

Development of Low Cost and Safe Cathode Material for High Energy Storage Lithium-ion Battery

Kuldeep Rana*, Shivangi Kosta

Abstract: Spinel LiMn_2O_4 is a low-cost, eco-friendly, and highly abundant cathode materials for Li-ion battery, however it has a drastic capacity loss with cycling due to the distortion in crystal structure during discharge. In order to overcome the capacity loss, Mg-doped manganese oxide was synthesised and investigated in order to have a structure with suppressed Jahn- Teller distortion. The distorted Li-Mg-Mn complex has potential merit for lithium ion battery cathode. To fulfil this objective, oxides of Mg and Mn were prepared in different compositions. The synthesized compounds are found to consist of MgMn_2O_4 as a major phase along with a minor fraction of Mg_6MnO_8 . Lithium insertion was carried out by adding Li_2CO_3 in appropriate proportion to MgMnO mixture in order to form a single phase LiMgMnO complex. The LiMgMnO complex as a cathode material was successfully demonstrated in a coin cell.

Keyword: Cathode materials, Electrochemical, Energy Storage; Li-ion Battery.

1.0 INTRODUCTION

The performance characteristics of Lithium-ion batteries directly depends on the properties of active cathode materials such as chemical potential, good ionic and electronic conductivities as well as large storage capacity for lithium ions. Moreover, excellent chemical and structural stability of the cathode materials is necessary for capacity retention. In this regard, a detailed study has been carried out by Thackeray *et al* [1]. The cathode materials typically used in earlier rechargeable lithium ion batteries are transition metal chalcogenides TiS_2 and oxides V_6O_{13} [2]. These materials offer channel like structure which facilitates lithium ion insertion and de-insertion. The different types of cathode materials presently used are two dimensional layered such as LiCoO_2 [3], LiNiO_2 [4] and three-dimensional spinel structure LiMn_2O_4 [5–8]. Structural properties of pure as well as doped lithium-cobalt [9], lithium-nickel [10], and lithium manganese oxides [11–14] were reported to be widely used as cathode material. The LiMO_2 (where $\text{M}=\text{Co}, \text{Ni}, \text{V}, \text{Cr}$) material has layered rock

salt structure consisting of two-dimensional array, edge sharing octahedrons. Commercial lithium ion batteries generally use LiCoO_2 as cathode. However, this has certain drawbacks such as high cost and toxicity. Therefore, an attempt is being made by researchers to replace LiCoO_2 by LiNiO_2 which is less expensive and less toxic. Meanwhile, several studies indicated that the use of LiCoO_2 limits the performance of the cathode and therefore, a partial replacement of Co with Ni was found to appear as a better solution for novel cathode development [15, 16]. Among all three-cathode materials stated above, LiMn_2O_4 remains the most attractive choice considering its low cost, easy availability (of raw materials) and very low toxicity. LiMn_2O_4 is a normal spinel with space group $Fd\bar{3}m$ (at room temperature), containing lithium on tetrahedral $8a$ sites and manganese on octahedral $16d$ sites. However, main challenges with this spinel structure material are its poor storage capacity at higher temperature (i.e. about 55°C) in its charged state and capacity fading [17]. The primary reason for the capacity fading was attributed to (i) the presence of a cooperative Jahn– Teller (J–T)

*Scientific Officer Electrical Appliances Technology Division, Central Power Research Institute, Prof. Sir. C.V. Raman Road, P.O.Box : 8066, Bengaluru – 560080 Email: kuldeeprana@cpri.in, Ph: 08884079854.

distortion when Mn^{3+} in the structure fraction exceeds 50%, (ii) structural instability in the high delithiation range. One of the ways to reduce this fading is partial substitution of manganese by transition metals (M) and the possibility was thoroughly studied [7]. Therefore, successful development of the cathode material bears strong correlations with establishing the structure of the material during discharge.

In order to overcome the capacity fading problem of LiMn_2O_4 oxide spinel structure cathode substitution of Mg in the manganese oxide structure was considered. Such substitution suppresses J–T distortion in the crystal structure of the cathode material during its discharging stage and consequently extends the voltage plateau at higher voltage. In the present study, a mixed oxide host was prepared in the system $(\text{MnO}_2)_{1-x} - (\text{MgO})_x$ where $x=0.31, 0.33, 0.35, 0.37$ and 0.39 for lithium insertion. Mg ions can easily facilitate high lithium ion mobility due to its large ionic radius (7.2mm). Involved Mg will improve the cyclic performance of the spinel LiMn_2O_4 . This will further lead to the distortion of molecules which is concomitant with the change in the electronic configuration. The changes leads to high capacity loss and is determined by Jahn-Teller. Solid-state reaction sintering process was followed for the preparation of both insertion and lithiated compounds. The compositions chosen corresponds to the exact and near spinel phase, so as to examine the extent of compositional variation over which the desired spinel phase can be obtained as a primary content in host structure prepared after reaction sintering. Lithium insertion was carried out in the host compound of relatively high phase purity in spinel MgMn_2O_4 .

2.0 EXPERIMENTAL

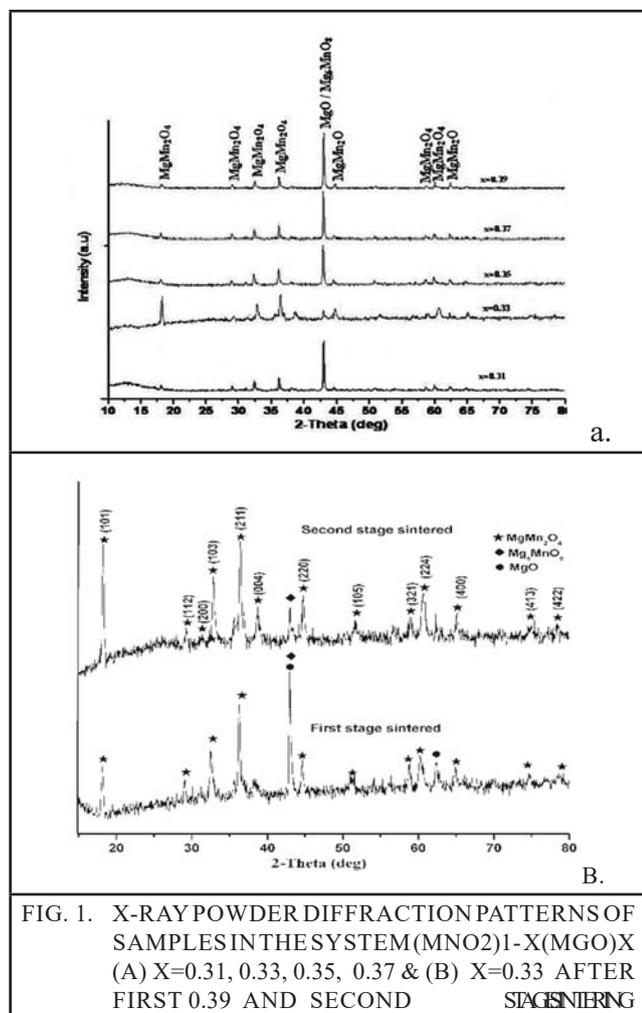
The samples in the system $(\text{MnO}_2)_{1-x}-(\text{MgO})_x$; $x=0.31, 0.33, 0.35, 0.37$ and 0.39 were prepared from MnO_2 and MgO powders (purity 99%, Sigma-Aldrich). The required amount of constituent powders for each composition was weighed and mixed in liquid medium

(acetone) using mortar and pestle. The dried powder mixtures were compacted in the form of cylindrical pellets. The green compacts were sintered in a muffle furnace first at 400°C for 1 h and then at 900°C for a soaking period of 10 h. The sintered samples were characterized by X-Ray Powder Diffraction. The diffraction data was collected from a diffractometer (Bruker AXS, D8 Advance) with CuK_α radiation at a moderate scan rate of $1^\circ 2\theta/\text{min}$ between 10° and 90° . The host compound synthesized was lithiated by thoroughly mixing with required amount of Li_2CO_3 powder (purity 99%, Sigma-Aldrich) and heating the powder mixture at 850°C for 10 h. The phase identification of the lithiated powder was carried out by XRD which consists primarily of spinel phase and relatively low secondary impurity phases. Morphology of the lithiated powder was observed by FE–SEM (FEI QUANTA 200 F). The compounds were also analysed by FTIR (Nicolet 710 FTIR) to know the coordination and configuration of molecules in the system from the vibration of individual bonds or groups in species. The samples were diluted in KBr for recording the FTIR spectra. The electrical conductivities of the MgMn_2O_4 and the lithiated compound were determined by Impedance Spectroscopy technique using LCR meter (HIOKI 3532-50 LCR Hi Tester). Charge/discharge studies have been carried out by using electrochemical analyser (Arbin BT200) using a coin cell holder.

3.0 RESULTS AND DISCUSSION

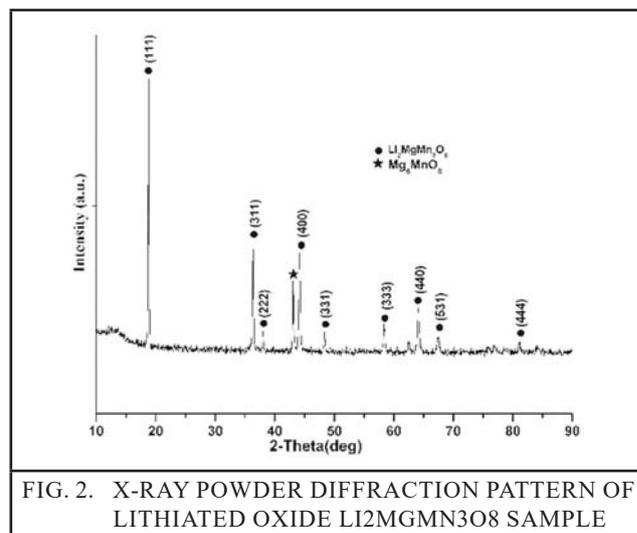
XRD patterns of sintered samples of all the compositions is shown in Fig. 1a. It can be seen from the Fig. 1a that majority of the peaks for all the compositions are of MgMn_2O_4 along with a secondary phase Mg_6MnO_8 . It can be mentioned that one of the characteristic peak of MgO is almost same angular position as that of Mg_6MnO_8 . In order to increase phase purity in the desired compound MgMn_2O_4 , the reaction sintered sample of $x=0.33$ was reground and further reaction sintered at the same temperature and for same time period as was followed in first sintering.

The samples after second sintering were analysed by XRD and pattern obtained is given in Fig. 1b. It can be seen from the Fig. 1b, that the intensity of the Mg₆MnO₈ peaks were suppressed to a substantial extent and the intensities of the MgMn₂O₄ peaks were increased sufficiently.

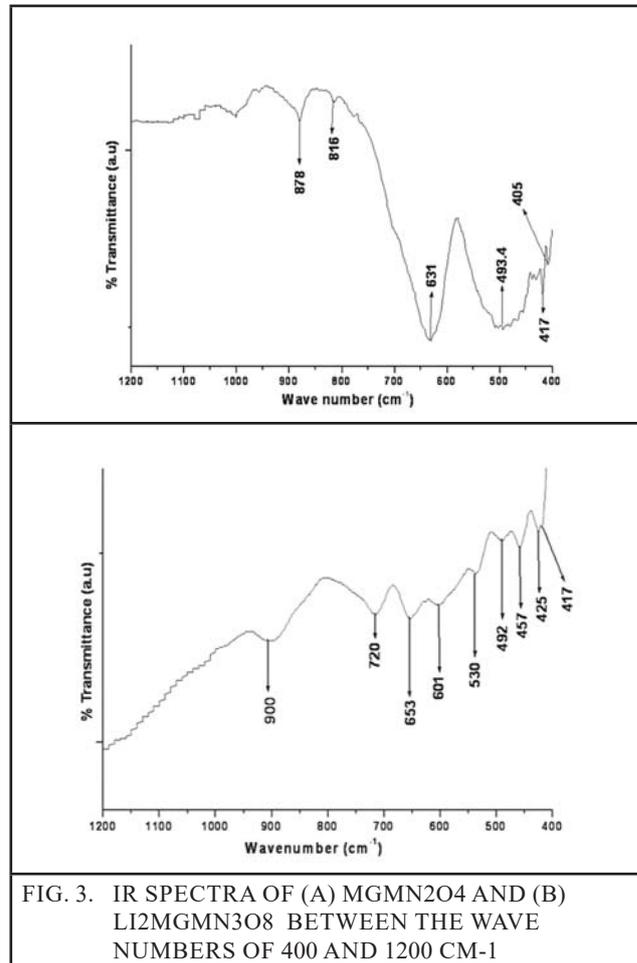


This powder was mixed thoroughly with required quantity of Li₂CO₃ using mortar and pestle and reaction sintered at 950°C for about 10 h. The sintered compound was subjected to XRD analysis and the pattern is shown in Fig. 2, which indicates that the material is phase pure to a high degree of Li₂MgMn₃O₈ phase with a minor constituent (only one peak) of secondary Mg₆MnO₈ phase. The crystal structure of Li₂MgMn₃O₈ phase is cubic spinel with space group of Fd3m. In this arrangement lithium ion resides the tetrahedral (8a) sites and magnesium and manganese occupy octahedral (16d) sites.

Fig. 3a and 3b shows FTIR spectra of the compounds MgMn₂O₄ and Li₂MgMn₃O₄ between 400 and 1200 cm⁻¹.



It can be seen that for MgMn₂O₄, two primary bands at around 493 cm⁻¹ and 631 cm⁻¹ appear and they are attributed to asymmetric stretching in the vibration of octahedron MnO₆.



The bands around 350-450 cm^{-1} indicates the vibration of lithium cations. The broad bands at around 500 cm^{-1} and 610 cm^{-1} are the characteristics of LiMn_2O_4 [18]. Therefore, the bands at 493 cm^{-1} and 631 cm^{-1} observed in the present study are very close to these characteristic bands of LiMn_2O_4 and can consequently be interpreted as due to Mn–O vibration in MgMn_2O_4 structure. The minor absorption bands observed on either side (i.e. on lower and higher wave numbers) of these two characteristic bands are perhaps appearing from $\text{Mg}_6\text{Mn}_3\text{O}_8$ phase. In the case of $\text{Li}_2\text{MgMn}_3\text{O}_8$ phase (Fig. 3b), though there are relatively a large number of absorption bands, none of these bands are very intense which can indicate the formation of ordered structure after lithiation. Therefore, the ionic configuration in the compound host and lithiated compound structures can well be visualized from IR results

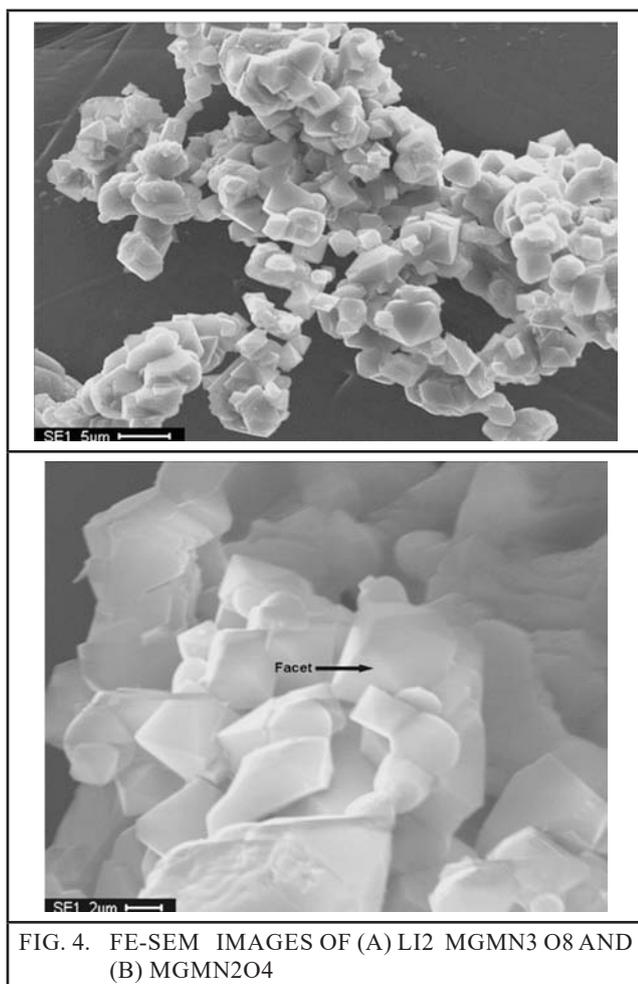


FIG. 4. FE-SEM IMAGES OF (A) $\text{Li}_2\text{MgMn}_3\text{O}_8$ AND (B) MgMn_2O_4

The powder morphology of $\text{Li}_2\text{MgMn}_3\text{O}_8$ was observed under FE–SEM (FEI QUANTA 200F)

and the micrographs are shown in Fig. 4a and 4b. The particles are of prismatic shape with clear faceted faces which are favourable for high energy storage. The particle size of the compound which was estimated by linear intercept method was in the range of 2–7 μm . The smaller particle size or larger surface area of sample is desirable for good reversibility and power capability. The particles are in agglomerated form which will further help in good packing density, leading to high capacity.

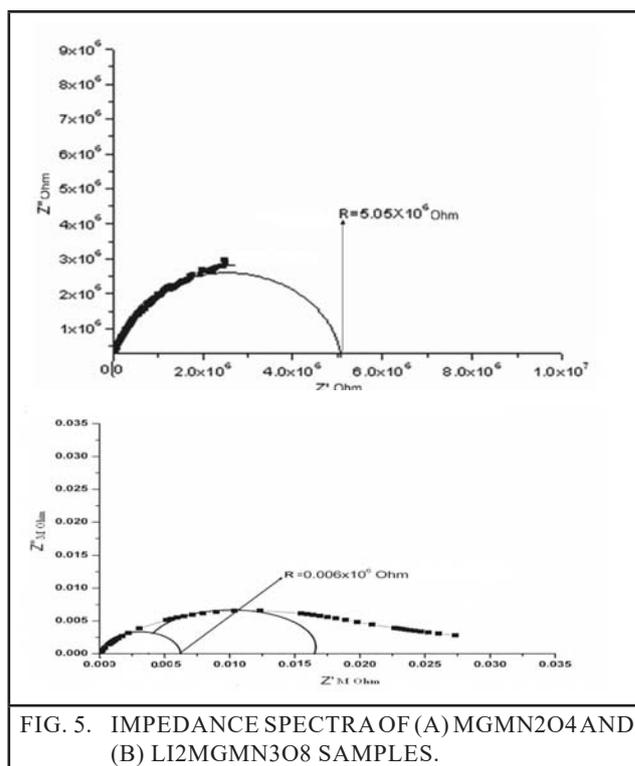


FIG. 5. IMPEDANCE SPECTRA OF (A) MgMn_2O_4 AND (B) $\text{Li}_2\text{MgMn}_3\text{O}_8$ SAMPLES.

The EIS data of the MgMn_2O_4 and $\text{Li}_2\text{MgMn}_3\text{O}_8$ samples in the form of cylindrical pellets at room temperature obtained by plotting real and imaginary part of complex impedance measurements at different frequencies as shown in Fig. 5a and 5b. It can be seen that the measurement points lie on depressed semicircles. The DC bulk resistance of the grain was estimated from the interception of semi-circular extrapolation of the higher frequency data points on the real (Z') axis. The conductivities of the samples were calculated from the following relationship $\sigma = t/(R \times A)$, where A is cross-sectional area, t is the sample thickness, and R is the bulk resistance of the sample $5.05 \times 10^6 \Omega$, $6.1 \times 10^3 \Omega$ for MgMn_2O_4 and $\text{Li}_2\text{MgMn}_3\text{O}_8$ respectively.

The conductivity values of $MgMn_2O_4$ and $Li_2MgMn_3O_8$ were found to be $\sigma = 4.0 \times 10^{-8} S cm^{-1}$ and $1.2 \times 10^{-5} S cm^{-1}$ respectively. The EIS analysis has shown that insertion of Li into $MgMn_2O_4$ has lowered the resistance and increased the conductivity of $Li_2MgMn_3O_8$ [19].

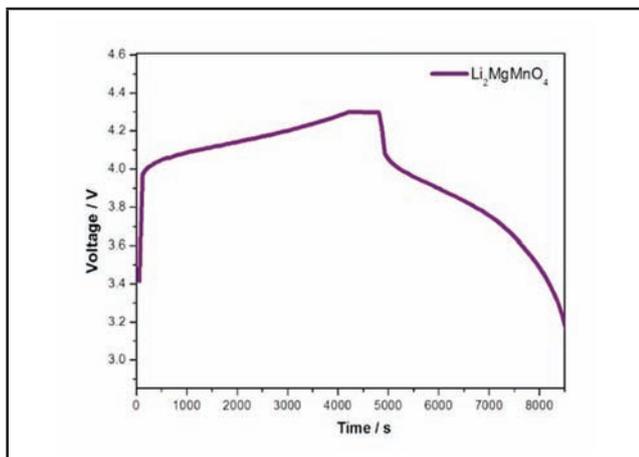


FIG. 6. CHARGE-DISCHARGE CHARACTERISTIC OF $Li_2MgMn_3O_8$

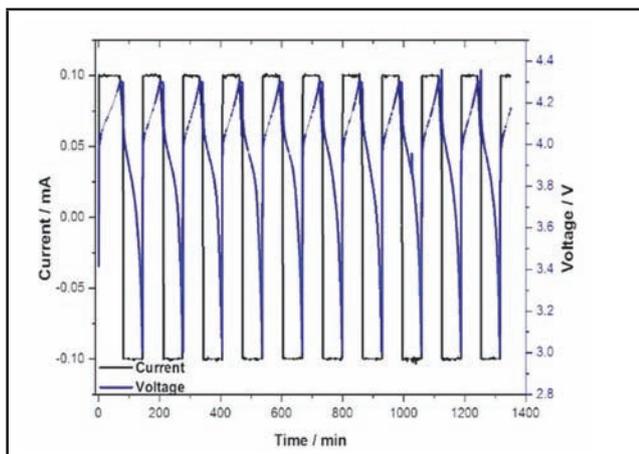


FIG. 7. CHARGE-DISCHARGE CYCLES OF $Li_2MgMn_3O_8$

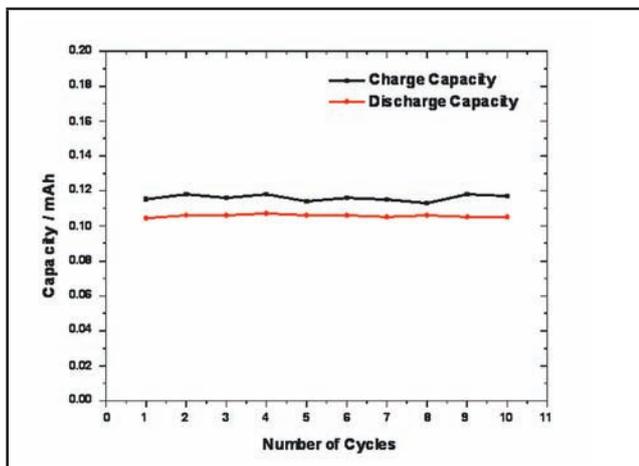


FIG. 8. CHARGE-DISCHARGE CAPACITY OF $Li_2MgMn_3O_8$

Fig. 6 shows the charge discharge curve of $Li_2MgMn_3O_8$. The charging current was 1A at ambient temperature conditions ($25 \pm 2^\circ C$). The Charging cycle displayed a steep raise in voltage from 3.4 V to 3.9 V, as the time progresses the voltage was further increased upto 4.3V and was stabilised. The discharge curve has shown step fall of voltage from 4.3V to 4.0 V. This may be because during discharge the Li inserted in $MgMnO$ matrix might undergo phase transitions and this phenomenon has been studied further [20]. The total charge-discharge cycle time was 8,000 s (133 min). The performance of the $MgMn_3O_8$ has increased with insertion of Li. Fig. 7 represents the charge-discharge cycles with constant current mode. During all the 10

cycles the $Li_2MgMn_3O_8$ gave very stable performance. It can be concluded that the insertion of Li into the $MgMn_3O_8$ has shown promising results. The capacity retention of the $Li_2MgMn_3O_8$ has been studied by constant charge/discharge studies, a current of 0.1 mA has been applied and the cell was cycled between 4.2 V to 3.4 V at room temperature. Fig. 8 shows the charge discharge curves of the $Li_2MgMn_3O_8$. The charge capacity stayed at 0.115 mAh and discharge capacity stayed at 0.104 mAh [21]. It also shows that the charge and discharge capacity versus cycle number of $Li_2MgMn_3O_8$ sample at a constant current of 0.1 A, and cut off voltage from 3.0 V to 4.3 V. The charge and discharge capacity of the $Li_2MgMn_3O_8$ were run for 10 cycles and it has shown stable results [22].

4.0 CONCLUSIONS

The present study addresses the solid-state synthesis of magnesium manganese oxide host compound and subsequent lithium insertion in the prepared host for lithium ions. The lithiation carried out by solid state process yields the compound $Li_2MgMn_3O_8$ which also consist of the spinel structure. The compound was characterized by FESEM, XRD and FT-IR spectroscopy which confirmed the required morphology and phase formation, i.e. spinel structure. The electrochemical performance of $Li_2MgMn_3O_8$ as a cathode material successfully

demonstrated in coin cell using Li-metal as counter electrode, which is suitable cathode material for high voltage, low cost and safer lithium ion battery

REFERENCES

- [1] M. M. Thackeray, Manganese oxides for Lithium batteries, *Prog. Solid. State Chem.*, Vol 25, pp. 1–71, 1997.
- [2] D.H. Doughty, *Sample J.*, Vol 32 (2), Iss. 2, pp. 75, 1996.
- [3] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Li_xCoO_2 ($0 < x < 1$): A New cathode material for batteries of high energy density *Mater. Res. Bull.*, Vol 15, pp. 783–789, 1980.
- [4] J.R. Dahn, U.V. Saken, M.W. Juzkow, Al-Janaby, Rechargeable $\text{LiNiO}_2/\text{Carbon}$ Cells, *J. Electrochem. Soc.*, Vol 138, pp. 2207–2211, 1991.
- [5] M.M. Thackeray, P.J. Johnson, L.A.D. Picciotto, Electrochemical extraction of Lithium from LiMn_2O_4 , *Mater. Res. Bull.*, Vol 19, pp. 179–187, 1984.
- [6] D. Guyomard, J.M. Tarascon, Li Metal-Free Rechargeable $\text{LiMn}_2\text{O}_4/\text{Carbon}$ Cells: Their Understanding and Optimization, *J. Electrochem. Soc.*, Vol 139, pp. 937–948, 1992.
- [7] H. Kawai, M. Nagata, H. Tukamoto, A.R. West, High-voltage lithium cathode materials, *J. Power Sources*, Vol 81–82, pp. 67–72, 1999.
- [8] Y.M. Chiang, Y.I. Jang, H. Wang, B. Huang, D.R. Sadoway, P. Ye, Synthesis of LiCoO_2 by Decomposition and Intercalation of Hydroxides, *J. Electrochem. Soc.* Vol 145 (3), pp. 887–891, 1998.
- [9] G.X. Wang, S. Zhong, D.H. Bradhurst, S.X. Dou, H.K. Liu, $\text{LiAl}_{1-\delta}\text{Ni}_{1-\delta}\text{O}_2$ solid solutions as cathodic materials for rechargeable lithium batteries, *Solid State Ionics*, Vol 116, pp. 271–277, 1999
- [10] L. Feng, Y. Chang, L. Wu, Electrochemical behaviour of spinel LiMn_2O_4 as positive electrode in rechargeable lithium cells, *J. Power Sources*. Vol 63, pp. 149–152, 1996.
- [11] W. Liu, K. Kowal, G.C. Ferrington, Electrochemical Characteristics of Spinel Phase LiMn_2O_4 -Based Cathode Materials Prepared by the Pechini Process, *J. Electrochem. Soc.*, Vol 143, pp. 3590–3596, 1992.
- [12] Y. Xia, M. Yoshio, An Investigation of Lithium Ion Insertion into Spinel Structure Li-Mn-O Compounds, *J. Electrochem. Soc.*, Vol 143, pp. 825–833, 1996.
- [13] Y. Shimakawa, T. Numata, J. Tabuchi, Verwey-Type Transition and Magnetic Properties of the LiMn_2O_4 Spinel, *J. Solid State Chem.*, Vol. 131, pp. 138–148, 1997.
- [14] C. Delmas, I. Saadoune, A. Rougier, The cycling properties of the $\text{Li}_x\text{Ni}_{1-y}\text{CO}_y\text{O}_2$ electrode, *J. Power Sources*. Vol 43–44, pp. 595–602, 1993.
- [15] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komari, Comparative study of LiCoO_2 , $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ and LiNiO_2 for 4 Volt secondary lithium cells, *Electrochem. Acta*. Vol 38, pp. 1159–1167, 1993.
- [16] A.D. Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gerand and J.-M. Tarascon, Mechanism for Limited 55°C Storage Performance of $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ Electrodes, *J. Electrochem. Soc.*, Vol 146 (2), pp. 428–436, 1999.
- [17] T.J. Richardson, S.J. Wen, K.A. Striebel, P.N. Ross, E.J. Cairns, FTIR Spectroscopy of metal oxide insertion materials: Analysis of LiXMn_2O_4 spinel electrodes, *Mater. Res. Bull.* Vol. 32, pp. 609–618, 1997.
- [18] B. Ammundsen, G.R. Burns, M.S. Islam, H. Kanoh, J. Roziere, Lattice Dynamics and Vibrational Spectra of Lithium Manganese Oxides: A Computer Simulation and Spectroscopic Study, *J. Phys. Chem. B.*, Vol 103, pp. 5175–5180, 1999.

- [19] X. Li, R. Xiang, T. Su, Y. Qian, Synthesis and electrochemical properties of nanostructured LiMn_2O_4 for lithium-ion batteries, *Mater. Lett.* Vol. 61, pp 3597–3600, 2007.
- [20] H. Liu, H. Yang, T. Huang, Synthesis, structure and electrochemical properties of one-dimensional nanometre materials LiV_3O_8 , *Mater. Sci. & Engg. B.* Vol. 143, pp 60–63, 2007.
- [21] R. Sathiyamoorthi, T. Vasudevan, Synthesis and electrochemical behavior of nanosized $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode materials for high voltage secondary lithium-ion cells, *Mater. Res. Bull.* Vol 42, pp. 1507–17, 2007.
- [22] Priti Singh, Anjan Sil, Mala Nath, Subrata Ray, Synthesis and characterization of $\text{Li}[\text{Mn}_{2-x}\text{Mg}_x]\text{O}_4$ ($x = 0.0-0.3$) prepared by sol-gel synthesis, *Ceramics–Silikáty*, Vol 54, pp. 38-46, 2010.

