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Preparation and characterization of nanosize LiMn_2O_4 cathodes for lithium ion battery

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ABSTRACT

The LiMn_2O_4 nanosized particles were synthesized using sol-gel, solid state reaction followed by hydrothermal method and traditional solid state method. The obtained nanosized particles were characterized by XRD and SEM. The samples were found to possess pure spinel phase with different particle size and shape. The electrochemical characterization of the nanosized particles was analyzed using charge-discharge cycling. The discharge capacity values were 120 mAh g⁻¹, 110 mAh g⁻¹ and 90 mAh g⁻¹ for nanorods, nanoparticles and micron sized particles respectively. Cathode made with nanorods exhibits better cycling performance than the cathodes made with nanoparticle and micro particles. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Synthesis;
Nanosized particles;
Cathode;
Li-Battery.

INTRODUCTION

LiMn_2O_4 compounds are most capable material in lithium insertion electrode for rechargeable lithium batteries. These electrodes are cost-effective and feasible when compared to LiNiO_2 and LiCoO_2 . LiMn_2O_4 cathode shows high cell voltage, long cycle life, non-toxicity and environmentally safe^[1]. The traditional synthesis method of LiMn_2O_4 is the solid-state reaction method. In this method, lithium and manganese salts of oxides or carbonates are ground well followed by calcining at high temperature. Generally LiMn_2O_4 produced in this method are chemical in-homogeneity, broad particle size distribution and long reaction time or unwanted phases.

Nowadays, sol-gel technique, Pechini method and combustion method have been developed to overcome the above-mentioned disadvantages caused by solid-

state reaction. However, most of those methods involve complicated steps during the preparation and hence unsuitable for large scale production^[2, 3]. Physical and chemical properties of the nanocrystalline materials having 1 – 100 nm range exhibits greater ductility, larger thermal expansion, high diffusivity and reactivity relative to the corresponding bulk materials so researchers focused on this field^[4]. Spinel LiMn_2O_4 cathode material have been prepared by different methods such as laser deposition^[5, 6], electrospraying^[7, 8], radio frequency magnetron sputtering^[9].

In this paper, the LiMn_2O_4 powders synthesized by the sol-gel method and solid state reaction followed by hydrothermal method in comparison to the conventional solid-state reaction have been investigated. Besides, the electrochemical properties of the Li/ LiMn_2O_4 cells, which prepared by the three different methods,

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are also examined. The results reveal that the LiMn_2O_4 powders obtained from the sol-gel method and hydrothermal method have a larger initial capacity and show better reversibility than one formed in the solid-state reaction, due to its better crystallinity and morphology.

EXPERIMENTAL

LiMn_2O_4 cathode material was prepared by three different methods. In sol-gel method, 0.5 mol lithium acetate and 0.25 mol manganous acetate and 0.75 mol citric acid were dissolved in distilled water. Each 10 mL of the solution was taken in a beaker. To this solution, 0.2 g of CTAB was added as a surfactant. The solution was heated at 80°C upto getting white colour gel. This gel was transferred to a crucible and heated at 350°C for 4 hours. It was then heated at different temperatures ranging from 600 to 800°C for 12 hours to get LiMn_2O_4 .

In solid state method, stoichiometric mixture of lithium acetate and manganese acetate were mixed by grinding the reactants. This mixture was heated at 350°C for 4 hours and then heated at 800°C for 12 hours to get LiMn_2O_4 .

Analytical grade $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8$ (99.99% Aldrich), and distilled water were used to prepare $\beta\text{-MnO}_2$ nanorods by hydrothermal reaction as reported elsewhere^[10]. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_8$ were dissolved at room temperature with a molar ratio of 1:1 in 80 mL of distilled water by magnetic stirring to form a homogeneous clear solution. The mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 120°C for 24 hours in a preheated electric oven for the hydrothermal reaction. After the reaction, the final precipitated products were washed sequentially with distilled water. The obtained powder was subsequently dried at 100°C for 12 hours in air. Preparation of LiMn_2O_4 nanorods by solid state reaction as reported elsewhere^[11]. In this method 1:2 molar concentration of $\text{LiOH} \cdot \text{H}_2\text{O}$ and synthesized $\beta\text{-MnO}_2$ nanorods were ground to form a fine mixture for several hours. The powder was then calcined at 800°C in air for 8 hours.

Electrochemical performance of the electrodes was tested by assembling coin-type (CR2032) cells with a battery test system (Maccor series 4000). The cath-

ode was normally composed of 75wt% composites, 20wt% acetylene black and 5wt% polyvinylidene difluoride (PVDF) as a binder in N-methylpyrrolidinone (NMP), the mixed slurry was spread on a thin aluminum foil and dried in oven at 80°C for 3h and then pressed and dried in vacuum for 24 hours. A metal lithium foil was used as a counter-electrode and the electrolyte was 1M LiPF_6 dissolved in a 1:1 v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cell was assembled in a glove box under argon atmosphere and cycled galvanostatically on a multichannel battery test mode.

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray diffraction patterns of spinel LiMn_2O_4 prepared using the citric acid assisted sol-gel method. The LiMn_2O_4 calcinated at 800°C is well crystallized and all the diffraction peaks matches with standard JCPDS value (JCPDS 35-0782), but the powders calcinated lower than 800°C contains impurity of Mn_2O_3 phase and also they are not well crystalline in nature. By increasing the calcination temperature, the manganese oxide phase disappears gradually. As could be seen from Figure 1 the powders calcinated at 800°C were well crystallized into the cubic spinel structure without impurities.

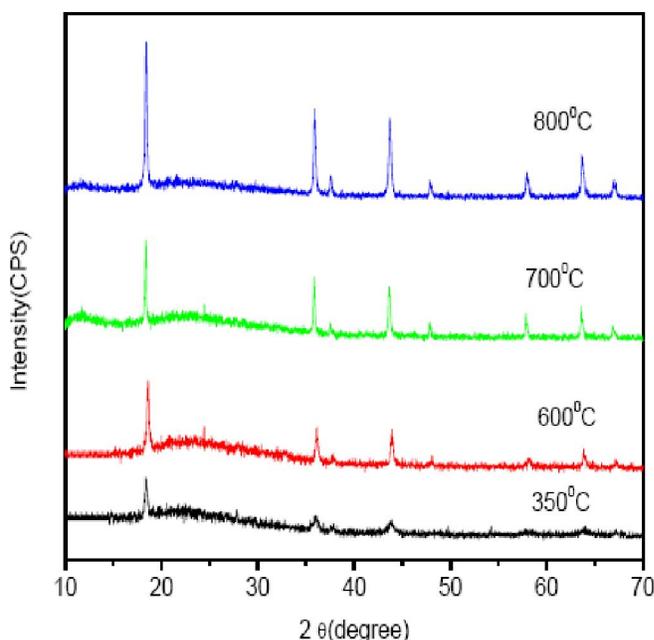


Figure 1 : XRD pattern of LiMn_2O_4 at different temperature prepared by Sol-gel method

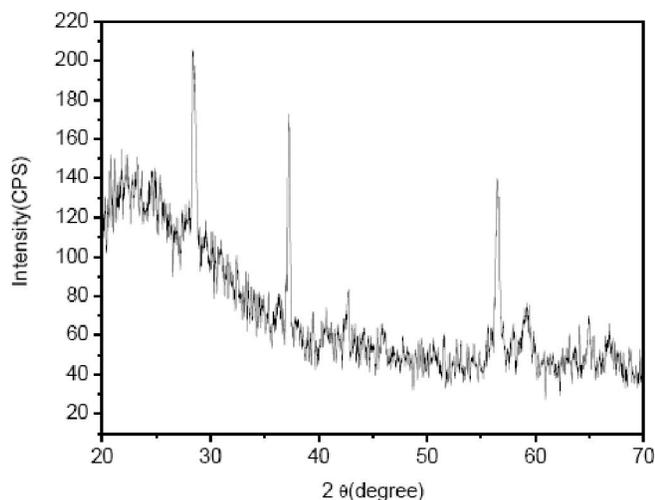


Figure 2 : XRD pattern of β - MnO_2 prepared by hydrothermal method

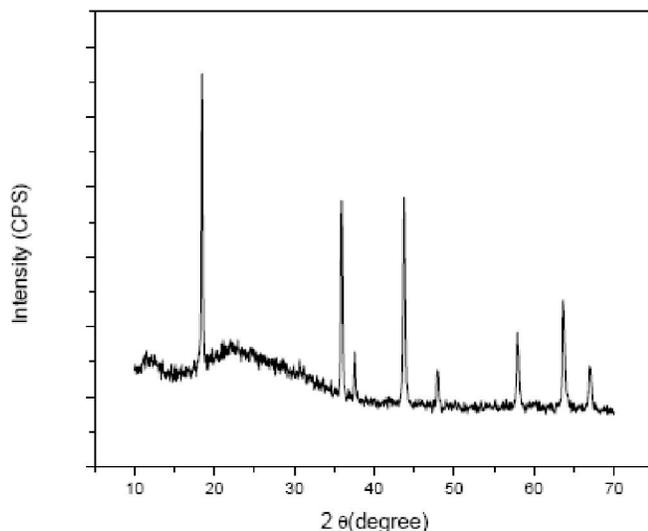


Figure 3 : XRD pattern of LiMn_2O_4 prepared by solid state method using β - MnO_2

Figure 2 shows XRD of β - MnO_2 prepared by hydrothermal method. All the diffraction peaks matches with standard JCPDS file (JCPDS 24-0735) having tetragonal symmetry. Figure 3 shows the XRD pattern of LiMn_2O_4 prepared by solid state reaction followed by hydrothermal method. The XRD diffratogram of LiMn_2O_4 shows features of the spinel structure with no peaks of the β - MnO_2 phase detected (Figure 2). The reaction between β - MnO_2 and LiOH at 800°C produced the pure LiMn_2O_4 phase.

Figure 4 shows SEM image of LiMn_2O_4 prepared by Sol-gel method. It is found that the spinel crystals can be observed in the particle morphology with uniform structure with narrow size distribution. These can

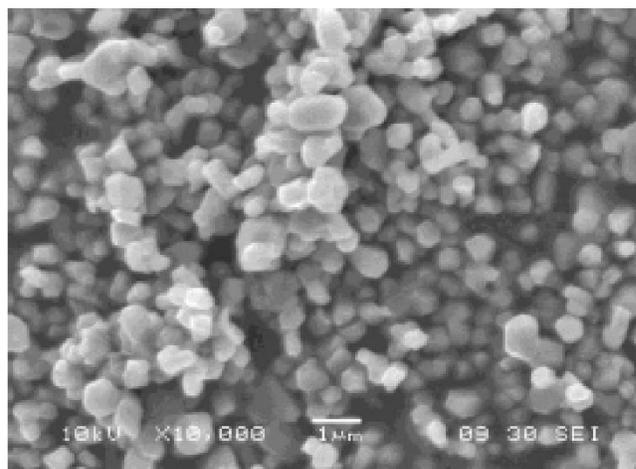
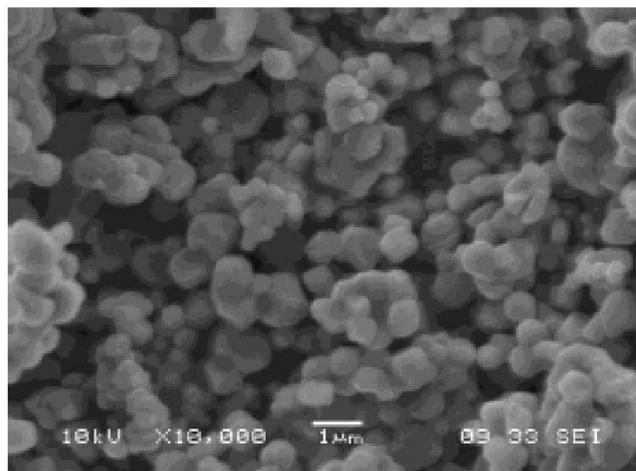


Figure 4 : SEM of LiMn_2O_4 prepared by Sol-gel method

be attributed to the chelating action of citric acid and that forms complex network, where the metal ions are uniformly distributed in the matrix, and the gel precursors are of atomic scale and homogeneously mixed with each other. Thus, during thermal decomposition it prevents phase separation and leads to the formation of homogeneous sized particles. This mechanism was also controlled by surfactant. So it helps to give more uniform and well crystalline compound.

SEM image of the LiMn_2O_4 prepared by solid state reaction was shown in Figure 5. It is around 1 micron in size and it is also well crystalline in nature.

SEM Image of β - MnO_2 is shown in Figure 6. SEM images showed that the particles consisted of nanorods with an average diameter of 30 nm and an average length of 2 μm . Figure 7 shows the SEM image of LiMn_2O_4 prepared by using β - MnO_2 . The LiMn_2O_4 particles also consisted mainly of nanorods which appear to have a larger average diameter and a

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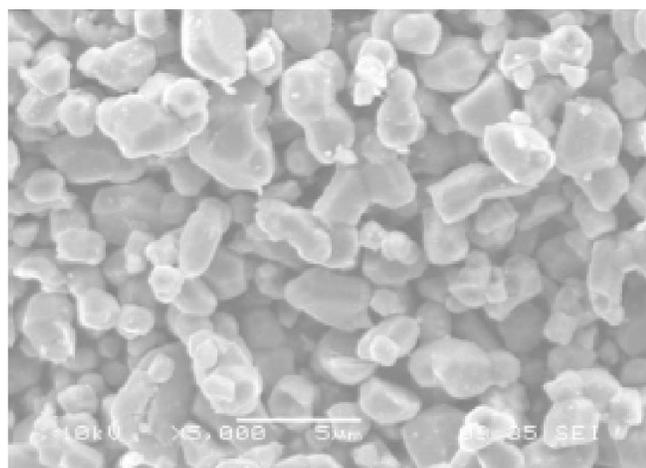
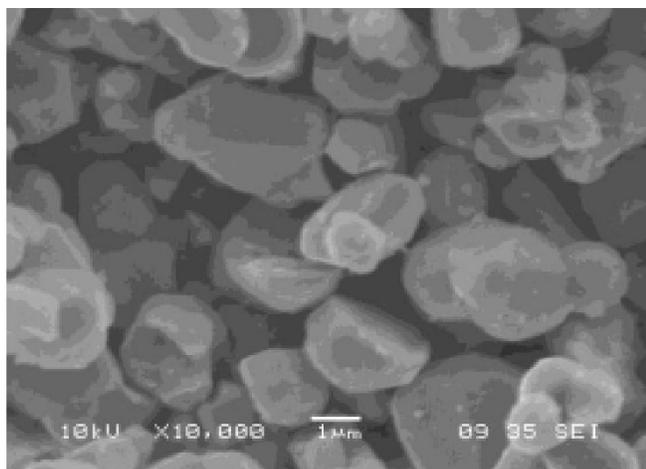


Figure 5 : SEM of LiMn_2O_4 prepared by solid state method

shorter average length than $\beta\text{-MnO}_2$ nanorods. These LiMn_2O_4 nanorods are well crystalline and homogenous in nature.

Electrochemical properties of the obtained LiMn_2O_4 are preliminarily evaluated using 2025 coin-type cell. Representative charge–discharge curves of the obtained LiMn_2O_4 are shown in Figure 8. Charge–discharge tests in a potential range from 3.3 to 4.5V in the first cycle were carried out to measure the electrochemical performance of the prepared samples shown in Figure. In order to avoid the transformation from cubic $\text{Li}[\text{Mn}_2]\text{O}_4$ to tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$, under limit value was fixed at 3.3V^[12]. It can be easily observed that two distinct potential plateaus in both charge and discharge curves. The insertion and extraction of lithium ions occur in two stages is indicated by two voltage plateaus^[13]. The first voltage plateau is attributed to the removal of lithium ions from half of the tetrahedral sites in which Li–Li interactions occur. The second voltage plateau is due to the removal of lithium ions from the other tetrahedral

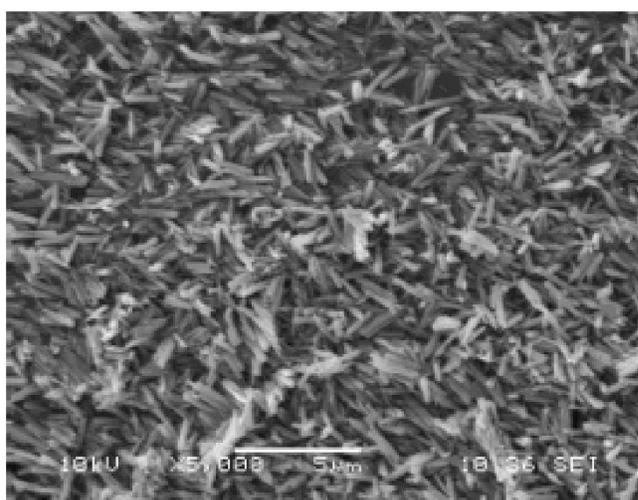
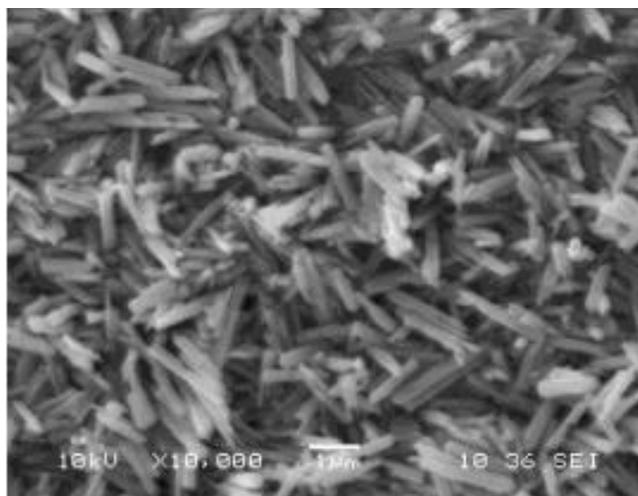


Figure 6 : SEM of $\beta\text{-MnO}_2$ prepared by Hydrothermal method

sites in which lithium ions do not have Li–Li interactions^[14, 15].

The discharge capacity values of LiMn_2O_4 depends on the method of preparation and conditions of charge–discharge cycling. Ahn et al synthesized LiMn_2O_4 by solid-state reaction and they reported discharge capacity values between 90 and 100 mAh g^{-1} ^[16]. Lanz et al synthesized LiMn_2O_4 by ceramic process and their discharge capacity of about 115 mAh g^{-1} at C/5 discharge rate^[17]. Park et al. reported about 115 mAh g^{-1} at C_1 rate for a commercial sample^[18].

The initial discharge capacity of spinel LiMn_2O_4 for a nanorods, nanoparticle and micron sized particles is 92, 109 and 118. mAh g^{-1} , respectively. The result indicates that the discharge capacity of first cycle increases with decreasing in size of the particle. The cycling ability of LiMn_2O_4 spinel of different samples was evaluated and cyclic performance of LiMn_2O_4 is shown in

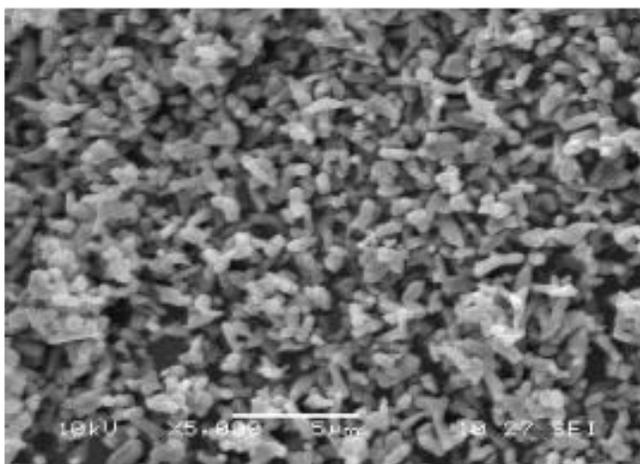
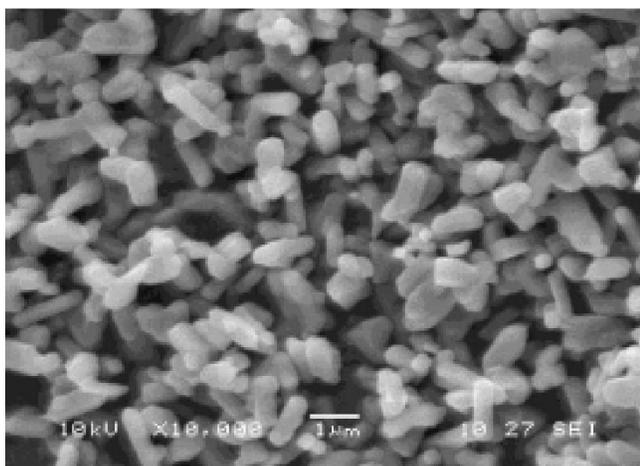


Figure 7 : SEM of LiMn_2O_4 prepared by solid state method using $\beta\text{-MnO}_2$

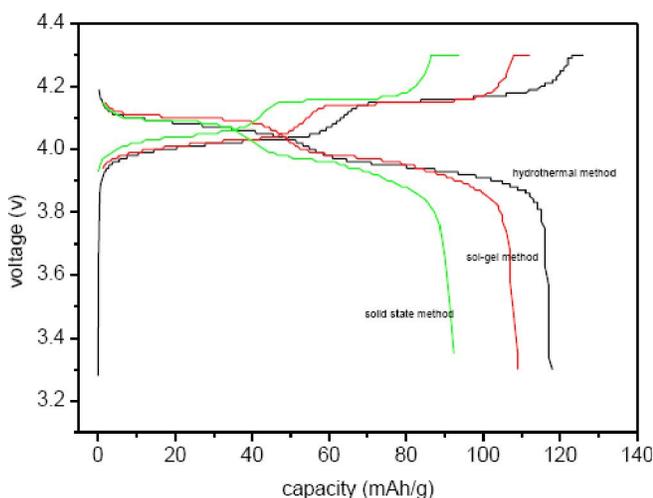


Figure 8 : Charge- Discharge curves of LiMn_2O_4

Figure 9. The capacity retention is better in nanorods than nanoparticles and micro particles. The results of electrochemical cyclic performance of samples prepared by different methods were inferred that long-term

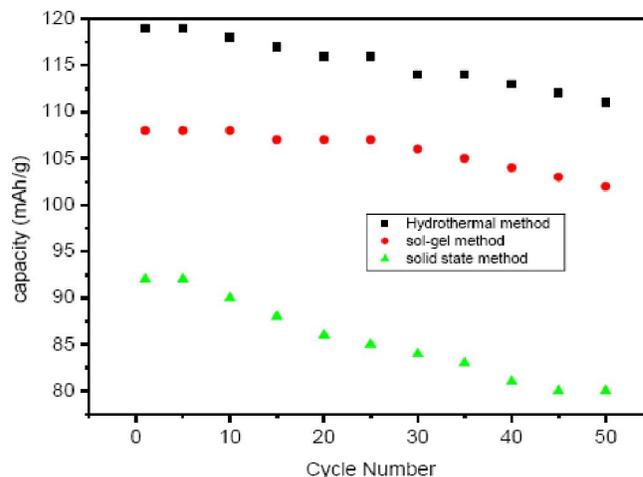


Figure 9 : Variation of capacity of LiMn_2O_4 as a function of cycle number

cyclic performance of sample prepared by hydrothermal method was better than that of sample prepared by sol-gel method and it was better than sample prepared by solid state reaction method at the same current density. The increase of capacity in sample prepared by hydrothermal method may be attributed to the $\text{Li}^+\text{-Li}^+$ Coulomb repulsion that is lower at the surface of sample enhancing local Li capacity because there is no neighbouring Li^+ outside the particle.

Therefore, the results obtained above confirm that smaller particle size in diameter delivers higher capacity. The improvement of the discharge capability of the sample prepared by hydrothermal method is mainly attributed to shorter and easier diffusion path of Li^+ in a material with small grain size as mentioned above. Therefore, the LiMn_2O_4 synthesized by hydrothermal method has the best electrochemical performance among three samples, which is closely related to its structural characteristics, such as, smaller unit cell volume, higher crystallinity, and smaller particle size.

CONCLUSIONS

Nanostructured LiMn_2O_4 spinel phase was synthesized by hydrothermal method, sol-gel method and micro sized particle was prepared by traditional solid state method. Nanorods were prepared by hydrothermal method and nanoparticles were prepared by sol-gel method. The spinel LiMn_2O_4 prepared by hydrothermal method shows a good discharge capacity. Electrochemical data demonstrated that electrochemical re-

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action activity and diffusion property of the electrode material with nanostructure synthesized by hydrothermal route are dramatically improved, which is related to the strong interaction of sample. The results showed that the LiMn_2O_4 powders prepared by the hydrothermal method possess good electrochemical properties than the sample prepared by sol-gel method and sample prepared by traditional solid state method.

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