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# Variations of the Electrochemical Properties of $LiMn_2O_4$ with the Calcining Temperature

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**ABSTRACT**

$LiMn_2O_4$ compounds were synthesized by calcining a mixture of LiOH and $MnO_2$(CMD) at 400°C for 10 h and then calcining again at 650°C to 900°C for 48 h in air with intermediate grinding. All the synthesized samples exhibited XRD patterns for the cubic spinel phase with a space group Fd3m. The lattice parameter increased gradually as the sintering temperature rose. The electrochemical cells were charged and discharged for 20 cycles at a current density 300 $\mu A/cm^2$ between 3.5 V and 4.3 V. The voltage vs. discharge capacity curves for all the samples showed two plateaus. The $LiMn_2O_4$ sample calcined at 900°C had the largest first discharge capacity. This sample exhibited the best crystallinity, had relatively large lattice parameter and had relatively large particles with relatively homogeneous size. All the samples showed good cycling performances. Among all the samples, the $LiMn_2O_4$ calcined at 850°C had relatively large first discharge capacity and very good cycling performance. The addition of excess LiOH and the mixing in ethanol considered to help the formation of the more $LiMn_2O_4$ phase per unit weight sample and the more stable $LiMn_2O_4$ phase. These led to the larger discharge capacities and the better cycling performances. The cyclic voltammograms for the second cycle of the $LiMn_2O_4$ samples showed the oxidation and reduction peaks around 4.05 V and 4.18 V and around 4.08 V and 3.94 V, respectively. The larger first discharge capacity of the sample calcined at the higher temperature is related to the larger lattice parameter.

***Key words : $LiMn_2O_4$, Solid-state method, Discharge capacity, Cycling performance***

## 1. Introduction

The transition metal oxides such as $LiCoO_2$,[1-3] $LiNiO_2$[4,5] and $LiMn_2O_4$[6-10] have been investigated in order to apply them to the cathode materials of lithium secondary battery. $LiCoO_2$ has large diffusivity and high operating voltage and it can be easily prepared. However, it contains an expensive element Co. $LiNiO_2$ has a large discharge capacity[11] and is relatively excellent from the view points of economics and environment. However, its preparation is very difficult as compared with $LiCoO_2$ and $LiMn_2O_4$. $LiMn_2O_4$ does not have a good cycling performance. However, it is very cheap and does not bring about environmental pollution.

Usually, $LiMn_2O_4$ is synthesized using a solid-state reaction which used mechanical mixing followed by high-temperature sintering. $LiMn_2O_4$ compounds are made from stoichiometric amounts of Li salts such as LiOH, $LiNO_3$, $Li_2CO_3$, mixed with manganese oxides[Chemical Manganese Dioxides(CMD) or Electrochemical Manganese Dioxides(EMD)].[12-16] The starting materials and synthesis temperature have effects on the electrochemical characteristics of $LiMn_2O_4$. By optimizing the $LiMn_2O_4$ synthesis, its electrochemical and cycling behavior can be improved. Guyomard *et al.*[14,17] prepared the spinel manganese oxide by sintering a stoichiometric mixture of $Li_2CO_3$ and $MnO_2$ at 800°C in air. The $LiMn_2O_4$ compounds (particle size 1 to 2 μm) were prepared by three consecutive annealings at 800°C for 24 h. Manev *et al.*[18] also prepared $LiMn_2O_4$ by sintering a mixture of $MnO_2$ (CMD) and $LiNO_3$ for 48 h in the temperature range between 450°C and 900°C. The results of the long-term cycling of $LiMn_2O_4$ synthesized at different temperatures showed the good cycling performance for the samples synthesized at 650°C and 750°C. These reports suggest that the electrochemical characteristics are sensitive to the microstructure of electrode material, which varies with the synthesis condition.

In this work, we synthesized $LiMn_2O_4$ samples by a solid-state reaction of LiOH with $MnO_2$ (CMD) at various temperatures from 650°C up to 900°C and then examined their electrochemical properties.

## 2. Experimental

$LiMn_2O_4$ compound was synthesized by the solid-state reaction. LiOH and $MnO_2$ (CMD) with a 1.1:2 molar ratio were mixed in a mortar filled with ethanol. Excess LiOH was added in order to compensate the quantity of evaporated Li during preparation. The mixture was calcined at 400°C for 10 h and then calcined again at 650, 700, 750, 800, 850 or 900°C for 48 h in air with intermediate grinding. The

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samples were slowly cooled at a cooling rate of 1°C/min. The phase identification of the prepared samples was carried out by X-Ray Diffraction (XRD, Rigaku III/A type) analysis using Cu Kα radiation. The morphologies of the samples were observed using a Scanning Electron Microscope(SEM). To measure the electrochemical properties, the electrochemical cells consisted of the prepared sample as a positive electrode, Li metal as a negative electrode and an electrolyte of 1 M LiPF6 in a 2:1 (volume ratio) mixture of Ethylene Carbonate(EC) and Dimethyl Carbonate(DMC). A Whatman glass-fiber was used as a seperator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, 89 wt% active material, 10 wt% acetylene black and 1 wt% Polytetrafluoroethylene(PTFE) binder were mixed in an agate mortar. By introducing Li metal, the Whatman glass-fiber, the positive electrode and the electrolyte, the cell was assembled. All the electrochemical tests were performed at room temperature with a battery charge-discharge cycle tester (WonATec WBCS 3000) at a current density 300 μA/cm$^2$ in a potential range from 3.5 V to 4.3 V. Fig. 1 summarizes the experimental procedure.

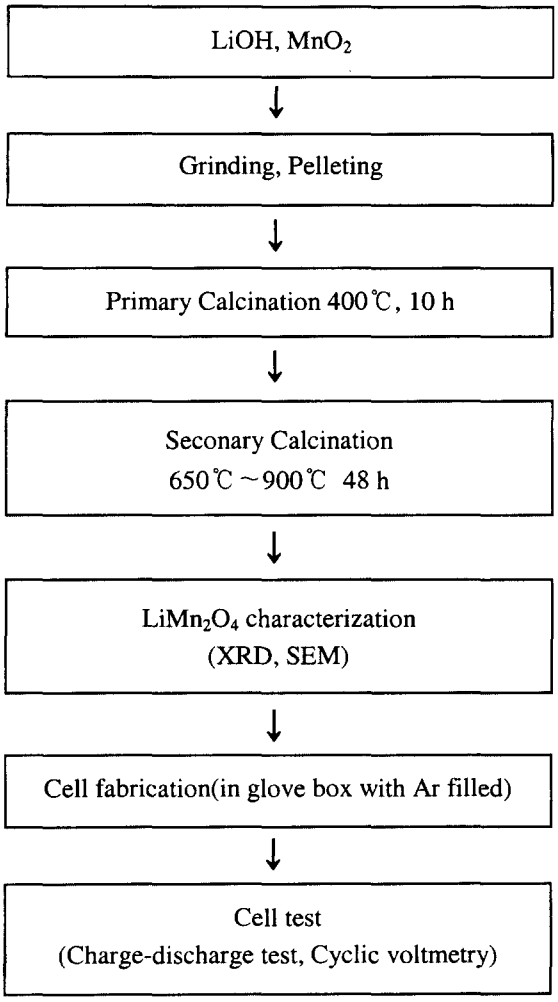


**Fig. 1.** Experimental procedure.

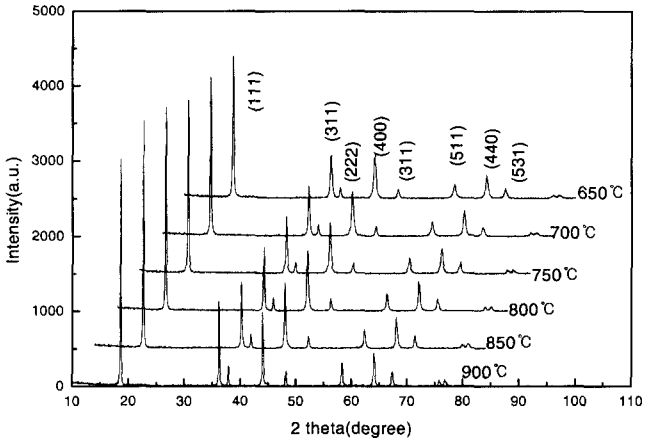


**Fig. 2.** XRD patterns of the $LiMn_2O_4$ samples calcined between 650°C and 900°C.

**Table 1.** Lattice Parameters of the $LiMn_2O_4$ Samples Calcined at Different Temperatures

| Secondary calcination temperature | Lattice parameter(Å) |
|---|---|
| 650°C | 8.18386 |
| 700°C | 8.19244 |
| 750°C | 8.19983 |
| 800°C | 8.21443 |
| 850°C | 8.21443 |
| 900°C | 8.21643 |

## 3. Results and Discussions

Fig. 2 shows XRD patterns of the $LiMn_2O_4$ calcined for 48 h between 650°C and 900°C. All the samples exhibit similar patterns. They were identified as the cubic spinel phase having a space group Fd3m. As the calcining temperature rises, the peaks become sharper. The sample calcined at 850°C and 900°C exhibited the sharpest peaks, showing that it has the best crystallinity.

The lattice parameter of each sample was obtained by the least-squares method. Table 1 gives the lattice parameters of the $LiMn_2O_4$ samples calcined at different temperatures. It increases gradually as the sintering temperature rises. The lattice parameters of $LiMn_2O_4$ calcined at 650°C and 900°C were $a_c$=8.18 and 8.22 Å, respectively.

Fig. 3 shows SEM microstructures of the $LiMn_2O_4$ samples calcined at 650°C to 900°C. The samples calcined at 650-750°C consist of very small particles and large ones. As the temperature increases, the particles grow and their sizes become more homogeneous. The samples calcined at 850°C and 900°C have relatively large particles with relatively homogeneous size.

Fig. 4 shows the voltage vs. discharge capacity curves at a current density 300 μA/cm$^2$ in a potential range from 3.5 V to 4.3 V for the first cycle of the $LiMn_2O_4$ samples calcined between 650°C and 900°C. The discharge capacity of the sample calcined at 900°C is larger than those of the other

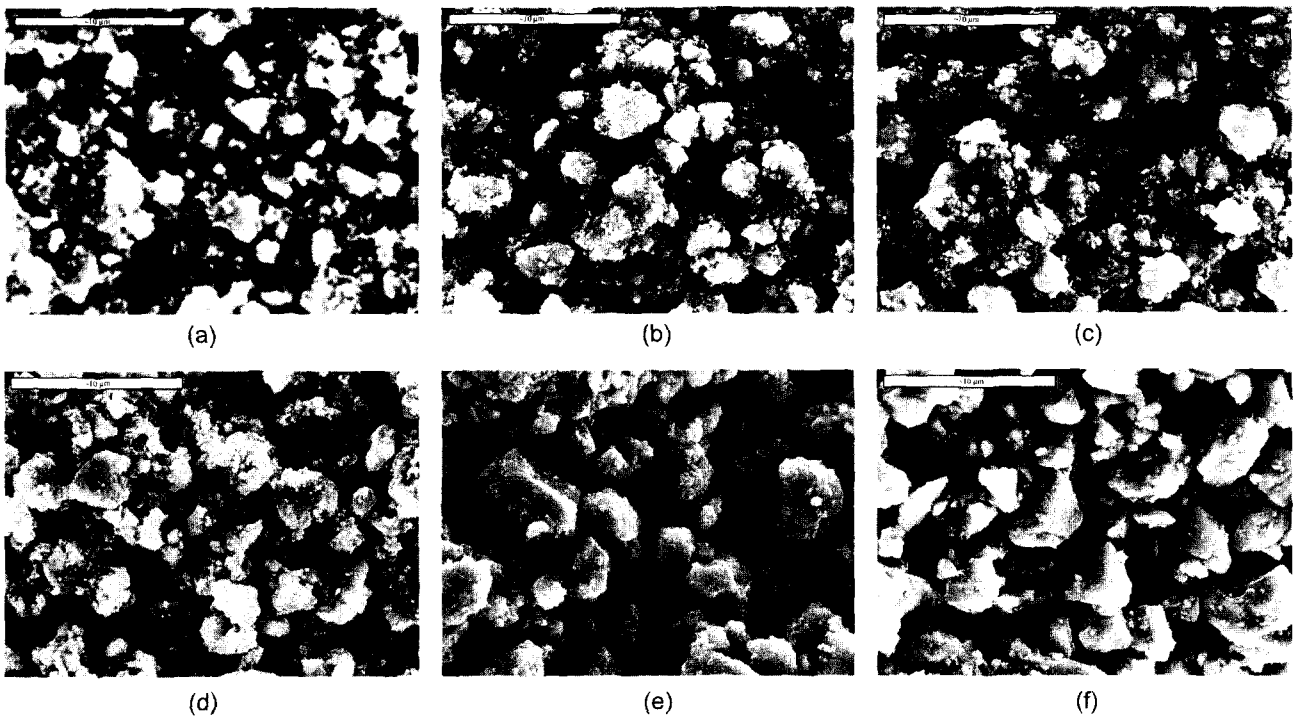


**Fig. 3.** SEM microstructures of the $LiMn_2O_4$ samples calcined at (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) 850°C and (f) 900°C.

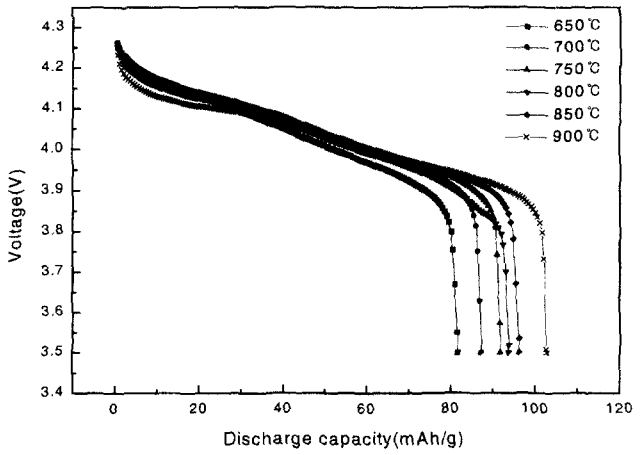


**Fig. 4.** Voltage vs. discharge capacity curves for the first cycle of the $LiMn_2O_4$ samples calcined between 650°C and 900°C.

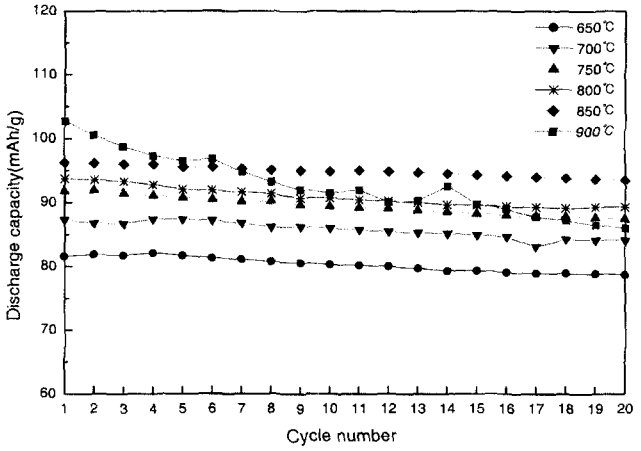


**Fig. 5.** Variations of discharge capacities with cycle number for the $LiMn_2O_4$ samples calcined between 650°C and 900°C.

samples. The discharge curves of all the samples showed two plateaus.

Fig. 5 shows the variations of discharge capacities for $LiMn_2O_4$ sintered at different temperatures with the number of discharge cycle. The cells were cycled for 20 cycles at a current density 300 $\mu A/cm^2$ between 3.5 V and 4.3 V. The $LiMn_2O_4$ calcined at 900°C has the largest first discharge capacity 102.7 mAh/g, which is a larger value than that reported earlier.[9] All the samples except that calcined at 900°C show good cycling performances. The $LiMn_2O_4$ sample calcined at 850°C has the first discharge capacity 96.2 mAh/g and the discharge capacity at the 20$^{th}$ cycle 93.5 mAh/g, showing the maintenance of 97.2% of the first discharge capacity. In this work excess LiOH was added in order to compensate the quantity of the evaporated Li during preparation. The mixture were mixed in a mortar filled with ethanol in order to get a homogeneous mixing. It is considered that these helped the formation of the more $LiMn_2O_4$ phase per unit weight of sample and the more stable $LiMn_2O_4$ phase. These led to larger discharge capacities and better cycling performances than those reported earlier.

Fig. 6 shows cyclic voltammograms for the second charge-

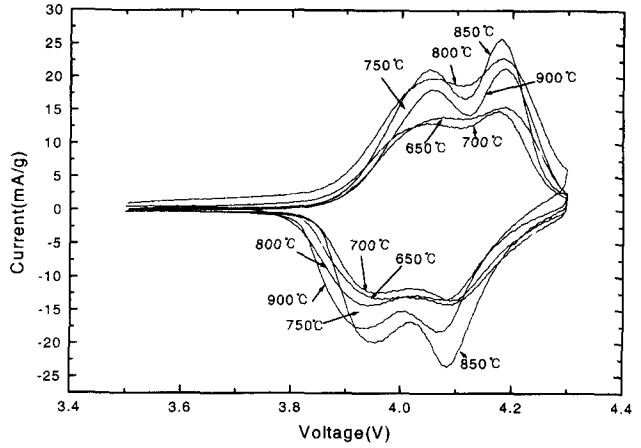


**Fig. 6.** Cyclic voltammograms for the second cycle of the $LiMn_2O_4$ samples sintered between 650°C and 900°C.

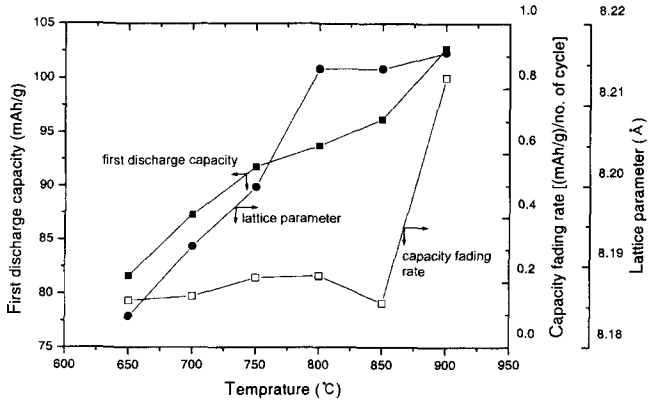


**Fig. 7.** Variations, with calcining temperature, of lattice parameter, the first discharge capacity and capacity fading rate.

discharge cycles of the $LiMn_2O_4$ samples calcined between 650°C and 900°C in the potential range from 3.5 V to 4.3 V. The oxidation and reduction peaks are located around 4.05 V and 4.18 V and around 4.08 V and 3.94 V, respectively, showing that oxidation and reduction proceed in two stages. The potentials for the oxidation in the cyclic voltammogram agree well with the plateau potentials of the V vs. x curve in Fig. 4.

The $LiMn_2O_4$ calcined at 900°C has the largest first discharge capacity. This sample shows the best crystallinity, has the largest lattice parameter and has relatively large particles with relatively homogeneous size. These are considered to be related with the largest first discharge capacity. Among all the samples, the $LiMn_2O_4$ sample calcined at 850°C has a relatively large first discharge capacity and a very good cycling performance.

Fig. 7 gives the variations, with calcining temperature, of lattice parameter, the first discharge capacity and capacity fading rate. The capacity fading rate, i.e. the decrease in the discharge capacity per no. of cycle, is obtained from the first to the twentieth cycle. The lattice parameter and the first discharge capacity decrease as the value of calcining temperature rises. The capacity fading rate increases, except at 850°C, as the calcining temperature rises. This shows that the sample with a larger lattice parameter has the larger first discharge capacity, suggesting that the spinel structure with a larger lattice parameter intercalates and deintercalates the more Li ions. The larger first discharge capacity is related to the wider range of the value of x $Li_xMn_2O_4$. The larger range of the value of x will cause the larger expansion and contraction of the spinel phase $LiMn_2O_4$ due to the intercalation and deintercalation. This will make the unit cell the more strained and distorted. With cycling, the more interstitial sites and thus the spinel structure will be destroyed. This decreases the larger fraction of the spinel phase, leading to the more capacity fading with cycling.

## 4. Conclusions

All the synthesized samples exhibited XRD patterns for the cubic spinel phase with a space group Fd3m. The lattice parameter increased gradually as the sintering temperature rose. The electrochemical cells were charged and discharged for 20 cycles at a current density 300 $\mu A/cm^2$ between 3.5 V and 4.3 V. The voltage vs. discharge capacity curves for all the samples showed two plateaus. The $LiMn_2O_4$ sample calcined at 900°C had the largest first discharge capacity. This sample exhibited the best crystallinity, had a relatively large lattice parameter and had relatively large particles with relatively homogeneous size. All the samples showed good cycling performances. Among all the samples, the $LiMn_2O_4$ calcined at 850°C had relatively large first discharge capacity and a very good cycling performance. The addition of excess LiOH and the mixing in ethanol considered to help the formation of the more $LiMn_2O_4$ phase per unit weight sample and the more stable $LiMn_2O_4$ phase. These led to the larger discharge capacities and the better cycling performances. The cyclic voltammograms for the second cycle of the $LiMn_2O_4$ samples showed the oxidation and reduction peaks around 4.05 V and 4.18 V and around 4.08 V and 3.94 V, respectively. The larger first discharge capacity of the sample calcined at the higher temperature is related to the larger lattice parameter.

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## REFERENCES

1. R. Alcantara, P. Lavela, J. L. Tirado, R. Stoyanova and E. Zhecheva, "Structure and Electrochemical Properties of Boron-doped $LiCoO_2$," *J. Solid State Chem.*, **134** 265-73 (1997).
2. Z. S. Peng, C. R. Wan and C. Y. Jiang, "Synthesis by Sol-gel

Process and Characterization of $LiCoO_2$ Cathode Materials," *J. Power Sources*, **72** 215-20 (1998).
3. M. K. Kim, K. S. Park, D. S. Kim, J. T. Son and H. G. Kim, "Effects of Drying Temperature on the $LiCoO_2$ Thin Films Fabricated by Sol-gel Method(*in Kor.*)," *J. Kor. Ceram. Soc.*, **38** 777-81 (2001).
4. J. M. Tarascon, E. Wang, F. K. Shokoohi, W. R. McKinnon and S. Colson, "The Spinel Phase of $LiMn_2O_4$ as a Cathode in Secondary Lithium Cells," *J. Electrochem. Soc.*, **138** 2859-64 (1991).
5. H. Rim, S. G. Kang, S. H. Chang and M. Y. Song, "A Study on the Synthesis and the Electrochemical Properties of $LiNi_{1-y}Co_yO_2$ from $Li_2CO_3$, $NiCO_3$ and $CoCO_3$(*in Kor.*)," *J. Kor. Ceram. Soc.*, **38** 515-21 (2001).
6. J. R. Dahn, U. von Sacken, M. W. Juzkow and H. Al-Janaby, "Rechargeable $LiNiO_2$/Carbon Cells," *J. Electrochem. Soc.*, **138** 2207-12 (1991).
7. M. Y. Song and D. S. Ahn, "On the Capacity Deterioration of Spinel Phase $LiMn_2O_4$ with Cycling around 4 V," *Solid State Ionics*, **112** 21-2 (1998).
8. M. Y. Song, D. S. Ahn and H. R. Park, "Capacity Fading of Spinel Phase $LiMn_2O_4$ with Cycling," *J. Power Sources*, **83** 57-60 (1999).
9. D. S. Ahn and M. Y. Song, "Variations of the Electrochemical Properties of $LiMn_2O_4$ with Synthesis Conditions," *J. Electrochem. Soc.*, **147** [3] 874-79 (2000).
10. Y. S. Han, J. T. Son, H. G. Kim and H. T. Jung, "Combustion Synthesis of $LiMn_2O_4$ with Citric Acid and the Effect of Post-heat Treatment(*in Kor.*)," *J. Kor. Ceram. Soc.*, **38** 301-07 (2001).
11. Y. Nishida, K. Nakane and T. Stoh, "Synthesis and Properties of Gallium-doped $LiNiO_2$ as the Cathode Material for Lithium Secondary Batteries," *J. Power Sources*, **68** 561-64 (1997).
12. Y. Xia and M. Yoshio, "An Investigation of Lithium Ion Insertion into Spinel Structure Li-Mn-O Compounds," *J. Electrochem. Soc.*, **143** 825-34 (1996).
13. A. Momchilov, V. Manev and A. Nassalevska, "Rechargeable Lithium Battery with Spinel-related $MnO_2$ II. Optimization of the $LiMn_2O_4$ Synthesis Conditions," *J. Power Sources*, **41** 305-14 (1993).
14. J. M. Tarascon, W. R. McKinnon, F. Coowar, T. N. Bowmer, G. Amatucci and D. Guyomard, "Synthesis Conditions and Oxygen Stoichiometry Effects on Li Insertion into the Spinel $LiMn_2O_4$," *J. Electrochem. Soc.*, **141** 1421-32 (1994).
15. Z. Jiang and K. M. Abraham, "Preparation and Electrochemical Characterization of Micron-sized Spinel $LiMn_2O_4$," *J. Electrochem. Soc.*, **143** 1591-98 (1996).
16. G. Pistoia, D. Zane and Y. Zhang, "Some Aspects of $LiMn_2O_4$ Electrochemistry in the 4 Volt Range," *J. Electrochem. Soc.*, **142** 2551-58 (1995).
17. D. Guyomard and J. M. Tarascon, "Li Metal-free Rechargeable $LiMn_2O_4$/Carbon Cells: Their Understanding and Optimization," *J. Electrochem. Soc.*, **139** 937-48 (1992).
18. V. Manev, A. Momchilov, A. Nassalevka and A. Kozawa, "Rechargeable Lithium Battery with Spinel-related $\lambda$-$MnO_2$ I. Synthesis of $\lambda$-$MnO_2$ for Battery Applications," *J. Power Sources*, **44** 551-59 (1993).