

## Effect of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on Hydrothermal Synthesis of $\text{LiMnPO}_4$

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### Introduction

Lithium metal phosphates ( $\text{LiMPO}_4$ ,  $M = \text{Fe, Mn, Co and Ni}$ ) have been investigated as promising cathode materials for lithium ion batteries. The distinctive features of this kind of cathode materials are good thermal and structural stability due to a strong covalent bond between oxygen and phosphorus atoms. Actually, a good cycle performance of  $\text{LiFePO}_4$  has been demonstrated in many practical applications [1]. However, the operating potential of  $\text{LiFePO}_4$  (3.4 V vs.  $\text{Li}/\text{Li}^+$ ) is lower than that of conventional  $\text{LiCoO}_2$ . Therefore, there is a strong demand to develop  $\text{LiMPO}_4$  cathodes with higher redox potentials than that of  $\text{LiFePO}_4$  to achieve higher energy density of lithium ion batteries. So far, many efforts have been paid to develop  $\text{LiMnPO}_4$  because of its high redox potential of 4.1 V vs.  $\text{Li}/\text{Li}^+$ . The electrical conductivity of  $\text{LiMnPO}_4$  is two orders of magnitude lower than that of  $\text{LiFePO}_4$  [2]. This makes it difficult to prepare  $\text{LiMnPO}_4$  with adequate electrochemical performance for practical use. In our previous study, we synthesized carbon-coated  $\text{LiMnPO}_4$  via hydrothermal process with different carbon sources, and found that the electrochemical performance of  $\text{LiMnPO}_4$  with several hundred nm or less particle size depended on the state of carbon coating [3]. In this study, we focused on  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as a catalyst for appropriate carbon-coating on  $\text{LiMnPO}_4$  and investigated its role in the hydrothermal synthesis of carbon-coated  $\text{LiMnPO}_4$ .

### Experimental

$\text{Li}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  and sodium salt of carboxymethylcellulose were mixed in a molar ratio of 1.5 : 1 : 1 : 0.03. The amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  added to those starting materials was changed from 0 to 40 wt%. The mixture was then dissolved in pure water to prepare  $\text{LiMnPO}_4$  precursor solution, in which the concentration of  $\text{Mn}^{2+}$  was controlled to be  $3.0 \text{ mol dm}^{-3}$ . For comparison, a precursor solution without  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was also examined. The precursor solution was transferred into an autoclave, and then hydrothermally treated at 200 °C for 3 h. The product was collected by filtration and freeze-drying. The obtained sample was then ball-milled for 10 h at 400 rpm using a planetary-type ball mill and heated at 700 °C for 1 h under 97 % Ar + 3%  $\text{H}_2$  atmosphere. The crystal structure and morphology of samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The carbon on  $\text{LiMnPO}_4$  samples was analyzed by Raman spectroscopy. The electrochemical performance of samples was investigated by using 2032 coin-type cell with lithium metal anode and composite cathode including  $\text{LiMnPO}_4$ , Ketjen Black and polyvinylidene fluoride (PVdF). The mixing ratio of  $\text{LiMnPO}_4$ , Ketjen Black and PVdF was 75:15:10 in weight. A mixed solvent between ethylene carbonate (EC) and diethyl carbonate (DEC) (1:2 in vol.) with  $1 \text{ mol dm}^{-3}$

$\text{LiPF}_6$  in was used an electrolyte solution. The charge - discharge measurement was performed in a potential range of 2.0 ~ 4.5 V at 30 °C.

### Results and discussion

Figure 1 shows XRD patterns of the samples prepared without and with 2 wt%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Both samples were crystallized in an orthorhombic olivine structure with a  $Pnma$  space group. However, the sample prepared without  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  showed two small peaks due to impurities. Figure 2 shows Raman spectra for the samples prepared without and with 2 wt%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The peaks attributable to G and D bands of carbon were clearly observed for both samples. However, the sample prepared without the Ni catalyst showed a small peak of  $\text{PO}_4^{3-}$ . This result suggests that the particle surface is roughly coated with carbon. In other words,  $\text{LiMnPO}_4$  is not covered with carbon, perfectly. On the contrary, the  $\text{PO}_4^{3-}$  peak was hardly observed for the sample prepared with the Ni catalyst. This difference supports that  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  works as a carbon coating catalyst and provides  $\text{LiMnPO}_4$  sample with a uniform carbon layer.

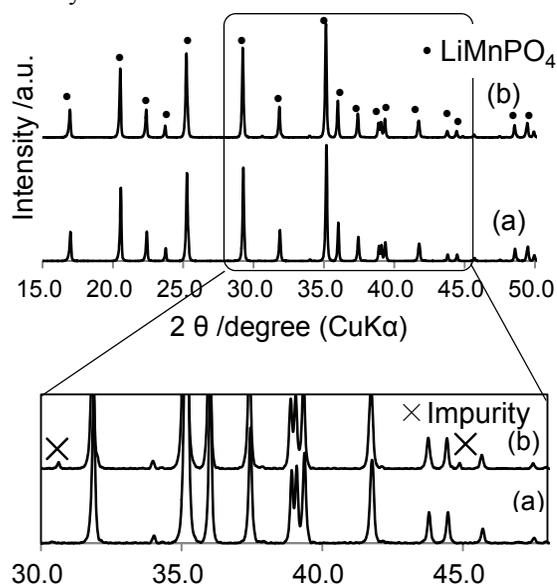


Fig. 1 XRD patterns of the products obtained from precursor solutions (a) with and (b) without 2 wt%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

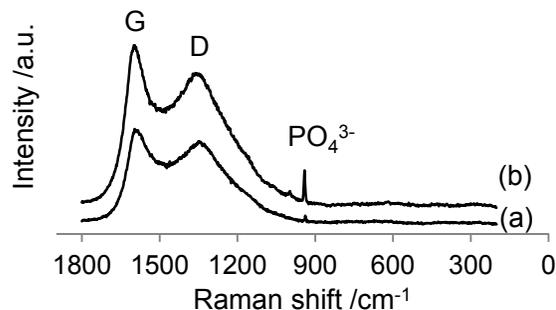


Fig. 2 Raman spectra of the products obtained from precursor solutions (a) with and (b) without 2 wt%  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

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