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Solution Combustion Synthesis of Lithium Manganese Oxide Nanospheres

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ABSTRACT

$LiMn_2O_4$ has been explored as a cathode material for Li-ion batteries. The usual method to produce $LiMn_2O_4$ has been the solid state reaction process. We report the synthesis of spinel phase lithium manganese oxide ($LiMn_2O_4$) nanoparticles through a template-free starch-glycine assisted solution combustion synthesis (SCS). The method is a single step method. The resultant powder was characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) techniques, which were studied in details to observe the structural and electrochemical properties.

Introduction

The tremendous challenges in energy and environment are known to everybody and there is no single solution to these challenges. Currently, we heavily rely on the energy from fossil fuels to satisfy the demands. These fossil fuels are non renewable energy sources and hence, in near future we would be devoid of these sources. Further, as the population is increasing at faster rates so is the consumption of these fuels and hence more is the required demand. Nearly 65% of the current energy demand is being fulfilled by petroleum and coal. The consumption of which not only diminishes these sources of energy but also produce hazardous green house gases and toxins thus, affecting life on all fronts (economically and technically, ecology and health, present and future) [1,2].

Renewable energy resources such as wind, tidal, geothermal and solar energy have been investigated as alternatives to fossil fuels. The energy produced from these sources not only is boundless but also clean. Though the energy density of these sources are not comparable to the fossil fuels but their abundance make them highly interesting. For example, solar energy, being the most abundant of renewable energy source is also the most easily available source of energy on the earth. It is envisaged that the solar energy received by the earth in a single day is sufficient enough to fulfill the energy demands of current world's population for nearly sixteen years [2,3]. Even though the renewable energy harvesting is very interesting but it is not easy at the same time. The renewable energy conversions are of very low efficiency and this energy is not same throughout the year neither is it available at all places nor at all times. The renewable energy utilization may be divided into three main steps: harvesting, conversion and storage. Thus storing renewable energy after harvesting is an important aspect in the energy utilization.

Significant progress has been made, in recent years both in terms of renewable energy harvesting, conversion and storage.

Nanomaterials based novel designs have demonstrated very promising results in increasing the efficiency in energy utilization [4,5] and as such, electrical energy storage is a key technology. It maintains the key to promote the use of renewable energy and to curb the green house gas emissions. During the last twenty years, great progress has been made in the electrical storage systems, but no current system is able to meet the targets set for the demanding applications, with regards to energy and power density, price and life time [6]. Lithium ion batteries (LIBs) are among the most promising storage devices, offering high energy and power densities, long cycle life, no memory effects and slow self-discharging, finding applications in portable power tools, wireless communication devices and hybrid electric vehicles etc [7-11]. Lithium ion batteries also do posses advantages of safety, low cost and environmental friendliness [12-23]. Much interest has been drawn towards the electrode materials of the lithium ion batteries. The electrode material should be capable of operating at elevated temperatures and at large current densities [8, 24-26].

The most commercialized cathode material for lithium ion batteries has been the lithium cobalt oxide ($LiCoO_2$). However, the high cost and toxicity of cobalt prevents its use in green LIBs. Among various cathodes proposed for LIBs, the most promising one is the spinel lithium manganese oxide ($LiMn_2O_4$). It makes its way due to its non-toxicity, low cost, abundance and ease of synthesis, besides being environmental friendly [7,27,28]. The intercalation and deintercalation of lithium ion is easy because of the 3D tunnel structure of spinel lithium manganese oxide [8-11, 29] as shown in fig. 1. The framework was first demonstrated by Thackeray et. al. for lithium insertion host in $LiMn_2O_4$ for a rechargeable electrode in a lithium ion battery [30-32]. It has an arrangement of fd3m space group in which lithium ion occupies a 8a tetrahedral sites, manganese at 16d sites and oxygen at 32e sites [33-35]. The edge-shared octahedral Mn_2O_4 host structure being highly stable and because of face-sharing of tetrahedral lithium (8a)

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sites and empty octahedral (16c) sites, possesses a series of tunnels which intersect each other.

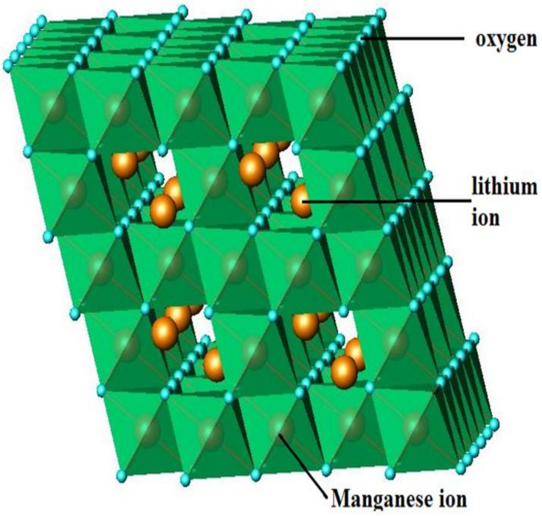

Figure 1. $LiMn_2O_4$ spinel structure. Adapted from: http://people.cst.cmich.edu.

Lithium diffusion occurs through such tunnels. At about 4 V, the lithium intercalation/deintercalation into/from the 8a tetrahedral sites occurs while maintaining the cubic spinel symmetry [36].

The usual method to produce $LiMn_2O_4$ has been the solid state reaction process [37-44]. But this method has several disadvantages of in-homogeneity, irregular morphology, broader particle size distribution, poor control of stoichiometry and longer periods of calcinations [45]. Spray pyrolysis has been considered as the versatile process to synthesize homogeneous $LiMn_2O_4$, but it leads to the discharge of toxic and corrosive gases [46]. Numerous other wet chemical methods, which include co-precipitation method [47,48], emulsion drying [49,50], hydrothermal method [51], the sol-gel method [45,52], pechini process [53] and combustion synthesis method [54] etc have been explored to synthesize $LiMn_2O_4$ powders to overcome the drawbacks of other methods. Among these methods, solution combustion synthesis method, solution mixture of aqueous metal salts and fuels, based on exothermic and self sustaining reaction is a promising method to synthesize $LiMn_2O_4$ powders. It is a single step method to yield nanosize particles having large specific surface area and homogeneous doping of trace amounts of various elements, besides being an environmental friendly synthesis method [55].

We report the synthesis of $LiMn_2O_4$ nanoparticles by using a glycine, urea and starch assisted solution combustion process (SCS). The as synthesized powder were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), to confirm the formation of $LiMn_2O_4$ nanoparticles and to study the morphology, crystallite size and structure.

Materials

Lithium Acetate (Thomas Baker), Manganese Acetate (Qualigens), Glycine (SD fine Chemicals), Starch (Fisher Scientific), Urea (Fisher Scientific) and Distilled water. All the reagents were used without any treatment or purification.

Experimental Procedure

In the solution combustion synthesis of $LiMn_2O_4$, stoichiometric amounts of lithium acetate, manganese acetate, glycine, starch and urea were added in a beaker with 650 ml of distilled water. The solution was magnetically stirred for 3 hours and then transferred to the muffle furnace and heated up to 700 °C. A schematic approach of the solution combustion synthesis of $LiMn_2O_4$ is depicted in the flow chart as shown in fig. 2.

The heat was increased at a rate of 1.5 °C per minute, starting from 0 °C. The final temperature (700 °C) was Maintained for 2 hours. All the thermal treatment of the solution was done in open air conditions only. Without removing the product from the furnace, it was allowed to cool down naturally, under open air conditions for 12 hrs. The porous foam like product was retrieved, ground into fine powder using mortar and pestle and characterized without any further treatment.

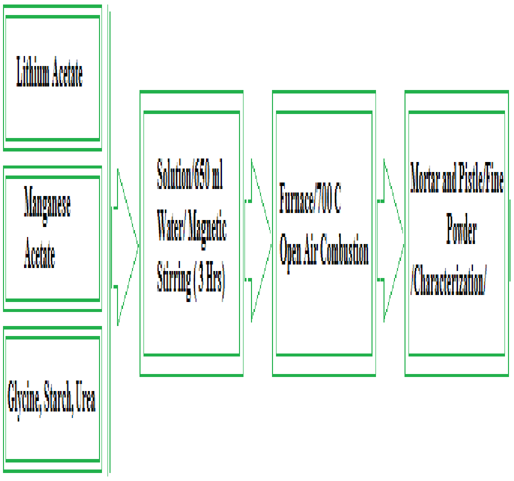

Figure 2. Flow chart showing various steps in the synthesis of $LiMn_2O_4$ by solution combustion method.

Characterization, Results and Discussions

X-Ray Diffraction Analysis

The X-ray diffraction profile of the as synthesized $LiMn_2O_4$ powder is shown in fig.1. The X-ray diffraction profile was determined by X-Ray diffractometer (Model-D8, Advance Bruker AXS).

The XRD profile can be assigned to the well crystallized spinel $LiMn_2O_4$, with all the reflection peaks perfectly matching with the Joint Committee of Powder Diffraction Standard (JCPDS Card No. 35-0782), confirming the formation of spinel $LiMn_2O_4$. The observed 2theta values and relative intensities were compared with the available JCPDS data as in table 1. All the diffraction peaks are indexed to the cubic spinel with the fd3m space group wherein lithium ion occupies the 8a tetrahedral sites, manganese occupies the 16d sites and oxygen the 32e sites [47]. The peaks corresponding to 2θ = 18.65, 36.14, 37.82, 44.03, 48.14, 58.43, 63.89 and 67.25 were assigned to (111), (311), (222), (400), (331), (551), (440), and (531) reflection planes [57-60]. No (222) reflection peak can be seen in the XRD profile, which arise from the tetrahedral (8a) sites [61]. It indicates that the lithium atoms occupy all the tetrahedral 8a sites and thus no (222) peak is observed as lithium has very low X-ray scattering ability. A small characteristic peak corresponding to Mn_3O_4 also appears at $2\theta = 32.84$, though it is of a small value. Its presence can be attributed to the presence of excess manganese oxide [17]. The high peak intensities as observed from the XRD plot can be referred to the higher crystallinity [29]. It has also been demonstrated that the intensity ratio of (111) and (311) reflection planes can be calculated to determine the mixing degree of Mn in $LiMn_2O_4$ and the lattice growth direction.

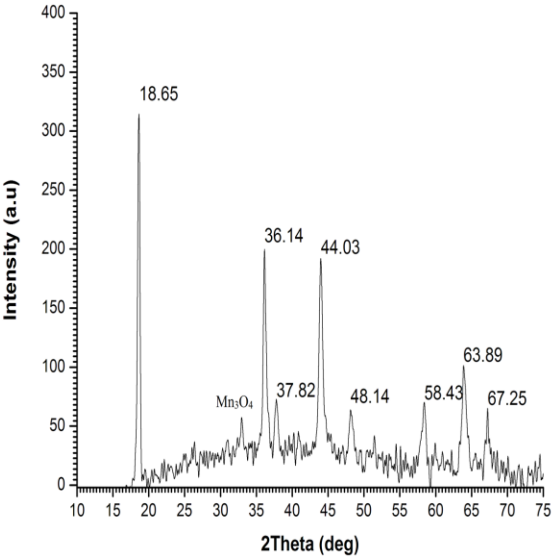

Figure 3. XRD spectrum of the as synthesized spinel $LiMn_2O_4$

Table 1. Comparison of observed and JCPDS data

Reflection Planes (hkl)	2 Theta		Relative intensity	
	JCPDS data	Observed data	JCPDS data	Observed data
(111)	18.611	18.65	100	100
(311)	36.085	36.14	38	38.3
(222)	37.747	37.82	10	10.51
(400)	43.869	44.03	33	36.58
(331)	48.047	48.14	7	8.79
(511)	58.056	58.43	10	12.65
(440)	63.780	63.89	16	19.53
(531)	67.079	67.25	7	11.7

The more immaculate are the elements lithium and manganese arranged if the intensity ratio of (111) and (311) reflections planes is a high value and it also indicates that the $LiMn_2O_4$ crystal grows preferentially along (111) direction [62]. This growth orientation of lattice is beneficial for the intercalation and deintercalation of lithium ions during electrochemical processes. As calculated in table 2, the intensity ratio of (111) and (311) reflection plane is calculated to be 1.5802, which is a moderate value when compared to other reports [29], indicating a good mixing degree of Mn in $LiMn_2O_4$ and that elements lithium and manganese are better arranged in the as synthesized $LiMn_2O_4$ spinels. Fig. 4 demonstrates the positions and intensities of (111), (311) and (400) reflection planes and the corresponding observations are tabled in table 2. Using the JCPDS data from table 1 and observable data from fig. 4 of reflection planes (111), (311) and (400), it can be easily be demonstrated that the characteristic peaks of (111), (311) and (400) reflection planes are shifted towards right that is , to higher 2θ values. It explains the fact that the crystal cell of as synthesized $LiMn_2O_4$ spinel is contracted and arranged closely. It also implies to the strengthening of cell structure, which relates to better cycling performance of $LiMn_2O_4$ [63].

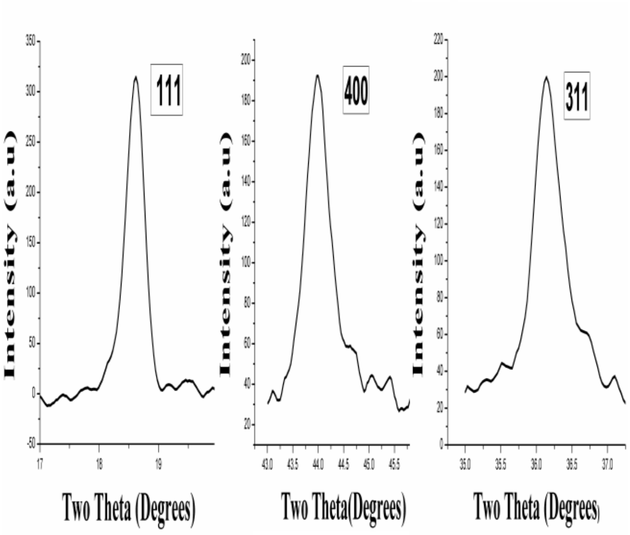

Figure 4. Peak position of (111), (400) and (311) respectively

The peak intensity ratio of (311) and (400) has also been demonstrated to determine the degree of crystallinity of $LiMn_2O_4$. A ratio within 0.96-1.1 range implies that the cycling performance of the $LiMn_2O_4$ is enhanced [64]. As calculated in table 2, this intensity ratio of the as synthesized lithium manganese oxide spinel is 1.034, which is within the prescribed limits and suggests good crystallinity and cycling performance and hence, good electrochemical properties. The lower full width at half maximum (FWHM) value of (400) peak also relates to the crystallinity and hence electrochemical properties in $LiMn_2O_4$ spinel [57,64,65]. As such, the FWHM of (400) peak was calculated as in table 2. A low value of 0.345 (degrees) was obtained and when compared to the earlier results is found to be the lowest [16,24,65]. Thus, from the XRD analysis, it is clearly examined that the $LiMn_2O_4$ spinels synthesized by this solution combustion synthesis method are highly crystalline and hence may possess good electrochemical properties as has been demonstrated by earlier reports.

Table 2. Peak parameters.

Peak Intensity Ratio I_{111}/I_{311}	Peak Intensity Ratio I_{311}/I_{400}	FWHM of (400) peak/(degrees)
1.5802	1.034	0.345

The crystallite size 'D' was calculated using Scherer's formula:

$$D = 0.94\,\lambda/B\ Cos\theta$$

Where λ is the wavelength of CuK_α radiations (1.54 A^o), B is the line width at half maximum (in radians), and θ is the Bragg angle corresponding to the maximum intensity peak (111) in the XRD profile. The crystallite size was calculated to be 24.1 nm.

Electron Microscopy

The morphology and the structure of the as synthesized spinel $LiMn_2O_4$ were determined by FE-SEM (Model Hitachi, S-4800). The FE-SEM images of the as synthesized $LiMn_2O_4$ powder are shown in fig. 2. The electrochemical properties of cathode materials are influenced by the crystallinity and the particle size. It has been observed that the high crystalline and moderate particle size may result in good electrochemical properties because of better mass-electrolyte contact and shortened diffusion routes for Li^+ ions and electrons [54, 66].

The morphology and size of the lithium manganese oxide particles is very important in the sense that the electrochemical properties are influenced by these as has been demonstrated by earlier reports [67, 68, 69]. The advantages of using nanomaterials as cathodes in the lithium ion batteries are: (a) they offer increased surface area for increased reaction sites; (b) nanostructured cathodes provide shorter diffusion lengths for electronic transport; (c) these can very well remain stable even after large volume expansion and contraction. All these factors do influence the electrochemical behavior of lithium manganese oxide as cathode material.

The reactions at the electrode take place at the surface of it and hence require charge transport into the electrode. So, small particles, providing large surface area and shorter diffusion distance would be desired [70,71]. However, if particles become too small, the stability and safety becomes a concern [72]. Thus, a moderate particle size would exhibit the best performance [73-75].

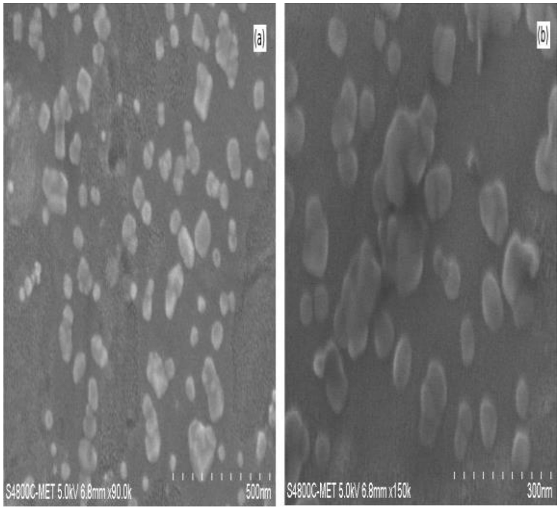

Figure 5. Typical (a) low and (b) high resolution FE-SEM images of as synthesized spinel $LiMn_2O_4$.

Particle shape has also been reported to be an important parameter for the electrode of better electrochemical performance. For lithium manganese oxide spinel electrodes, the spherical morphology has been mentioned to have good electrochemical properties [76,77]. The FE-SEM images of the as synthesized spinel $LiMn_2O_4$ (Fig.2) clearly reveal that the particles are more or less spherical in shape with a diameter in the range of $30 \pm 5\ nm$. The size and morphology are within the criterion limits for good electrochemical performance.

Conclusion

Single phase spinel $LiMn_2O_4$ nanoparticles with spherical shape have been successfully synthesized by starch-glycine assisted solution combustion synthesis method. The synthesis has proved to produce high crystalline $LiMn_2O_4$ nanospheres at an optimum temperature of 700 ^oC. All the parameters of the as synthesized lithium manganese oxide spinels are of desirable characteristics as per the previous reports. The diameter of the spherical particles is neither too large nor too small which is considered to be an effective parameter in determining the enhanced properties of cathodes in lithium ion batteries. This facile solution combustion synthesis method would be appropriate to synthesize lithium manganese oxide spinel structures for of the lithium ion batteries cathodes for enhanced electrochemical performance and reduced cost.

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