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Synthesis and Electrochemical Improvement of Nanocrystalline $LiMn_{2-X}Mg_XO_4$ Powder Using Sol-Gel Method

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With the advancement of nanotechnology, there is an interest in the replacement of conventional materials by nanomaterials. There is a reasonable chance that as the active mass of electrode for lithium batteries is comprised of smaller particles, they will perform better in terms of capacity, power, rate capability and stability. The "bottom–up" approach of $LiMn_{2-X}Mg_XO_4$ (X=0.5) Nano material was synthesized and characterized by electrochemical techniques. $LiMn_2O_4$ is inexpensive material but it shows rather poor cyclic performance. The electrochemical performance of spinel type $LiMn_2O_4$ has been effectively improved with doping of Mg by Sol-Gel method. Their structural and textural properties of $LiMn_{2-X}Mg_XO_4$ (X=0.5) was determined by using X-ray diffraction (XRD), Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), Cyclic Voltammetry technique was used to characterize the reversibility of the cathode material. Cells made from the spinels have exhibited good rate of performance at C/10 rate charge – discharge studies.

Keywords: $LiMn_{2-X}Mg_XO_4$, Sol-Gel method, Lithium-ion battery, Nanomaterial

1. INTRODUCTION

Research in the field of rechargeable lithium-ion batteries has made a significant progress in the past decade through an increasing demand for using Nano materials. The structures of nanomaterials commonly used to prepare the positive electrodes for rechargeable lithium batteries, generally consist of three and two dimensional frame works capable to preserving the network upon insertion or exertion of lithium. Two paradigmatic compounds of these systems are $LiMn_2O_4$ and $LiCoO_2$, which have received much attention [1-4]. The explosive demand for portable electronic devices has brought about in the importance of compact, lightweight and reliable power sources. One of the most portable candidates for such requirements is Li-ion rechargeable battery, which employs two intercalation compounds for electrode materials. Lithiated transition metal oxides ($LiCoO_2$,

$LiNiO_2$ and $LiMn_2O_4$) have been extensively studied as cathode materials for commercialization of rechargeable lithium batteries. Among these, spinel lithium manganese oxide ($LiMn_2O_4$) has been considered as a promising candidate for cathode material due to its high intercalation voltage, low cost, abundance and non-toxicity [5-8]. $LiMn_2O_4$ powders are usually synthesized by a solid-state reaction of lithium and manganese salts [9-12]. Because of the several disadvantages of this method, viz. inhomogenity, irregular morphology, larger particle size distribution, poor control of stoichiometry and a longer period of calcinations followed by introduced for the synthesis of high performance cathode active materials for rechargeable lithium batteries [13-16]. To improve the performance of the spinel phase $LiMn_2O_4$ several research groups have studied the properties of manganese substituted $LiM_XMn_{2-X}O_4$ [M= Cr, Co, Ni, Fe, etc] [17-18]. Thackeray et al [19] has pointed out that the substitution of a metal cation for Mn enhances the stability of spinels. In this present work, the spinel nano $LiMg_xMn_{2-x}O_4$ has been prepared via Sol-Gel method. Magnesium was selected as the substitute material because of it low atomic weight compared with $LiMn_2O_4$. The structure and morphology of the product has been investigated and improve the electrochemical behaviour of $LiMn_2O_4$.

2. EXPERIMENTAL

Abundant Mg-doped $LiMn_{2-x}Mg_xO_4$ (x=0.5) spinel cathode material for lithium-ion batteries was prepared by Sol-Gel method. The solution for Sol-Gel method was obtained by dissolving stoichiometric ratios of $CH_3COOLi.2H_2O$ (99%), $Mg(CH_3COO)_2·4H_2O$ (99%) and Mn $(CH_3COO)_2.4H_2O$ (99%) in distilled water and mixed well with citric acid in distilled water. The resulting precursor solution was evaporated at 80°C under constant stirring for 6 hours. The evaporation increases the viscous of the solution and further heating lead to the formation of polymeric resin. Obtained polymeric resin was further heated at 175°C for 12 hours to obtained polymeric intermediates with solid mass nature. Calcining at 800°C for 6 hours, the polymeric intermediate caused the decomposition of organic derivatives due to the combustion and led to the formation of nano crystalline $LiMn_{1.5}Mg_{0.5}O_4$ powder. The flow chart diagram for the synthesis of nano crystalline $LiMn_{1.5}Mg_{0.5}O_4$ powder by citric acid through Sol-Gel route is given in Fig.1.

Synthesis of nano crystalline $LiMn_{1.5}Mg_{0.5}O_4$ powder by citric acid assisted Sol-Gel route was investigated through Thermogravimetric analysis (TGA) in TG/DTA Analyzer Model STA-1500 at heating rate of 10°C/min. XRD (JOEL Model JDX 8030 X-ray diffractometer using Cu-kα radiation), Scanning Electron Microscope (Philips Scanning Electron Microscope), Transmission Electron Microscope (TEM, JEM-2010) are to identify the structural co-ordination and crystalline phase.

The electrochemical performance of the as-prepared powder electrodes were estimated with two-electrode coin-type cell (2032) with lithium foil as the reference electrode. All testing electrodes were prepared by coating the slurry of a mixture (composed of 80 wt. % active cathode powders, 10 wt. % conducting agent (acetylene black) and 10 wt. % binders (polyvinylidene fluoride)) onto an copper foil current collector. After drying in air at 80°C for 4h, the electrodes were pressed under 20MPa for 1 min, and then dried at 120°C for 24h in a vacuum drier. The weight of the active materials in the electrode sheet was about 10mg cm^{-2}. The cells were assembled in an Ar filled glove box. The electrolyte was 1M $LiClO_4$ in the mixture of ethylene carbonate (EC) and propylene carbonate (PC) with mass ratio being 1:1. A polypropylene (PP) film (Cellgard 2300) was used as the separator. Galvanostatic charge–discharge tests were conducted on a WPG instrument, South Korea battery program-control test system with the cut-off voltages of 3 and 5V (versus Li/Li$^+$) under a specific current density (a nominal specific capacity of 120mAhg^{-1} was assumed to convert the current density into C rate). The cyclic voltammogram (CV) test was performed on EG&G PARC model 6310, Electrochemical Impedance Analyzer coupled with M398 software at room temperature with a scan rate of 0.1mVs^{-1}.

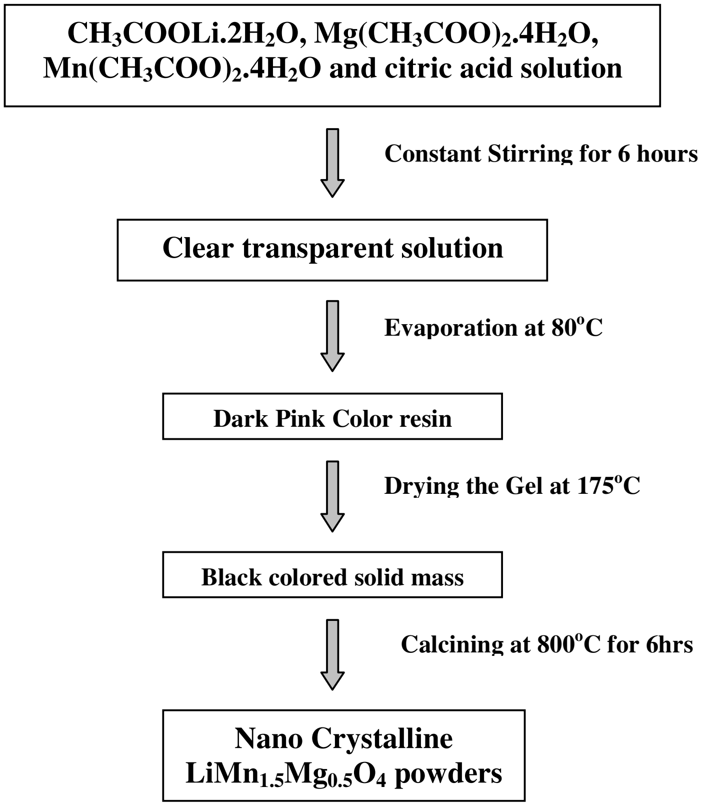

Figure 1. Schematic representation for the preparation of nanocrystalline $LiMn_{1.5}Mg_{0.5}O_4$ powders

3. RESULTS AND DISCUSSION

3.1 Thermal Studies

Fig.2 Shows the typical TGA and DTA curves of $LiMn_{1.5}Mg_{0.5}O_4$ powder. TGA curve which exhibit three distinct weight loss steps and the DTA curve shows one endothermic peak and exothermic peaks. The first weight loss step in the temperature range about 150-200°C is accompanied by an endothermic peak around 190°C on the DTA curve, which is due to the loss of residual water in the gel. The second weight loss step in the temperature range of 200-400°C is associated with the decomposition of chelating agent, nitrate and acetate ions. Third step conform the formation of the nanocrystalline $LiMn_{1.5}Mg_{0.5}O_4$ powder.

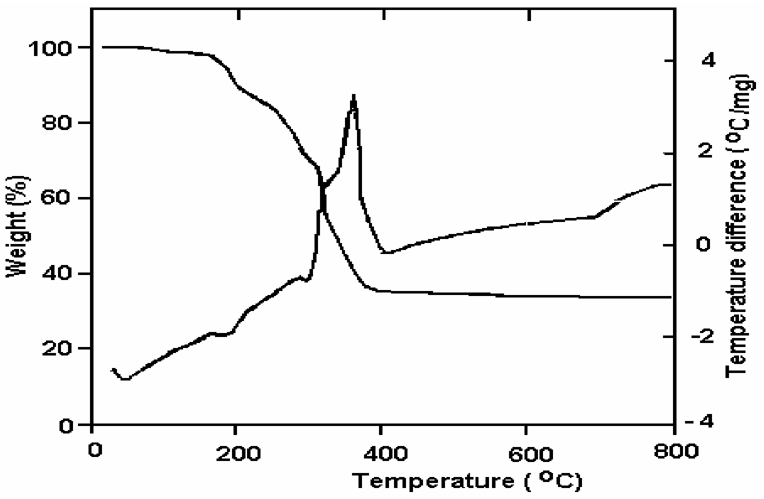

Figure 2. TGA / DTA Curves for $LiMn_{1.5}Mg_{0.5}O_4$ powder

3.2 X-ray diffraction

Fig.3 shows the X-ray diffraction pattern of $LiMn_{1.5}Mg_{0.5}O_4$ powder, calcined at 800°C. The diffraction peaks are much sharper, the width of the peaks is narrower and the positions which indicate the increase in crystallinity and the formation of single phase are confirmed. The crystal phase of the sample is identified from XRD data, which as an ordered spinal structure indexed by cubic Fd-3m and no other secondary products are detected. This fact indicates that the Mn site in $LiMn_2O_4$ is substituted full by Mg doping. For $LiMn_{1.5}Mg_{0.5}O_4$, the lattice parameter 'a' (8.2211A$^{o)}$ was calculated using a least square fit method.. According to the literature [20], the decrease is due to the increase in the concentration of Mn^{4+} ions in the spinel structure as Mn^{3+} ions are substituted by Mg^{2+} ions.

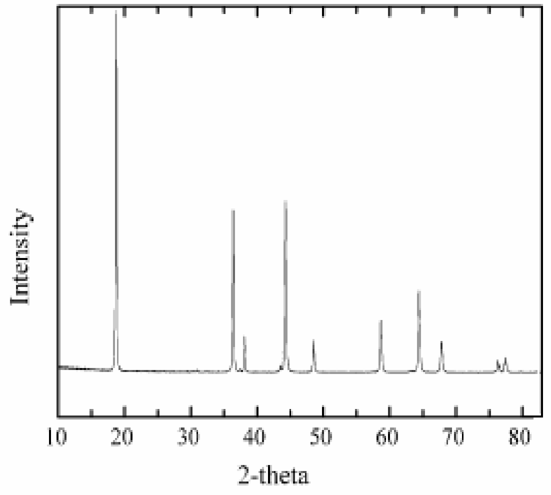

Figure 3. X-ray diffraction pattern of $LiMn_{1.5}Mg_{0.5}O_4$ powder

3.3 SEM and TEM

Fig.4 shows SEM and TEM images of $LiMn_{1.5}Mg_{0.5}O_4$ powder. The images also exhibit typical morphologies for the as-prepared powder. The particles have an average size of about 100-150nm and show uniform particle distribution. But from both images, it is obviously seen that the agglomeration takes place among the particles. Also, both in the TEM and SEM image, the powders prepared by Sol-Gel method have regular shapes with dell defined crystal faces. Especially, in SEM image, the particles exhibit single crystals of octahedral shape with well developed [111] planes [21]. This suggests that the products are in a good crystalline state. The presences of voids indicate that the product is porous in nature and it facilitates easy access of the battery electrolyte to increase the number of active sites favourable for good battery activities.

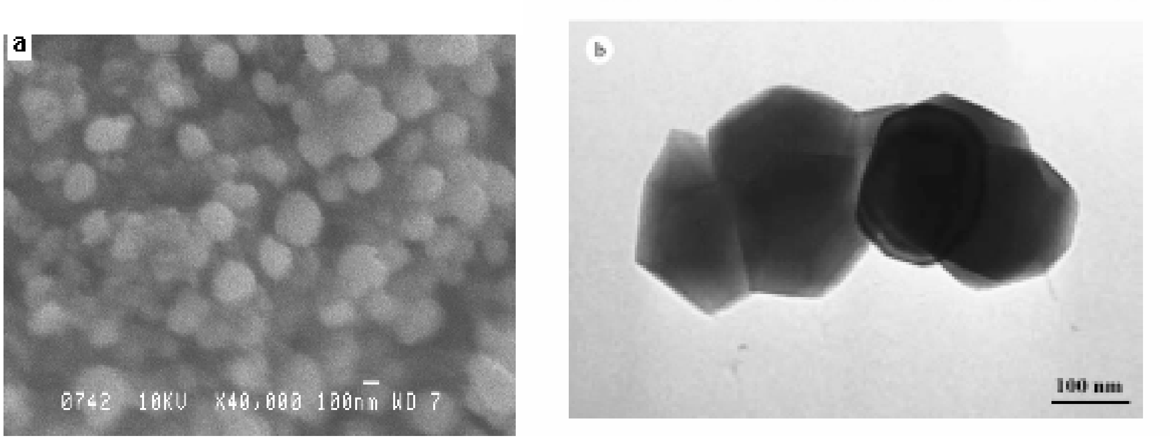

Figure 4. Images of $LiMn_{2-X}Mg_XO_4$ powders prepared by Sol-Gel method : (a) SEM and (b) TEM

3.4 Cyclic Voltammetry

In order to evaluate the electrochemical characteristics of the as-prepared powder of doped Mg ion, a series of electrochemical tests were performed. Fig.5 shows the cyclic voltammogram of the $LiMn_{1.5}Mg_{0.5}O_4$ powder at a scan rate of 0.1mVs-1. As can be seen in Fig.4 each one smooth and sharp reversible peak is obtained. In the region of 4.5V, the peaks obtained which indicate the maximum amount of Mg ion is doped with Mn. During the electrochemical process, the oxidation and reduction of Mg is responsible for the 4.5V which is superimposed in the redox couple peak of Mn^{3+}/Mn^{4+}, as compared to $LiMn_2O_4$ the peak current is high (1.467mA).

3.5 Charge / discharge

Typical initial charge-discharge profiles of $Li/LiMn_{1.5}Mg_{0.5}O_4$ cells are obtained as a function of Mg content in the $LiMn_{1.5}Mg_{0.5}O_4$ (Fig.6). At the end of first cycle, decrease in capacity from 140 to $128mAhg^{-1}$. The fading capacity is almost12% in the original capacity. After the 100th cycle, the capacity was decreased very minimal as compared to first cycle it decreases only 10% of its capacity. It is due to the formation of a passivation film on the electrode surface. Hence, substitution of Mg reduces such a loss and improves the capacity. Powder prepared by the Sol-Gel method, have an excellent initial capacity.

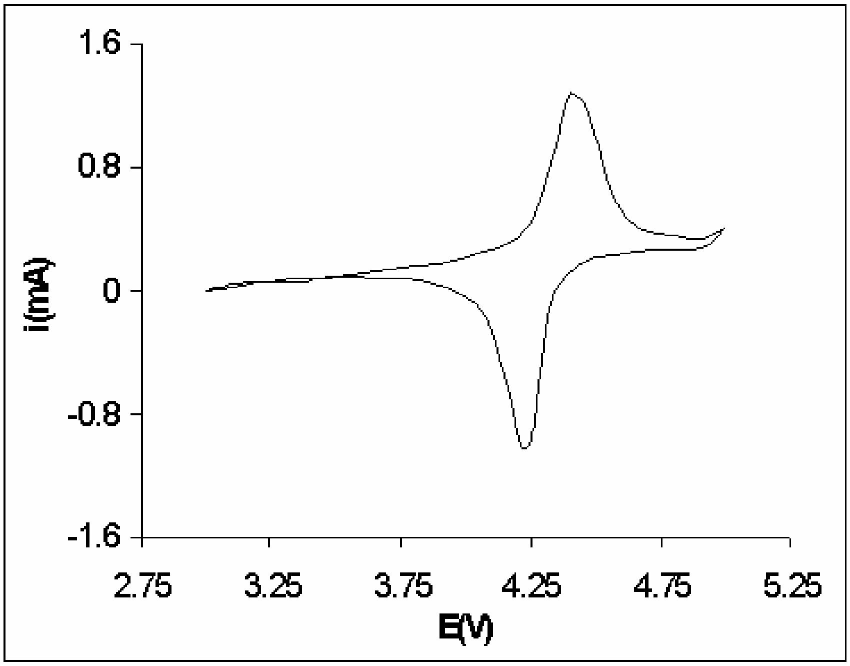

Figure 5. Cyclic Voltammogram of $LiMn_{2-X}Mg_XO_4$ electrode at $0.1mVs^{-1}$

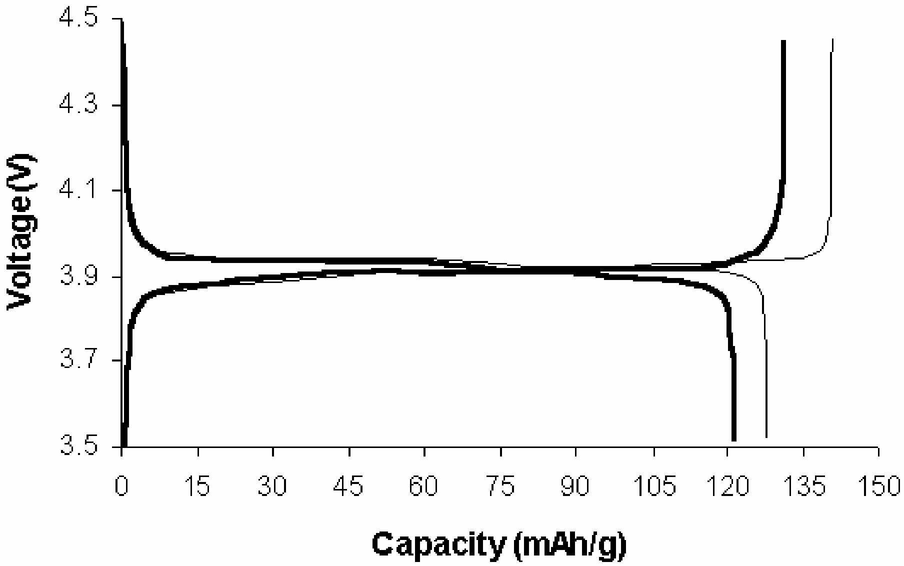

Figure 6. Charge – discharge curve of $LiMn_{2-X}Mg_XO_4$ electrode

4. CONCLUSION

The electro active nano $LiMn_{1.5}Mg_{0.5}O_4$ spinel has been synthesized by the sol-gel method using citric acid as a chelating agent with the subsequent calcination at 800°C for 6h. The synthesized powder has good spherical morphology and uniform particle size. Powder X-ray diffraction analysis shows that the sample is pure single phase and good crystallization. The initial discharge capacity of $LiMn_{1.5}Mg_{0.5}O_4$ spinel at C/10 rate is $140mAhg^{-1}$ and it exhibits good cycle stability.

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