of the first discharge capacities at 1 C.

Conclusion

C/LiMnPO₄ precursors were prepared by the complex polymerized method using a solution of citric acid and ethylene glycol. XRD measurements revealed that the crystal phase of calcined C/LiMnPO₄ powders was in agreement with an orthorhombic olivine structure. The first discharge capacities of C/LiMnPO₄ cathodes calcined at 973 K were 135 mAh/g and 60.0 mAh/g at 0.1 C and 1 C, respectively. After 100 cycles at 0.1 C and 1 C, the discharge capacities reduced to 85.1% and 80.0%, respectively, of the first discharge capacities.

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doi:10.4028/www.scientific.net/KEM.485

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doi:10.4028/www.scientific.net/KEM.485.115