

Cathodic Capacity Promotion Via Narrow Range of Nano- Te(IV)-Dopings on $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ -Spinel

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ABSTRACT

Samples with general formula $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ (where $x= 0.025,0.05$ mole) were successfully synthesized through thermal decomposition of LiMnC_2O_4 (OAc) precursor. The structural , micro-structural and electrochemical features of pure spinel and tellurium doped samples were investigated . The electrochemical investigations included cyclic voltammetry, charge–discharge cycling of coin model cells were performed. Capacity retentions (loss with recycleability for first twenty nine cycles) were promoted with tellurium doping recording maximum for $x = 0.025$ mole (0.31 % loss per cycle) and 0.93 % loss per cycle for $\text{LiMn}_{1.95}\text{Te}_{0.05}\text{O}_4$ and minimum one for the undoped parent LiMn_2O_4

Keywords: Li-ion Batteries ;Doped-Spinel ;Crystal Structure; SEM; XRD.

INTRODUCTION

The lithium ion batteries are widely available for portable consumer applications such as lap top computers and cellular telephones. are under consideration for the electric vehicle and the hybrid electric vehicle applications. The technological challenges confronting their scale up and commercialization are the capacity fade characteristics and the thermal safety. The cathode materials such as LiCoO_2 [1 , 2], LiNiO_2 [3 , 4], $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ [5 , 6] are currently used in the lithium-ion batteries. Although the commercially available lithium-ion cells for portable applications use LiCoO_2 and $\text{LiCo}_y\text{Ni}_{1-y}\text{O}$, they are considered to be more expensive and toxic than that having a LiMn_2O_4 cathode. The LiMn_2O_4 has been studied extensively as a cathode material for Li-ion batteries because it is relatively inexpensive and has environmental advantages, compared with LiCoO_2 , LiNiO_2 , and $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ [1, 2, 3, 4, 5 and 6]. However, LiMn_2O_4 shows problems related to poor cycling behavior because of a fast capacity fading in

the three voltage range due to the phase transformation from cubic structure to tetragonal structure and also in the four voltage range mainly due to the Mn (Mn^{3+}) dissolution during lithium ion intercalation/deintercalation [7]. Reducing the amount of the Mn^{3+} ion in structure may help in improving the cycling performance of Mn spinel [8, 9 and 10]. Transitional metals in the same row in the periodic table may be considered as the possible candidates for the substitution because of their similar ionic radii. The use of metal ions with similar radii will not cause a dramatic structural change as a result of the substitution [11, 12, 13, 14 and 15]. In an effort to better understand the performance issues of the Mn spinels, research was undertaken to prepare the manganese-substituted spinels by partially substituting Mn separately with Co, Ni, Fe and Cr studying their structures, electrochemical behavior, diffusion phenomena and thermal characteristics. A sol-gel process was used for the synthesis in order to achieve the homogeneity and narrow particle size distribution of the final product [16, 17, 18 and 19]. The electrochemical and thermal properties of the substituted $LiMn_2O_4$ spinels were compared with those of $LiMn_2O_4$.

The major goal of the present article is to investigate narrow range of tellurium (IV) ions doping on manganese sites ($0.025 \leq x \leq 0.05$) to promote :

- 1-Structural and micro-structural features of cubic spinel (Li-Mn-O) .
- 2- Cathodic features (specially charge/discharge specific capacity and cycleability) .

MATERIALS AND METHODS

II.I.Synthesis of Li-Mn-O spinels :

Li-Mn-O pure and Te-substituted spinels were prepared by thermal decomposition of $LiMnC_2O_4$ (AC) precursor which mixed with accurate molar ratios of TeO_2 whereas $LiMnC_2O_4$ (AC) precursor was synthesized by the room temperature solid state reaction. In this method, LiOH and oxalic acid were mixed in a molar ratio of 1:1 and ground in a gate mortar until the mixture becomes sticky. Then, manganese acetate (in solid state) was added to the sticky mixture with the same molar amount, and ground for 30 min. In this process, the vinegar odor could be smelt. The obtained materials were further dried at 80-100°C to remove water and acetic acid adsorbed on the product, and finally $LiMnC_2O_4$ (AC) precursor was obtained, then the $LiMnC_2O_4$ (AC) precursor was pressed into tablets, the lithium manganese oxides was prepared by sintering tablets of $LiMnC_2O_4$ (AC) precursor in air at 780°C for 50 hrs with a heating rate of 10°C / min without intermediate regrinding or other heating treatments, after sintering and cooling with a possible lowest rate (5°C/min.) .

II.II.Structural characterization :

II.II.A. X-Ray diffraction (XRD):

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground pure and Te-substituted spinels in the range ($2\theta = 10-90^\circ$) using Cu-K α radiation source and a computerized [Steo-Germany] X-ray diffracto-meter with two theta scan technique.

II.II.B. Scanning Electron – Microscope:

Scanning electron microscope (SEM) measurements were carried out using small pieces of prepared samples on different sectors to be the actual molar ratios by using "TXA-840, JEOL-Japan" attached to XL30 apparatus with EDX unit, accelerant voltage 30kv, magnification 10x up to 500.000x and resolution 3. nm. The samples were coated with gold.

II.III. Electrochemical measurements :

The coin cells model (2016 size) were used for electrochemical. The coin cells comprised of $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ as a cathode, lithium foil anode, and an electrolyte having 0.5 M LiPF_6 in a 1:1 wt.% of ethylene carbonate and diethyl carbonate (EC/DEC, EM Industry, Inc. $\text{H}_2\text{O} < 30$ ppm). A Celgard 2400 micro-porous polypropylene separator was used in these cells. The cell preparation was carried out in the Argon-filled dry box. The cyclic voltammetry curves were obtained at room temperature using the above coin cells at a scan rate of 0.02 mV s^{-1} . Another group of fresh coins cells were also cycled galvanostatically using an Arbin cycler in the potential range of 2.5–4.5 V for $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ ($\text{Te} = 0.025$ and 0.05 mole).

The cells were first cycled three times and then, charged to 4.4 V. The cells were charged using a constant voltage charging procedure for 40 h. The cut-off voltage for charging was 4.4 V. The charged coin cells were opened in an argon-filled glove box and the cathode material was recovered from the cells.

RESULTS AND DISCUSSION

III.I.Phase Identification:

Fig.1_{a-c} shows the X-ray diffraction patterns of pure spinel and Te-doped spinels with formula $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ (where $x = 0.025, 0.05$ mole) powders. Analysis of the corresponding 2θ values and the interplanar spacings d (Å°) proved that the compounds are mainly belong to a single-phase spinel structure. with Fd3m space group in which the lithium ions occupy the tetrahedral (9a) sites as clear in Fig.1_d. The Mn^{3+} and Mn^{4+} ions as well as the doping metal ions, as in LiMn_2O_4 structure, occupy the octahedral (16d) sites [19]. For simplicity, these structures can be expressed as $[\text{Li}]^{\text{tetrahedral}} [\text{M}_y\text{Mn}_{2-y}]^{\text{octahedral}} [\text{O}_4]$ [20] as described in fig.1_d and Table 1. Doping did not appear to change the basic LiMn_2O_4 structure, but slightly change the lattice parameters due to atom size effect.

As clear in Figs.1_{a-d} the Li-Mn-O spinel doped with Te(IV) of at the expense of Mn^{3+} crystallized in octahedral units $[\text{MnO}_6]$ without any kind of noticeable distortion as expected with Fd3m space group . Only tellurium oxide as secondary phase appears in minor trace in the back ground which confirm success of doping in the investigated range .

It is well known that spinel LiMn_2O_4 as a cathodic material is too poor to be substituted or replaced by LiCoO_2 due to the gradual degradation of its capacity on cycling. The degradation mechanisms have been proposed as (a) structural damage due to Jahn-Teller distortion, (b) dissolution of the spinel into the electrolyte, (c) oxidation of the electrolyte on the surface of the cathode at the highly charged state [21-25].

Accurate retvield analysis of structure indicated that all samples have the finger print peaks of Li-Mn-O spinel (red circles in Fig 1_{a-c}) with high degree of crystalline. The lattice constants of cubic spinels were calculated and found to be $a = 8.3679(1) \text{ Å}^\circ$ for $x = 0.025$ mole and $a = 8.388(4) \text{ Å}^\circ$ for $x = 0.05$ mole which are bigger than undoped one ($a = 8.269(3)$) since the ionic radii of the sixth coordinate Te^{4+} and Mn^{3+} are 0.097 and 0.064 nm, respectively. So that the unite crystal volume expands, that what was expected, but in opposite with Xu et al.[26] .

These results in full agreement with those reported by Wolska et al.[27] who stated that substitution with very small quantities of Fe^{+++} ions first restrains the partial ordering of Mn^{3+} and Mn^{4+} ions in the spinel super-lattice and then stabilizes cubic spinel structure of LiMn_2O_4 .

III.II.Scanning Electron Microscopy :

The morphology of powdered samples for undoped and doped sample fired at 750°C in air for 50 hr, were investigated by scanning electron microscope (SEM) after coating with gold. Fig.(2_{a-c}) represents the captured images for undoped LiMnO₄ powder and Te-doped spinels. With low – magnification of 750 times, the morphology of this powder reveals that the powder exhibits irregular porous agglomerates. It can be more clearly observed that there are many micro – holes in the surface of the particles, this porous morphology is beneficial for the diffusion of electrolyte into the interior of the particle during fabrication of the battery. The formation of porous morphology is attributed to the escape of the gases such as CO₂ and H₂O from the interior of the particles during the heat treatment. In other words, the organic constituents in LiMnC₂O₄(AC) precursor has bubbling effect. The morphology of the same sample (LiMn₂O₄) doped with tellurium (x = 0.025 and x = 0.05 mole) with magnification of 35000 times. Fig.(b,c), reveal that the sample have regular nano – sized grains of average size 149 nm and the average particle size is ~ 17.6 nm.

These averages of grain and particle size of pure and Te-doped spinels are fully consistent with those reported by Lu et al.[28] who synthesized uniform spinel by using emulsion technique with spherical powders with a size distribution which ranged from 0.1-0.15 μm .

II.III. Electrochemical measurements :

II.III.A.Specific Capacities Investigations :

Fig. 3_{A-C} shows the initial charge–discharge curves of Li/ LiMn_{2-x}Te_xO₄ coin cells where x = 0 ,0.025 and 0.05 mole respectively at a constant charge–discharge rate of C/20 over the voltage range of 4.5–3.5 V. The theoretical and experimental capacities are compared.

The theoretical capacity of the Li/LiMn₂O₄ cell is 148 mA h g⁻¹ [29] on the basis that one Li per Mn₂O₄ unit is reversibly intercalated and deintercalated at 4.12 V. But, LiMn₂O₄ shows actual value of about 126 mA h g⁻¹ corresponding to 0.82–0.90 of total Li in LiMn₂O₄ reversibly utilized within the voltage range of 3.5–4.5 V. While the specific capacities recorded for yttrium-substituted spinels were 128 and 91 mA h g⁻¹ respectively .

It was observed that for the first twenty nine cycles the capacity retentions (loss with recycleability) were promoted as Te-doping increases recording maximum for x = 0.025 mole (0.31 % loss per cycle) and 0.93 % loss per cycle for LiMn_{1.95}Te_{0.05}O₄ and minimum one for the undoped parent LiMn₂O₄ .

Accordingly the enhancement of specific capacity (see Fig.4) and recycleability of Te-doped samples specially that with optimal doping content x = 0.025 mole is due to Te(IV) resists redox reactions on its immersed electrolyte since Te (IV) could oxidize to Te(VI) and stabilize spinel crystal structure by reinforcing lattice stability towards Jahn-Teller distortion inside MnTeO₆ – poly-octahedrons .

II.III.B. Cyclic Voltammetry Measurements :

The potential scan for cyclic voltammetry for LiMn_{2-x}Te_xO₄ where x = 0 ,0.025 and 0.05 mole samples was conducted within a potential range from 3.5 to 4.5 V versus Li/Li⁺. The cyclic voltammetry curves as shown in Fig.5a-c have some important observations:

There are two anodic and cathodic peaks for pure spinel and Te-substituted spinels. The peak potentials of the substituted spinels in the anodic region slightly shifted to high potential and those in the cathodic region also shifted towards high potential with respect to the LiMn_2O_4 .

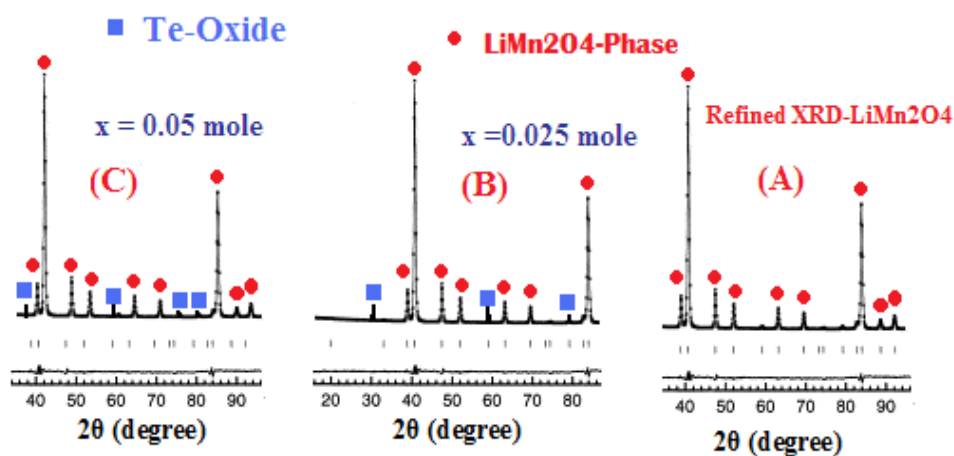


Fig.(1_{a-c}): X-ray diffraction patterns of $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ spinel doped with Te^{4+} .

- (a): undoped LiMn_2O_4 .
- (b): doped with $x = 0.025$ mole.
- (c): doped with $x = 0.050$ mole.

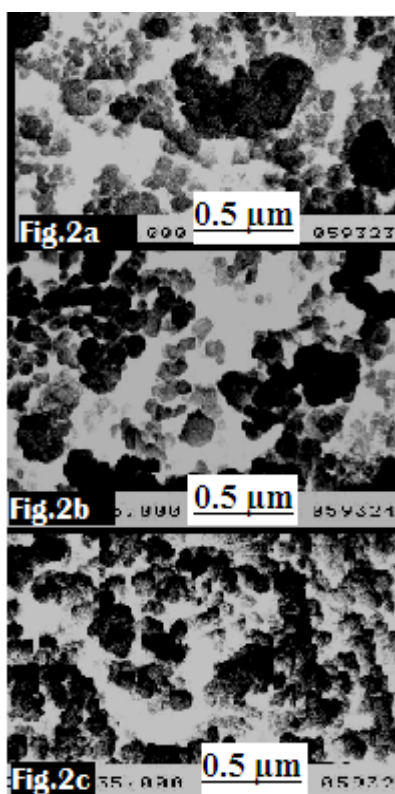


Fig.2. SE-micrographs captured for pure and Te-substituted spinels.

- Amplification factor = $0.5 \mu\text{m}$.
- (a): undoped LiMn_2O_4 .
- (b): doped with $x = 0.025$ mole.
- (c): doped with $x = 0.050$ mole.

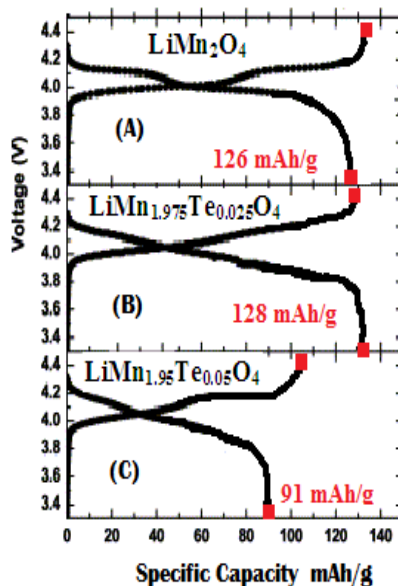


Fig. 3. First cycle charge and discharge curves of type 2016 coin cells at C/20 rate. Cell—Li—0.5 M LiPF₆ in (1:1 wt.% EC+DEC)—LiMn_{2-x}Te_xO₄ (where x =0.025, and x = 0.05 mole respectively).

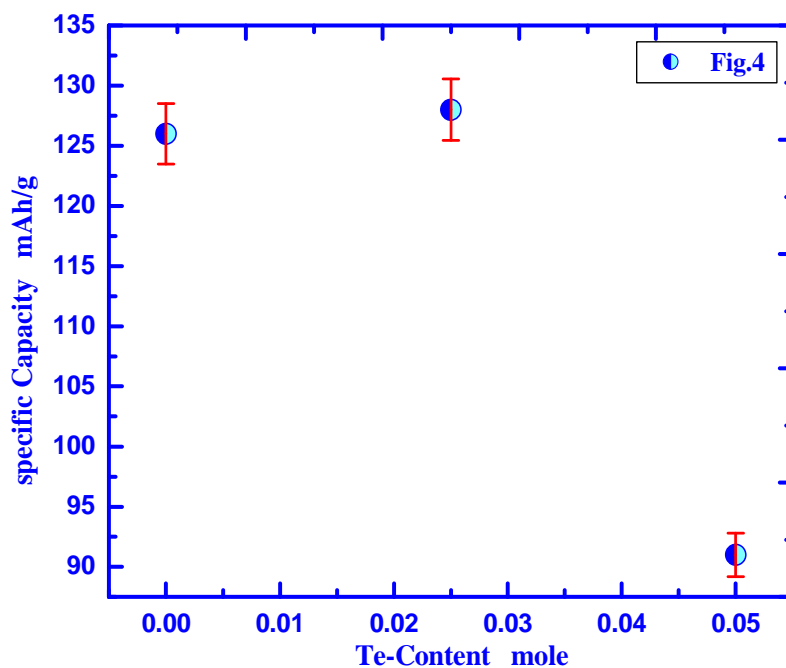


Fig.4: Specific Charging Capacity versus Te-IV-Doping Content

The peak current densities as well as the area under the current–voltage curve for the substituted spinels lower and smaller than those of LiMn₂O₄ by very small ratios.

The two pairs of the oxidation and reduction peaks of LiMn_2O_4 spinel were located around 4.21 and 4.06 V, corresponding to the two-stage reversible intercalation/deintercalation processes of lithium. The results obtained in this study are consistent with those reported previously [18 and 30]. The oxidation of Mn^{3+} to Mn^{4+} contributes to the oxidation peaks in the investigated voltage range for the LiMn_2O_4 and so it is reasonable to assume that only Mn^{3+} in both substituted spinels causes the oxidation and reduction peaks [20] and that the amount of Mn^{3+} is decreased by doping, thereby resulting in a decrease in the observed peak current.

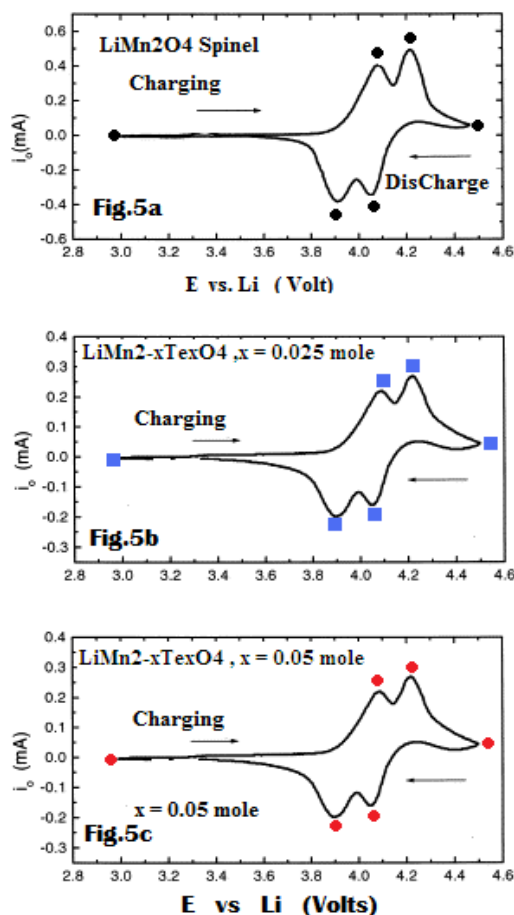


Fig. 5_{a-c}. Cyclic voltammetry curves of LiMn_2O_4 and substituted $\text{LiTe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.025$ and 0.05 mole) spinels in 0.5 M LiPF_6 in $1:1 \text{ wt.}\%$ EC+DEC electrolyte.

Scan RATE = 0.02 mV s^{-1} .

- (a): undoped LiMn_2O_4 .
- (b): doped with $x = 0.025$ mole.
- (c): doped with $x = 0.050$ mole.

CONCLUSION

Samples with general formula $\text{LiMn}_{2-x}\text{Te}_x\text{O}_4$ (where $x = 0.025, 0.05$ mole) were successfully synthesized through thermal decomposition of $\text{LiMn}_2\text{C}_2\text{O}_4$ (OAc) precursor. The structural, micro-structural and electrochemical features of pure spinel and tellurium doped samples were promoted. The electrochemical investigations proved that the capacity retentions (loss with recyclability for first twenty nine cycles) were promoted with tellurium doping recording maximum for $x = 0.025$ mole (0.31% loss per cycle) and 0.93% loss per cycle for $\text{LiMn}_{1.95}\text{Te}_{0.05}\text{O}_4$ and minimum one for the undoped parent LiMn_2O_4 .

REFERENCES

- [1] T. Nagaura and K. Tazawa *Prog. Batteries Solar Cells* 9 (1990), p. 20.
- [2] K. Ozawa *Solid State Ionics* 69 (1994), p. 212.
- [3] W. Ebner, D. Fouchard and L. Xie *Solid State Ionics* 69 (1994), p. 238.
- [4] J.R. Dahn, U. Von Sacken, M.R. Jukow and H. Al-Janaby *J. Electrochem. Soc.* 138 (1991), p. 2207.
- [5] C. Delmas, I. Saadoune and A. Rougier *J. Power Sources* 43–44 (1993), p. 595.
- [6] R.J. Gummow and M.M. Thackeray *J. Electrochem. Soc.* 140 (1993), p. 3365.
- [7] J.M. Tarascon, W.R. Mckinnon, F. Coowar, T.N. Boowner, G. Amatucci and D. Guyomard *J. Electrochem. Soc.* 141 (1994), p. 1421.
- [8] D. Guyomard and J.M. Tarascon *Solid State Ionics* 69 (1997), p. 22.
- [9] X. Qiu, X. Sun, W. Shen and N. Chen *Solid State Ionics* 93 (1997), p. 335.
- [10] Y.-K. Sun *Solid State Ionics* 100 (1997), p. 115.
- [11] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. Mckinnon and S. Colson *J. Electrochem. Soc.* 138 (1991), p. 2589.
- [12] T. Ohzuku, M. Kitagawa and T. Hirai *J. Electrochem. Soc.* 137 (1990), p. 769.
- [13] R. Bittihin, R. Herr and D. Hoge *J. Power Sources* 43-44 (1993), p. 223.
- [14] Y. Toyoguchi, Eur. Pat. Appl. 0390 (1990) 185.
- [15] S. Bach, M. Henry, N. Buffer and J. Livage *J. Solid State Chem.* 88 (1990), p. 325.
- [16] T. Tsumura, A. Shimizu and M. Inagaki *J. Mater. Chem.* 3 (1993), p. 995.
- [17] P. Barboux, J.M. Tarascon and F.K. Shokoohi *J. Solid State Chem.* 94 (1991), p. 185.
- [18] W. Liu, G. Farrington, F. Chaput and B. Dunn *J. Electrochem. Soc.* 143 (1996), p. 879.
- [19] G. X. Wang, H. K. Liu and S. X. Dou, *Solid State Ionics*, 120, 1-4, (1999), p. 95-101
- [20] L. Guohua, T. Uchida and M. Wakihara *J. Electrochem. Soc.* 143 (1996), p. 178.
- [21] A.R. West In: *Basic Solid State Chemistry*, Wiely, New York, (1991), p. 57.
- [22] R. Koksang, J. Barker, H. Shi and M.Y. Sa. *Solid State Ionics* 84 (1996), pp. 1–21.
- [23] M.M. Thackeray, W.I.F. David and J.B. Goodenough. *Mater. Res. Bull.* 17 (1982), p. 785.
- [24] M.M. Thackeray. *J. Electrochem. Soc.* 142 (1995), pp. 2558–2563.
- [25] R.J. Gummow, A. de kock and M.M. Thackeray. *Solid State Ionics* 69 (1994), p. 59.
- [26] C.Xu, Y. Tain, Y.C.Zhai, L.Y.Liu, *Materials Chemistry and Physics* 98(2006)p. 532-538.
- [27] E.Wolska, M.Tovar, B.Andrzejewski, W.Nowicki, P.Pisora, M.Knapp, *Solid State Science* 8(2006)p.31-36.
- [28] C.H.Lu and S.W.Lin, *Journal of Power Sources*, 93(2001)p.14-19.
- [29] H. J.Bang, V. S. Donepudi and J.Prakash, *Electrochimica Acta*, 48, 4, (2002),P. 443-451
- [30] J.M. Tarascon and D. Guyomard *J. Electrochem. Soc.* 138 (1991), p. 2864.