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Synthesis and Characterization of LiMnPO₄/Carbon Nanocomposite Material as Cathode Material

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Development of an eco-friendly, low cost and high energy density LiMnPO₄ cathode material has attracted much attention due to its high operating voltage vs. Li falling within the electrochemical stability window of conventional electrolyte solutions and offers more safety features due to the presence of a strong P-O covalent bond. Synthesis of battery materials integrates the battery technology specially in development of cathode materials. Solvothermal method is used for the synthesis of In LiMnPO₄ nanomaterials. The dried LiMnPO₄ nanoparticles were mixed with 10 wt% conductive carbon such as acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) binder for LiMnPO₄/C sample. The structure of the as-prepared LiMnPO₄ nanomaterial were studied by X-ray diffraction tool, morphology by scanning electron micrograph tool. The galvanostatic charge-discharge measurements of LiMnPO₄/C nanostructures is undertaken.

Keywords: LiMnPO₄, Solvothermal, X-ray diffraction, Scanning electron micrograph

INTRODUCTION

The cathode materials used in commercial rechargeable Li-ion batteries are the layered rock salt oxides LiCoO₂, LiNiO₂ and the spinel LiMn₂O₄. Recently, olivine structure based LiMPO₄ (M = Fe, Mn) [1-4] is attracted as alternative cathode materials for lithium-ion batteries because of its excellent cyclability, thermal stability, low cost and environmental benefits. However, these materials have a low electronic and ionic conductivity leading to the poor rate capability. Fortunately, these problems are overcome by coating conductive carbon on the surface of the particles. Presently, LiFePO₄ [5] has been extensively studied and developed as potential candidate for commercial Li ion battery. In fact, LiMnPO₄ seems more promising in performance than LiFePO₄ due to higher operating voltage (4.1V vs. Li+/Li), which contributes to a 20% increase in

energy density. However, due to poor electrochemical activity, the achievement of such high energy density [6] remains a challenge. In this study, LiMnPO₄ nanoparticles [7-8] were synthesized in low temperature synthesis *via* solvothermal technique and characterized.

Present study reports the synthesis of LiMnPO₄ nanomaterials using solvothermal method. LiMnPO₄/C battery material is prepared by carbon insertion in LiMnO₄ material using acetylene black and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) binder. The structure of the as-prepared LiMnPO₄ nanomaterial were studied by X-ray diffraction tool, morphology by scanning electron micrograph tool. The galvanostatic charge-discharge measurements of LiMnPO₄/C nanostructures is undertaken.

EXPERIMENTAL

Materials and Methods

All the chemicals used in the present study are of AR

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(Analytical Reagent) grade. Solvothermal method is used for the synthesis of LiMnPO₄ nanomaterials. Electrode materials of LiMnPO₄ are prepared by mixing with carbon.

Synthesis of LiMnPO₄ Nanomaterials

LiMnPO₄ nanomaterial was synthesized by solvothermal process. In a typical synthesis process, manganese acetates [Mn-(CH₃COO)₂], phosphoric acid (H₃PO₄) and lithium acetate [Li-CH₃COO] were added to suitable amount of Diethylene glycol (DEG) in the molar ratio of 1:1:1 (Li:M:P) and stirred separately for about 60 min at room temperature. Subsequently, the transition metal solutions were transferred into separate 60 ml Teflon-lined stainless steel bombs, which were then sealed and heated at 200 °C for 20 h. The resulting precipitates were thoroughly washed several times with acetone and methanol to remove organic compounds and the sample was dried to obtain powder.

Synthesis of LiMnPO₄/C Electrode

Electrochemical properties were studied by using coin type electrode cell. The dried LiMnPO₄ nanoparticles were mixed with 10 wt% conductive carbon such as acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) binder. The slurry was consistently mixed and pasted onto aluminium foil (for cathode) by doctor blade method and dried in an oven at 80-100 °C over night under vacuum. Electrodes prepared in this way were then pressed under 200 kg cm⁻² and kept in an argon filled glove box. For examining the electrochemical properties of the as-prepared electrodes, coin-type cells (CR2032) were used. The cells included the as-prepared electrode as the working electrode, lithium foil as the counter and reference electrode, a porous polypropylene (Celgard 2300) as the separator, and 1M LiPF₆ in a mixed aprotic liquid as the electrolyte. The cells were constructed in an argon loaded glove box with O₂ and H₂O levels less than 0.1 ppm [9-11].

Characterization. The structures of as-prepared LiMnPO₄ were studied by X-ray diffraction using Phillips X-ray diffractometer (PW3710) with Cu K α as source of radiation. Morphology and bonding of the above oxide was studied by Phillips XL 30 ESEM.

RESULTS AND DISCUSSIONS

X-ray Diffraction Study

The crystalline phases of the LiMnPO₄ nanostructure materials were determined by X-ray diffraction using Cu-K α radiation. Figure 1 shows XRD patterns of as-prepared material. All diffraction peaks can be indexed to an orthorhombic olivine phase, which matches well with the standard data (JCPDS card No: 81-1173). Results show that LiMnPO₄ nanomaterial prepared in the absence of carbon has strongest peak at 35 degree, indicating the formation of olivine structure. The unit cell parameters (*a*, *b* and *c*) for the orthorhombic cell pertaining to LiMnPO₄ were determined to be *a* = 10.4406, *b* = 6.0955, *c* = 4.7406 Å. Interestingly, the XRD results showed that the solvothermal process could produce phase pure LiMnPO₄ with no undesirable impurity phases such as Li₃PO₄ and transition metal compounds, thus avoiding the complex procedures for tedious and conventional post-heat treatments. Additionally, it indicates that LiMnPO₄ material with high crystallinity can be synthesized by the solvothermal method at lower temperatures than that in the polyol process [8].

Scanning Electron Micrograph Study

The morphologies of as-prepared materials were observed by scanning electron microscopy. Figure 2 shows SEM image of LiMnPO₄ nanoparticles. Most of the particles observed in the image are of spherical in shape and some are compacted each other. Crystalline nature of the sample is well defined, in agreement with XRD results. The LiMnPO₄ nanoplates obtained after a solvothermal reaction showed a plate shape with the length of ~800 nm.

Electrochemical Charging and Discharging Study

The electrochemical efficiency of the as-prepared materials was analyzed by galvanostatic charge-discharge and cyclability. The tests were carried out in coin cells (CR2032). The electrode composition was 80 wt% of the as-prepared materials, 10 wt% of carbon black and 10 wt% of polyvinylidene fluoride (PVDF). The electrolyte solution was 1 M LiPF₆ in a 1:1:1 combination of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate

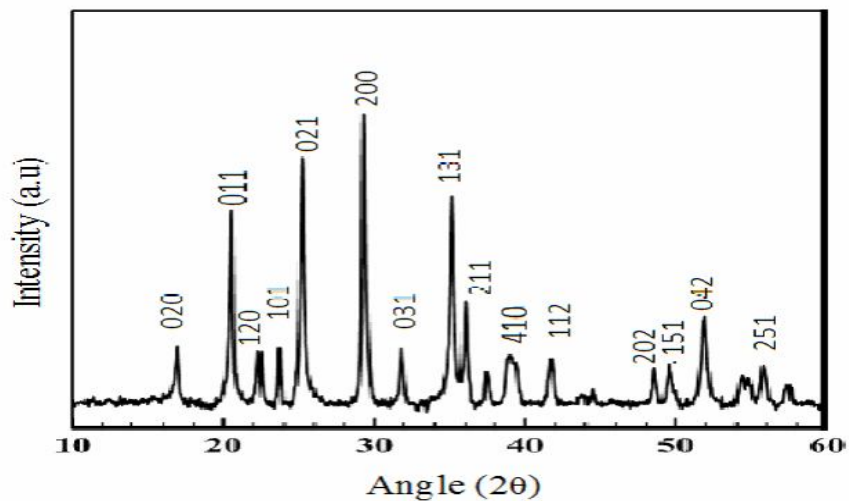


Fig. 1. XRD patterns of as-prepared LiMnPO₄ material.

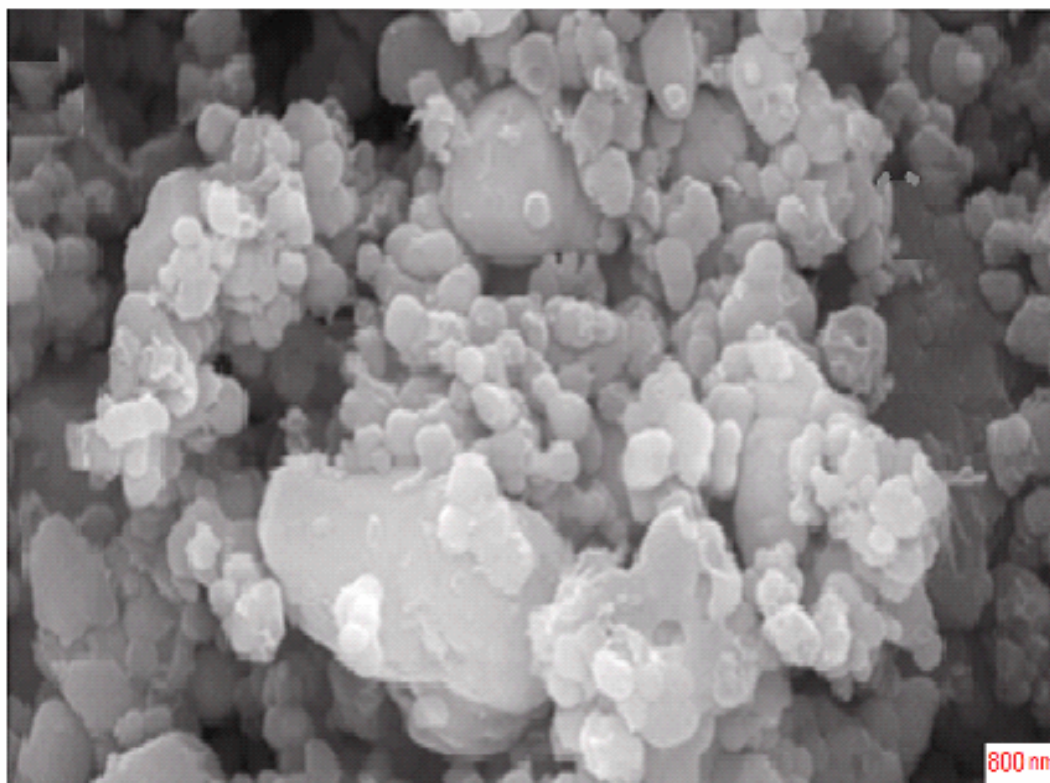


Fig. 2. The SEM image of LiMnPO₄ sample synthesized by solvothermal method.

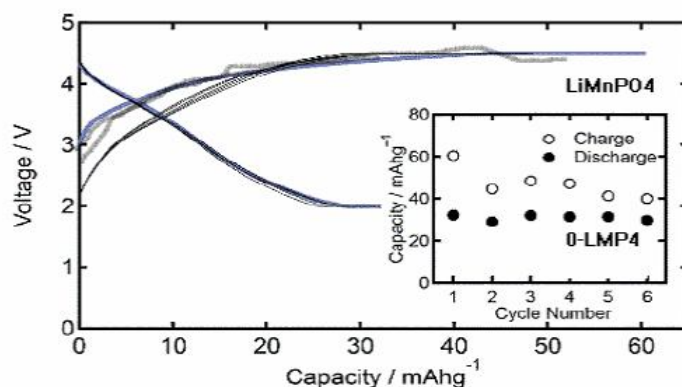


Fig. 3. The initial charge/discharge curves of LiMnPO₄/C samples at current density of 0.02 mA cm⁻² in voltage range of 2.5-4.5 V and Cyclability of LiMnPO₄.

(DMC). The galvanostatic charge and discharge experiment was conducted between 2.5-4.5 V at room temperature using a battery testing system. Figure 3 reveals the charge-discharge curves and cycling performance of the electrodes made of as-prepared materials at different C-rates. The charge procedure was performed at the same amount as the discharge procedure to 4.5 V followed by a constant voltage charge at 4.5 V. The cell discharge capacity increases with the charge cutoff voltage. The galvanostatic charge-discharge measurements of LiMnPO₄/C nanostructures shows the initial discharge capacity of ~65 mAh g⁻¹ at current density of 0.02 mA cm⁻², and LiMnPO₄ nanocrystals synthesized at 200 °C for 10 reactions shows a galvanostatic charging-discharging capacity of ~56 mAh g⁻¹ at 0.1 C rate.

CONCLUSIONS

This solvothermal method may be used for the preparation of other nanomaterials because of its simplicity.

- Applicable morphology of the sample may depend on the preparative technique
- Nanosized crystalline materials are prepared by this method
- Crystalline materials formed in simple way with charging and discharging capacity.

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