Combustion synthesis of LiMn$_2$O$_4$ by thermal decomposition of oxalate precursors

Arunkumar Lagashetty$^a$, Vijayanand Havanoo$^b$, S Basavaraja$^b$ & A Venkataraman$^b$

$^a$Appa Institute of Engineering & Technology, Gulbarga 585 102, India
$^b$Department of Materials Science, Gulbarga University, Gulbarga 585 106, India

Email: arunlagashetty@yahoo.com

Received 23 May 2006; revised received 3 October 2007; accepted 10 October 2007

Self-propagating low temperature combustion method for the synthesis of LiMn$_2$O$_4$ is reported. Synthesis of LiMn$_2$O$_4$ was carried out by thermal decomposition of lithium oxalate and manganese oxalate precursors employing poly(ethylene glycol) (PEG) as a fuel. The prepared LiMn$_2$O$_4$ was then characterized for structure by employing X-ray diffraction (XRD), morphology by scanning electron microscopy (SEM), particle size and shape by transmission electron microscopy (TEM) and bonding by Fourier transform infrared (FT-IR) spectral studies. The powders resulting from this method are pure, spinel-structure LiMn$_2$O$_4$ particles of regular shapes.

Keywords: Combustion, Synthesis, Morphology, Bonding

Recent research on materials has developed into a large interdisciplinary field in materials science. An important area of research in materials science is the synthesis of materials through different routes. The development of techniques such as sol-gel and other soft chemical methods viz., hydrothermal, microwave assisted and emulsion method etc., have led to the preparation of special engineering materials viz., pervoskites, garnets, spinel compounds etc. In recent years, efforts have been focused on preparation of metal oxide nanomaterials owing to their markedly different physical and chemical properties with respect to bulk materials.

LiMn$_2$O$_4$ is a promising positive electrode material for rechargeable lithium-ion batteries because of its high reduction potential (4 V), low cost and acceptable environmental impact. Attempts at improving the electrochemical response have been addressed in two ways: (i) by appropriate processing of composites having LiMn$_2$O$_4$ as active materials and (ii) by modifying the active materials in order to overcome the loss of capacity on cycling. Regarding the first point, the capacity can change from 0 to 135 mAhg$^{-1}$ as a function of the carbon black content according to percolation process. Regarding the second aspect, samples with a chemical composition slightly different from stoichiometric LiMn$_2$O$_4$ and/or samples of the nominal LiMn$_2$O$_4$ composition have been prepared by different synthesis procedures.

Self-propagating high/low temperature synthesis (SHS) is a combustion technique that has been used to prepare a wide range of refractory materials. Practically SHS is an ideal technique for the synthesis of representative hard (BaFe$_{12}$O$_{19}$) and soft (Li$_{10.5}$Fe$_{2.5}$O$_4$) ferrite materials. The SHS process is extremely rapid, producing ferrite materials in minutes, proceeding by a synthesis wave that moves through the precursors. The products after SHS require minimal treatment to produce single phase materials of high purity and figures of magnetic merit equivalent to commercially prepared materials.

Poly(vinyl alcohol) can be employed as an oxidizing agent along with urea, glycine etc., for the synthesis of ferrites, refractory materials and ceria etc., through combustion of citrate and nitrate precursors. However, this technique has some limitations viz., use of urea as fuel, and also that poly(vinyl alcohol) has a wide variation of molecular masses, both of these parameters may influence the combustion to undergo as a highly exothermic reaction. Hence, a new fuel which can also act as a controllable oxidant in a combustible reaction generating self-propagation is essential. In search of a suitable economic fuel, the use of polyethylene glycol (PEG) has given promising results in a single step. The reasons for employing PEG in the present study are: Polyethylene glycol has a sharp melting point (62°C) and distinct decomposition temperature, which are widely separated. The precursors get well dispersed in the molten polyethylene glycol. Polyethylene glycol is known to be a good surfactant and a dispersant and hence, ultrafine nanomaterials...
are expected to be formed as final product on combustion. Polyethylene glycol has alcoholic groups and it burns in air exothermically with precursors to form desired metal oxides.

Recently PEG has been successfully used for the synthesis of $\gamma$-Fe$_2$O$_3$ and other metal oxides from different precursors. In these studies different weight ratios of precursor and PEG were employed to synthesise the $\gamma$-Fe$_2$O$_3$ nanoaprticles. Among all the different ratios attempted a 1:5 ratio produced monophasic ultrafine particles of $\gamma$-Fe$_2$O$_3$. In the present investigation, therefore, for the preparation of LiMn$_2$O$_4$, the oxalate precursors of Li and Mn and PEG in 1:5 ratio have been used. Self-propagating low temperature combustion route was adopted for the synthesis of LiMn$_2$O$_4$ nanoparticles by auto ignition of oxalate precursors of Li and Mn employing polyethylene glycol as a fuel. The synthesized LiMn$_2$O$_4$ was characterized for its structure (XRD), morphology (SEM), metal-oxygen bonding (IR) and particle size and shape (TEM).

Experimental Procedure

Materials and methods

All the chemicals used were of AR grade. Poly(ethylene glycol) of molecular weight, 4000 was obtained from HiMedia, Mumbai. Double distilled water was used for the preparation of the required solutions.

Preparation of lithium oxalate and manganese oxalate

The precursors were prepared by dissolving equimolar quantities of lithium chloride and manganese chloride with oxalic acid separately and were stirred well. The resulting precipitates of lithium oxalate and manganese oxalate were filtered through sintered glass crucible and were washed with double distilled water till free from chloride ions and oxalic acid. The chloride free residue were finally washed with dry acetone and were then dried under vacuum.

Synthesis of nanosized LiMn$_2$O$_4$

The lithium oxalate, manganese oxalate and poly(ethylene glycol) were mixed in weight ratio of 1:1:5 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and heated in air. It was observed that initially poly(ethylene glycol) melted, then frothed and finally ignited to give LiMn$_2$O$_4$ as residue. On cooling to room temperature, no traces of carbon impurities were observed in the final residue of LiMn$_2$O$_4$ nanocrystalline material. As the reaction was fast i.e., completed within 10-15 min, and ignited auto-catalytically, the exact temperature of the reaction could not be measured. However, using a thermocouple the highest temperature achieved in the reaction was found to be around 500°C.

Characterization of LiMn$_2$O$_4$

The X-ray diffraction patterns were obtained employing a JEOL JDX-8p spectrometer using CuK$_\alpha$ radiation. The X-ray generator was operated at 30 kV and 20 mA. The scanning from 10°-90° range 20 was selected. The scanning speed 1° min$^{-1}$ was employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard.

The shape, microstructure and distribution of the powder of LiMn$_2$O$_4$ were examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope. The SEM was operated at 20 kV. The sample was made conducting by the sputtering of gold using a Polaron DC “sputtering unit” operated at 1.4 kV and 18-20 mA.

The TEM image was obtained from JEOL-1000 transmission electron microscope. The transmission electron microscope was operated at 190 keV. The Fourier transform infrared spectra of LiMn$_2$O$_4$ was recorded on a Perkin–Elmer FTIR spectrophotometer [Model 1000] in the range 300 to 4000 cm$^{-1}$.

Results and Discussion

X-ray diffraction study

Figure 1(a-c) presents XRD patterns of synthesized lithium oxalate, manganese oxalate and LiMn$_2$O$_4$ nanomaterials respectively. The XRD pattern of lithium oxalate and manganese oxalate does not show any Bragg’s reflections indicating amorphous nature, whereas the LiMn$_2$O$_4$ sample shows sharp peaks (indexed in the pattern) which are in well agreement with literature (JCPDS 35-782).

The mean particle diameter was calculated from the XRD pattern according to the line width of the (111) plane reflection peak using the following Debye-Scherer equation.

$$D = \frac{K\lambda}{\beta^{1/2} \cos \theta}$$

The equation uses the reference peak width at angle $\theta$, where $\lambda$ is the X-ray wavelength (1.5418 Å), $\beta_{1/2}$ is
the width of the XRD peak at half height and K is a shape factor, about 0.9 for spherical shaped particles. The particle size calculated from peak width is about 30 nm, which is in agreement with the observation from the TEM results discussed below.

**SEM study**

Figure 2 shows SEM image of synthesized LiMn$_2$O$_4$. This image shows irregular shaped nano-particles joined together to form agglomerates of sub-micron dimensions.

**Transmission electron microscopy**

Figure 3 shows the typical bright field TEM image of the synthesized LiMn$_2$O$_4$ nanoparticles. It is observed from this image that the particles are roughly spherical in shape and are in the range of 15-30 nm size. These particles are very closely joined together to form agglomerates.

**IR studies**

Infrared techniques has been employed to understand the metal-oxygen and metal-metal bond in the prepared lithium manganate sample. Figure 4 shows IR spectrum of the synthesized LiMn$_2$O$_4$ sample. The vibrational frequencies obtained for LiMn$_2$O$_4$ are 890, 800, 665, 425 and 310 cm$^{-1}$. The characteristic lines below 1000 cm$^{-1}$ show the metal-oxygen vibrational frequency. The sample shows absorption bands below 1000 cm$^{-1}$, confirming the
presence of M-O (Li-O, Mn-O) bond in the prepared sample. The peak at around 310 cm⁻¹ (finger print region) observed in the spectrum shows the metal-metal (Li-Mn) vibrational frequency. These two bonding sites confirm the formation of LiMn₂O₄.

**Conclusions**

The LiMn₂O₄ nanoparticles have been synthesized by a thermal decomposition of oxalate precursors employing self-propagating low temperature combustion route. The results obtained from XRD and TEM images confirm the nanocrystalline nature of the synthesized LiMn₂O₄. This process is less time consuming and allows preparation of practically pure nanocrystalline products.

**Acknowledgement**

The authors wish to thank the University Grants Commission (UGC), New Delhi for financial assistance. Authors thank Dr. Shashidhar, I.I.Sc, Bangalore, for providing XRD data. The author Arunkumar Lagashetty thanks Dr. Sharanabasavappa Appa, President Appa Institute of Engineering & Technology, Gulbarga for providing laboratory facilities.

**References**