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Synthesis of $LiMn_2O_4$ by molten salt technique

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Abstract Lithium manganese oxide powders have been successfully prepared by a molten salt synthesis using eutectic mixture of LiCl and MnO_2 salt at 900 °C. The synthesis was performed in open atmosphere. The crystalline powders were characterized for their phase identification using X-ray diffraction analysis. The physicochemical properties of the lithium manganese oxide powders are investigated by thermal analysis (thermo gravimetric analysis/ differential thermal analysis), Fourier transform infrared spectroscopy, Raman spectroscopy, atomic absorption spectroscopy, electron spin resonance spectroscopy, and scanning electron microscopy. This work shows the feasibility for obtaining lithium manganese oxide at low-temperature molten salt flux method.

Keywords $LiMn_2O_4$ · Molten salt synthesis · Cathode materials · Batteries · Cathodes · Li-ion batteries · Materials preparations

Introduction

Oxides with the spinel structure are some of the most studied compounds in solid state sciences due to their wide range of applications as magnetic materials, semiconductors, catalysts, and pigments [1]. Oxide spinels are represented by the general formula AB_2O_4, where A and B stands for tetrahedral and octahedral cation sites in a cubic close packing of oxygen. The unit cell contains eight unit formulas and the symmetry is cubic space group fd3m.

One of the most promising energy sources for many of the domestic and engineering applications is the rechargeable lithium-ion battery. High-performance lithium-ion batteries are favored where light weight with small volume is desired, e.g., laptop computers, cellular phones, and electric vehicles. A number of recent studies have focused on the synthesis, processing, and electrochemical characterization of cathode materials. Only three materials are identified as suitable cathode materials in 4 V lithium-ion batteries. They are spinel type $LiMn_2O_4$, the layered $LiCoO_2$, and $LiNiO_2$ [2].

Spinel $LiMn_2O_4$ is an attractive cathode material for Li/Li^+ rechargeable batteries which offers benefits such as low cost, natural abundance, and environmental friendliness of raw materials. It also possesses thermal stability at the working temperature and environment [3]. It may reversibly deintercalate one lithium per formula unit, with a theoretical capacity of 148 mAh/g [4]. The disadvantages persist on the decay of $LiMn_2O_4$ with extended cycling, especially at elevated temperatures, which prevents its wide use in the commercial field [1].

The spinel-type lithium manganese oxides are commonly prepared via a solid state reaction method. The oxide powders prepared by this route causes inhomogeneity, irregular morphology, and a broader particle size distribution of powder. To overcome these disadvantages, several solution routes have been developed such as sol-gel [5, 6], coprecipitation [7], Pechini process [8], and freeze-drying [9] methods. These methods require a large quantity of solvent and organic materials like citric acid, ethylene

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glycol, polyvinyl alcohol, and polyvinyl butyral [10]. The molten salt synthesis (MSS) or flux growth method has been found to be one of the simplest methods to prepare pure and stoichiometric powders of multicomponent oxides. In this method, the molten salts are utilized as solvent or reacting species, or sometimes both [11, 12]. Since the diffusion rate of the components in molten salts are much higher than those in the solid state reaction, various oxide powders and ferrites are prepared at significantly lower temperatures [13, 14]. The preparation of lithium manganese oxides by molten salt synthesis using γ-MnOOH as a manganese source and LiCl, $LiNO_3$, Li_2SO_4 or LiOH as flux has been reported [15].

In this study, we have reported the preparation of $LiMn_2O_4$ powder by molten salt route using simple oxide and chloride as the starting materials for the preparation of precursors. LiCl is a neutral salt, hence, it is expected to have high solubility for manganese and stabilize Mn^{3+} in the LiCl melt [15, 16] in contrast to salt containing oxygen [16]. The synthesized product has been characterized using various characterization techniques and the results are presented.

Experimental

For the preparation of lithium manganate, analytical grade anhydrous lithium chloride 99% (Loba Chemie, Mumbai, India) and manganese oxide 99% (Loba Chemie) powders were used as the starting materials. Stochiometric quantities of the starting materials were thoroughly mixed and placed in a high purity alumina crucible. Then, the crucible was placed in a programmable electrical resistance furnace and heated at 900 °C in air. The heating rate was 3 °C $min^{-1}$and the heating was continued at this temperature for 5 h. After cooling to room temperature, the product was removed from the crucible and thoroughly washed with 1 M acetic acid followed by triple distilled water for several times to remove the excess lithium salts. The residue was dried in a vacuum oven at 150 °C for 1 h and cooled to room temperature. Finally, fine crystalline free-flowing black powders were obtained.

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) of the synthesized samples were carried out using a STA 1500 PL Thermal Sciences, version V4.3o analyzer. The DTA/TGA curves were recorded from room temperature to 1,000 °C in air at a heating rate at 10 °C/min. The purified product was characterized by XRD (Philips 8030 X-Ray diffractometer) to identify the phase composition. The unit cell lattice parameters were obtained by the least-square fitting method of the d-spacing, and the hkl values. Fourier transform infrared (FTIR) spectroscopy was used to study the structure coordination of the calcined powders using Perklin Elmer UK paragon-500 spectroscopy. To record the spectra each sample was mixed with KBr and thoroughly ground in to fine product and examined in the wave number ranging from 400-4,000 cm^{-1}.

Raman spectroscopy measurements were performed using a Renishaw InVia microscope. Raman system equipped with a charge-coupled device detector. Atomic absorption spectroscopy (AAS) was performed using Varian Model Spectra 220 to analyze the compositional data of the synthesized powders. Carbon, hydrogen, nitrogen, sulphur analysis was carried out using elementar vario EL III-Germany to analyze the purity of the powders.

Electron spin resonance (ESR) spectroscopy was carried out with microwave frequency 9.857403 GHz with fields corresponding to about 6500.000G sweep width using a

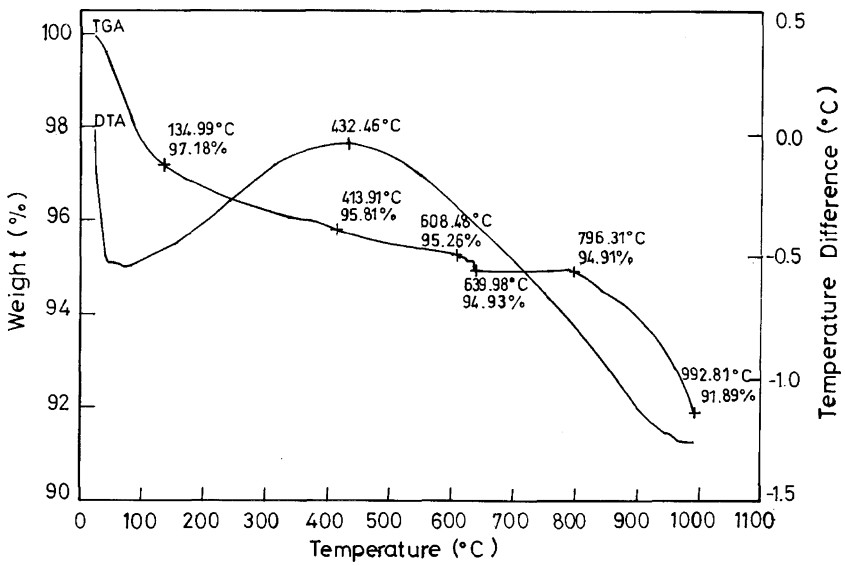

Fig. 1 TGA and DTA curves for $LiMn_2O_4$ synthesized by molten salt synthesis

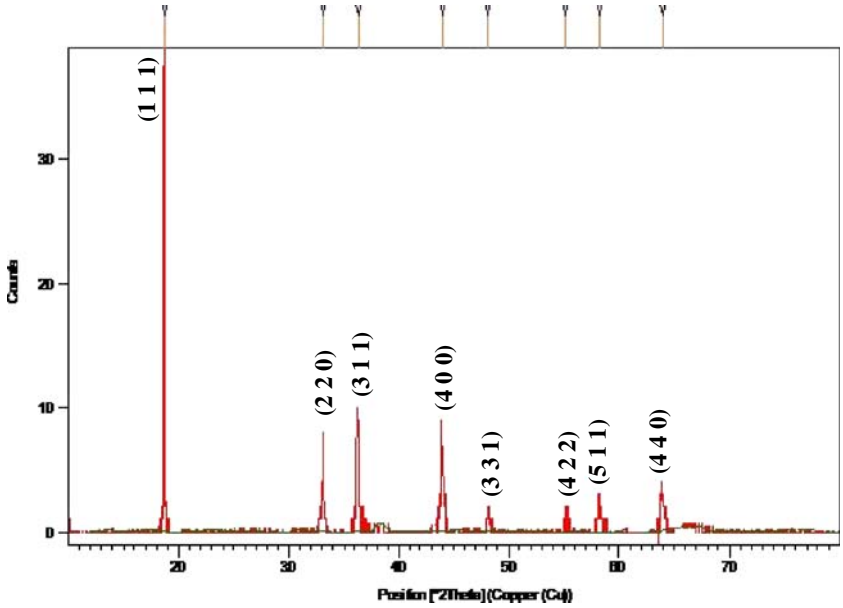

Fig. 2 X-ray powder diffraction pattern of the $LiMn_2O_4$

Bruker Bio Spin Gmbh EPR spectrometer. The morphology of the synthesized powders was scrutinized by SEM (JEOL-JSM-3.5 CF, Japan.)

Results and discussion

Figure 1 shows the TGA and DTA curves for $LiMn_2O_4$ synthesized by molten salt synthesis. There is an endothermic reaction observed at 134.9 °C which may be due to the dehydration of the water molecules present in the as synthesized compound. At this temperature, about 2.82% weight loss has been noticed. Thereafter, a gradual decrease in weight loss could be seen in TGA curve. Beyond 600 °C, it could be observed that a minor change in the weight loss in the compound and stabilized beyond 796 °C. After this temperature, the compound has completely transformed into a single phase $LiMn_2O_4$. The DTA curve, exhibits an exothermic peak at 432 °C which is responsible for the partial decomposition of MnO_2 into MnO, where the transformation starts to form the single phase $LiMn_2O_4$. It has been noticed that beyond 800 °C, the complete transformation of the precursor salts in to a single phase $LiMn_2O_4$.

The XRD pattern for the synthesized compound is shown in Fig. 2. Most of the peaks are found to match with the standard data. The XRD data were used to calculate the lattice constant. The calculated values are in good agreement with the published values for $LiMn_2O_4$ where a=8.2304 A° (JCPDS data card no. 88-1026).

The FTIR spectrum is shown in Fig. 3. In the spectrum we could see three prominent bands and four weak bands at different wavelength regions. From the FTIR spectra, it has been observed that the strong frequency bands at 615 and 509 cm^{-1}, which are responsible for the formation of $LiMn_2O_4$ (belonging to F_{1u} species). They are assigned to the asymmetric stretching of MnO_6 groups which has been reported in the literature [17, 18]. From the FTIR spectra, it is revealed that the synthesized product is a single phase $LiMn_2O_4$ compound.

The synthesized $LiMn_2O_4$ powders are examined using Raman spectroscopy. The Raman spectrum is shown in Fig. 4. The spectra exhibit a strong band centered at 657.3 cm^{-1} and three weak bands at 467.7, 371.8, and 316.9 cm^{-1} respectively. The strong band appeared at 657.3 cm^{-1} is attributed to A_1g mode corresponding to symmetric Mn-O stretching vibration of MnO_6 groups. The other three broad weak bands may be assigned to three modes of t_2g phonons as reported in literature [19, 20]. The band at 651 cm^{-1} is responsible for the presence of the single phase $LiMn_2O_4$ compound. It has been suggested that $LiMn_2O_4$ phase has been assigned by visualizing the group theory for the perfect spinel compound with fd3m

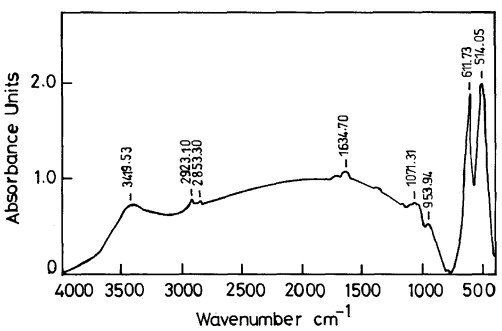

Fig. 3 FT-IR spectrum of $LiMn_2O_4$

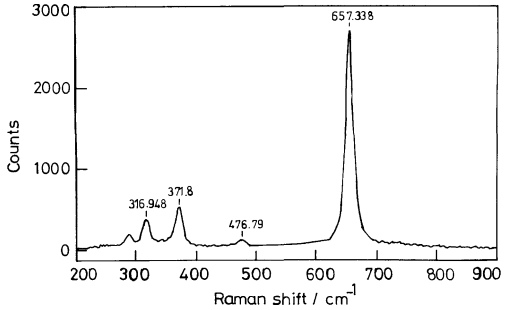

Fig. 4 Raman spectrum of $LiMn_2O_4$

symmetry. From the above studies, it has been concluded that the single phase $LiMn_2O_4$ compound is being synthesized by molten salt technique. The spectral data of the synthesized $LiMn_2O_4$ is in good agreement with the reported data, prepared by different preparation techniques [19–21].

The concentrations of Li and Mn ions are determined using atomic absorption spectroscopy. An aliquot quantity of the sample is dissolved in 1 N HCl solution and the concentration of the Li and Mn ions are assessed. It is revealed that the concentration of Li and Mn ions are in stochiometric ratio in the prepared compound $LiMn_2O_4$.The determined values are in good agreement with literature data [22].

The solid state elemental analysis has also been done using CHNS analyzer. It is revealed that the synthesized $LiMn_2O_4$ does not possess any impurity species. This analysis also proves that the compound prepared by molten salt technique is of pure $LiMn_2O_4$.

The paramagnetic behavior of the synthesized $LiMn_2O_4$ is determined using EPR studies. From the EPR spectrum, it has been noticed that the value of g factor is $g=1.88$ which is in good agreement with the reported value for $LiMn_2O_4$.The lone pair of electron state is identified from the EPR spectrum. The position of the signal is nearer to the value expected for uncorrelated spins with the giro-magnetic factor Mn^{4+}–Mn^{4+} dipolar interactions. The contribution of Mn^{4+}–Mn^{3+} and the broadening of the signal obtained from the EPR spectrum are correlated for this compound (Fig. 5). The signal is attributed to Mn^{4+} ions which are responsible for the paramagnetic entities exist in the compound. It is emphasized that the charge state

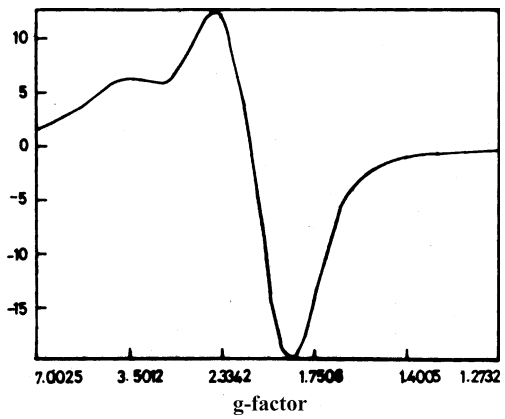

Fig. 5 EPR spectrum of $LiMn_2O_4$

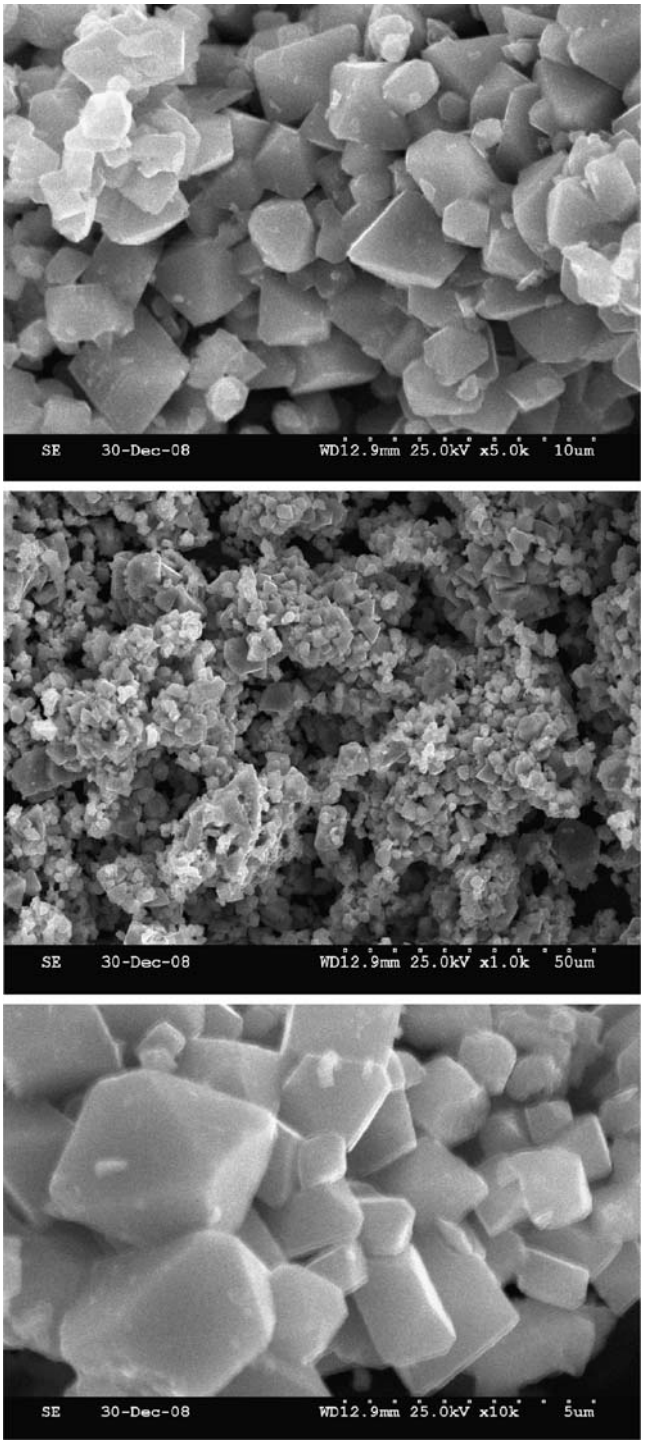

Fig. 6 SEM Micrographs of synthesized $LiMn_2O_4$ at various magnification

of the manganese localizes Mn^{3+}–Mn^{4+} state accounts for the electronic structure of $LiMn_2O_4$ [23–25].

The morphology of the synthesized $LiMn_2O_4$ crystals exhibits platelet of cubic structure (Fig. 6). The particles are found to be irregular in shape with irregular edges. The average crystalline size of the particle is ranging from 5–50 μm.

Conclusion

Crystalline $LiMn_2O_4$ is successfully synthesized using molten salt technique. The prepared compound possesses good physical properties. The synthesis process is economically viable which can be extended for the large scale preparation of this material.

References

1. Ferreira TAS, Waerenborgh JC, Mendonca MHR, Nunes MR, Costa FM (2003) Solid State Sci 5:383
2. Ozawa K (1994) Solid State Ionics 69:212
3. Broussely M, Biensan P, Simon B (1999) Electrochim Acta 45:3
4. Mohamedi M, Takahashi D, Itoh T, Chida IU (2002) Electrochim Acta 47:3483
5. Barboux P, Tarascon JM, Shokoohi FK (1991) J Electrochem Soc 94:185
6. Sun YK, Oh IH, Hong SA (1996) J Mater Sci 31:3617
7. Qui X, Sun X, Shen W, Chen N (1997) Solid State Ionics 93:335
8. Liu W, Wowal K, Farrington GC (1996) J Electrochem Soc 143:3590
9. Lemercier T, Gaubicher J, Bermejo E, Chabre Y, Quarton M (1999) J Mater Chem 9:567
10. Zhecheva E, Stoyanova R, Gorova M, Alcantara R, Mopales J, Tirado JL (1996) Chem Mater 8:1429
11. Chiu CC, Li CC, Desu SB (1991) J Am Ceram Soc 74:38
12. Yoon KH, Cho YS, Lee DH, Kang DH (1991) J Am Ceram Soc 76:1373
13. Kim SJ, Hong YS, Park HB, Park SY, Kim K (1996) J Mater Sci Lett 15:1443
14. Okamoto S, Narumiya Y, Yamaguchi T (1986) Ceram Int 12:209
15. Yang X, Tang W, Kahoh H, Ooi K (1999) J Mater Chem 9:2683
16. Yang X, Kanoh H, Tang W, Ooi K (2000) J Mater Chem 10:1903
17. Raja MW, Mahanty S, Paromita G, Basu RN, Maiti HS (2007) Mater Res Bull 42:1499
18. Kalyani P, Kalaiselvi N, Muniyandi N (2002) J Power Sources 111:232
19. Ammundsen B, Burns GR, Islam MS, Kanoh H, Roziere J (1999) J Phys Chem B 103:5175
20. Tang SB, Lai MO, Lu L (2007) J Power Sources 164:372
21. Chiu KF, Lin HC, Lin KM, Tsai CH (2005) J Electrochem Soc 152:A2058
22. Tang W, Yang X, Liu Z, Kasaishi S, Ooi K (2002) J Mater Chem 12:2991–2997
23. Capsoni D, Bini M, Chiodelli G, Massarotti V, Mozzatti MC, Anzoni C (2003) Solid State Commu 125:179
24. Amdouni N, Zaghib K, Gendron F, Mauger A, Julien CM (2007) J Magnetism and Magnetic Materials 309:100
25. Stoyanova R, Gorova M, Zhecheva E (2000) J Physics and Chemistry of Solids 61:609