

Preparation and electrochemical properties of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ material for lithium secondary battery

Yun-Sung Lee[†], Sung-Jun Cho and Masaki Yoshio*

Faculty of Applied Chemical Engineering, Center for Functional Nano Fine Chemicals (BK21 Program), Chonnam National University, 300 Yongbong-dong, Gwangju 500-757, Korea

*Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502, Japan

(Received 29 October 2005 • accepted 7 February 2006)

Abstract— $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ materials have been synthesized at 900 °C by using the melt-impregnation method. $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ showed fairly large capacity fading at room temperature; however, $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ exhibited excellent cycling performance for 85 cycles at room temperature. Doped fluorine ions increased the oxygen amount in $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$, which resulted in an increase of the average Mn oxidation state. We found that this indication was the main reason for the cycling performance improvement of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ compound.

Key words: Lithium Secondary Battery, Cathode Material, F-Doped, $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$

INTRODUCTION

Commercial lithium secondary batteries with high energy density and good cycle life have been used as a power source for portable electronic devices. Even though various cathode materials have been used in lithium secondary batteries, it is well known that LiMn_2O_4 spinel is more attractive than other materials, such as LiCoO_2 and LiNiO_2 , because of its low cost, easy preparation, and good environmental characteristics [Thackeray et al., 1983; Li et al., 1994; Xia et al., 1995; Jang et al., 1996].

However, LiMn_2O_4 still has some problems, such as poor long-term cycling performance and abrupt capacity fading at high temperature. Although Tarascon et al. reported that the lithium-rich spinel ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$) showed a fairly good cycleability at room temperature, it also showed poor cycle characterization at high temperature. Therefore, many research groups have been trying to improve the cycleability of the LiMn_2O_4 electrode at room and high temperatures, such as cation substitution for manganese and surface passivation treatment of the LiMn_2O_4 [Tarascon et al., 1995].

Recently, Amatucci et al. reported that the lithium rich oxyfluoride ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4-z}\text{F}_z$) and Al-substituted oxyfluoride spinel ($\text{LiAl}_{0.2}\text{Mn}_{1.8}\text{O}_{4-z}\text{F}_z$) materials showed excellent cycling performances both at room and high temperatures by preventing Mn dissolution into the electrolyte. They suggested that the main reason for the improved cycleability and high discharge capacity of $\text{LiAl}_{0.2}\text{Mn}_{1.8}\text{O}_{4-z}\text{F}_z$ was related to the retention of the small lattice parameters ($<8.21\text{ \AA}$) and reduced average Mn oxidation state by F substitution, respectively. However, they did not present the concrete results of the fluorine effect by $\text{LiAl}_{0.2}\text{Mn}_{1.8}\text{O}_{4-z}\text{F}_z$ material [Amatucci et al., 1997, 2001].

In this paper, we successfully synthesized the $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ material with an excellent cycle performance at room and high temperatures. We first report on the unique effect of doped fluorine ions and the electrochemical characteristics of the $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ material.

EXPERIMENTAL

$\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{LiMn}_2\text{O}_{3.9}\text{F}_{0.1}$ were synthesized by using LiOH , Mn_3O_4 , and LiF by melt-impregnation method. The mixture of starting materials was precalcined at 470 and 530 °C for 5 h in O_2 , respectively, and then post-calcined at 900 °C for 20 h in air. Powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation was employed to identify the crystalline phase of the synthesized material. The contents of Li and Mn in the resulting materials were analyzed with atomic absorption spectroscopy by dissolving the powder in the dilute nitric acid. The content of fluorine was measured by ion chromatography. A small amount of the two compounds was dissolved in 6 N HCl solution and add to 1 ml of H_2O_2 solution in order to accelerate the dissolution of precursor. Oxygen analyzer (RO-416DR, LECO Corporation, USA) was used to measure the oxygen content quantitatively. It could detect the oxygen amount within the CO and CO_2 gas when powder was calcined in the graphite capsule with tin as catalyst at 1600 °C. The electrochemical characterizations were performed with a CR2032 coin-type cell. The cathode was fabricated with 20 mg of accurately weighed active material and 12 mg of conductive binder (8 mg of Teflonized acetylene black (TAB) and 4 mg of graphite). It was pressed on 200 mm^2 stainless steel mesh used as the current collector under a pressure of 300 kg/cm² and dried at 180 °C for 5 h in an oven. The test cell was made of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film (Celgard 3401). The electrolyte used was a mixture of 1 M LiPF_6 -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 2 by vol., Ube Chemicals, Japan). The charge and discharge cycling was performed at a current density of 0.4 mA/cm² with a cut-off voltage of 3.0 to 4.3 V at room and high temperatures.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns (XRD) of the $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ materials which were calcined at 900 °C for 20 h in air. The two materials showed a single crystalline cubic spinel

*To whom correspondence should be addressed.

E-mail: leeys@chonnam.ac.kr

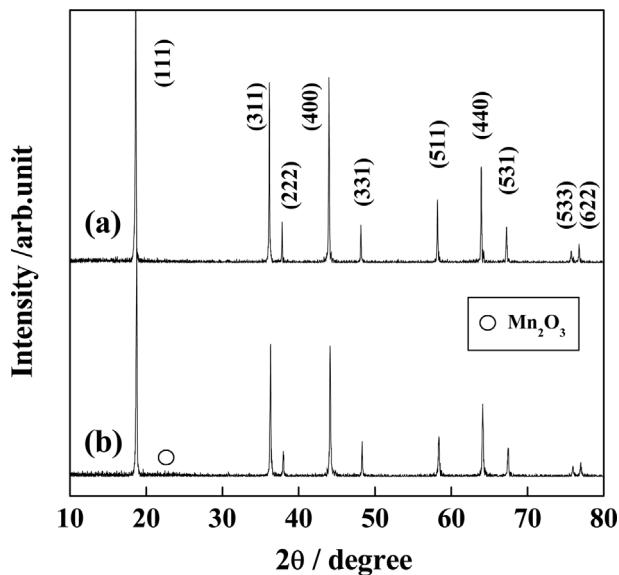
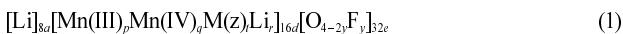


Fig. 1. X-ray diffraction patterns of powders calcined at 900 °C in air. (a) $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, and (b) $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$.

phase, although $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ exhibited a very small amount of impurity peak such as Mn_2O_3 in the XRD pattern. The chemical analysis showed that the ratio of the lithium and manganese in these two materials was 1.1 : 2.

Generally, it has been reported that the lattice constant of the LiMn_2O_4 spinel decreased with an increase in the lithium substitution [Tarascon et al., 1995]. Because the Li^{+} ion is larger than that of Mn^{3+} , the shrinkage in the lattice constant can be attributed to the formation of smaller Mn^{4+} cation due to the electro-neutrality retention as Li^{+} substitutes for Mn^{3+} . This results in the improvement of the cycling performance of the LiMn_2O_4 compound by increasing the Mn oxidation state. On the other hand, Amatucci et al. reported the synthesis of the anion-doped spinel materials, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4-z}\text{F}_z$ and $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_{4-z}\text{F}_z$ ($0 \leq x \leq 0.2$, $0 \leq z \leq 0.5$), which were calcined at 800 °C in air in order to improve their cycling performance at elevated temperature. The substitution of oxygen by fluorine resulted in a systematic increase in the lattice constant and reduced the average Mn oxidation state. This resulted in the increase of capacity of 120 mAh/g along with excellent cycle retention at high temperature (55 °C) [Amatucci et al., 2001]. This change also could be explained in the theoretical calculation. If we assume the metal-substituted oxyfluoride spinel (including lithium rich oxyfluoride), in which the fluorine ion occupies only the 32e site of the spinel structure, then we will indicate it as the following formula:



where p, q, t, and r are the number of molecules in the 8a or 16d site. If the mole ratio of the lithium/total metal ion, $\text{Li}/(\text{Mn}+\text{M(z)})$, equals n and the mole fraction of foreign ions, $\text{M(z)}/(\text{Mn}+\text{M(z)})$, equals f, then the following equations will be obtained.

$$(1+r)/(p+q+r)=n \quad (2)$$

$$t/(p+q+r)=f \quad (3)$$

$$p+q+t+r=2 \quad (4)$$

$$3p+4q+zt+r=7-y \quad (5)$$

when it is rearranged as p, we obtain the next equation.

$$p=y+\{4-5n-3(4-z)\}/(1+n) \quad (6)$$

Using Faraday's law, the theoretical capacity in the 4 V region (due to $\text{Mn}^{(III)} \rightarrow \text{Mn}^{(IV)}$ reaction) of the spinel compounds can be presented as follows:

$$\text{Cap (Ah/g)}=26.8 [y+\{4-5n-3(4-z)\}/(1+n)]/F \quad (7)$$

where F denotes the molecular weight of the spinel. Therefore, as the fluorine content (y) increases, the discharge capacity should increase as expressed by Eq. (7). The result of Amatucci et al. agrees well with the theoretical value.

However, we found that $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ in this study showed a unique behavior in the particle properties and cycle characterizations. Lithium fluoride (LiF) used as the fluorine source in this research forms a double salt, $\text{LiF}\cdot\text{LiOH}$, at 462 °C when it is reacted with lithium hydroxide. Furthermore, LiF was dissolved at 842 °C (melting point) and then impregnated into $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ particles which could form $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ over 842 °C.

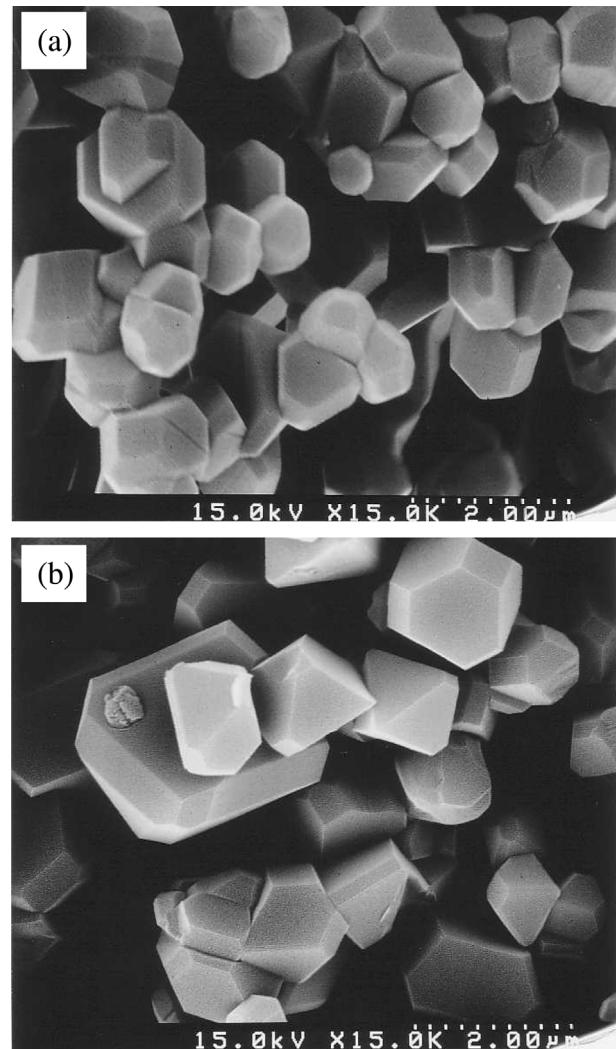


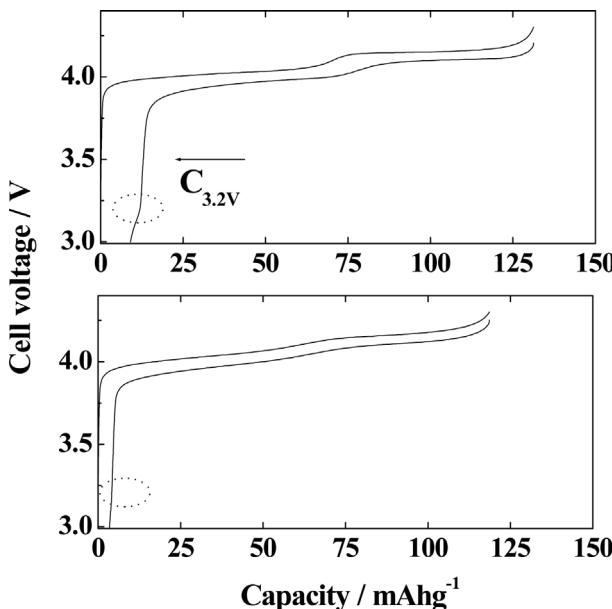
Fig. 2. Scanning electron microscope images of (a) $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, and (b) $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$.

Table 1. Lattice constants and chemical analysis of $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ materials

	Lattice constant (Å)	Fluorine content (wt%)	Oxygen content (wt%)
$\text{Li}_{1.1}\text{Mn}_2\text{O}_4$	8.24	-	36.572
$\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$	8.23	0.8	37.258

Fig. 2 shows scanning electron micrographs (SEM) for the $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ compounds calcined at 900 °C. The particles of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ are slightly larger and more crystallized than those of $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ due to the doped fluorine ions, although the two powders had the same polyhedron shape and showed similar particle sizes of about 1-2 μm . In order to investigate the characteristics of the two compounds, ion chromatography and an oxygen detector measured the contents of fluorine and oxygen, respectively. Table 1 is the lattice constant and chemical analysis of the spinel compounds obtained at 900 °C. The lattice constants of a cubic unit cell calculated by Rietveld refinement using the X-ray data were 8.24 Å and 8.23 Å for $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$, respectively. These values were very similar to those of Amatucci et al. However, the analysis of the fluorine and oxygen contents provided us with an interesting fact. The fluorine content of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ was as much as 10% below the theoretical value; moreover, it showed larger oxygen content than that of $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$. It is worth noting that this is a new observation different from previous reports [Amatucci et al., 2001].

Recently, Xia et al. and Yang et al. reported correlating the capacity fading and structural changes in the $\text{Li}_{1+y}\text{Mn}_2\text{O}_{4-y}$ spinel system [Xia et al., 2001; Wang et al., 2001]. They accurately controlled the composition of the LiMn_2O_4 spinel with accuracy between 700-800 °C for 24 h in flowing air or N_2 . They found that both the charge/discharge profile and structural change during cycling are very closely related to the degree of oxygen deficiency in the synthetic process.

**Fig. 3. The first discharge curves for the Li/1M LiPF₆-EC/DMC/Li_{1.1}Mn₂O₄ (a), and Li_{1.1}Mn₂O_{3.9}F_{0.1} (b) at room temperature.**

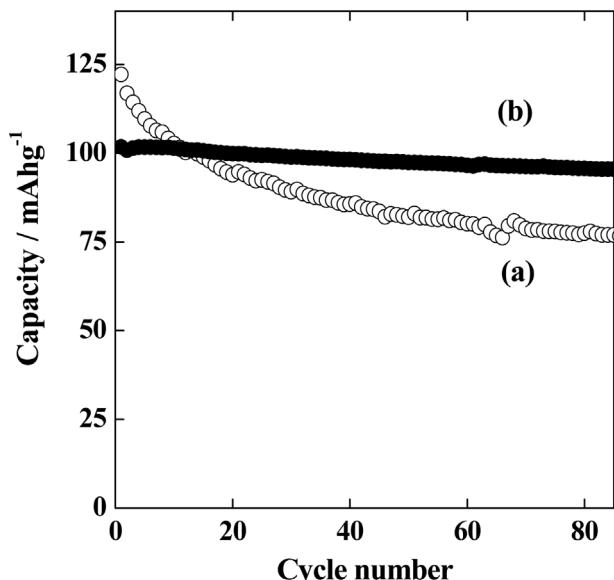
They also suggested that a higher degree of oxygen deficiency is accompanied by a faster capacity fading during cycling. Therefore, we assumed that the lithium doped spinel ($\text{Li}_{1.1}\text{Mn}_2\text{O}_4$) in this study, which was calcined at high temperature (900 °C), should exhibit a large $\text{C}_{3.2V}$ region in the 4 V region [Wang et al., 2001; Lee et al., 2002].

Fig. 3 shows the first charge/discharge curves for Li/1M LiPF₆-EC/DMC/Li_{1.1}Mn₂O₄ and Li_{1.1}Mn₂O_{3.9}F_{0.1} calcined at 900 °C for 20 h in air. Even though two distinct plateaus in the 4.0-4.15 V region disappeared due to the excess lithium content, the charge/discharge curve clearly shows that the $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ material might be an oxygen deficient spinel and easily shows the abrupt capacity fading in the 4 V region. On the other hand, the cycle curve of Li_{1.1}Mn₂O_{3.9}F_{0.1} exhibited a reduced initial discharge capacity as well as no $\text{C}_{3.2V}$ region, which were the opposite results compared to that of Amatucci et al. [2001].

Fig. 4 shows the specific discharge capacity vs. cycle number for the Li/1M LiPF₆-EC/DMC/Li_{1.1}Mn₂O₄ and Li_{1.1}Mn₂O_{3.9}F_{0.1} containing cells which were calcined at 900 °C in air. The charge/discharge current density was 0.4 mA/cm² with a cut-off voltage of 3.0 to 4.3 V at high temperature. As we expected, the Li_{1.1}Mn₂O₄ compound continuously showed a severe capacity loss and the retention rate after 85 cycles was 63% at high temperature. However, Li_{1.1}Mn₂O_{3.9}F_{0.1} showed a very stable cycling behavior and the cycling retention rate after 85 cycles was 94% as shown in Fig. 4. This means that the fluorine ions played an important role in synthesizing the Li_{1.1}Mn₂O_{3.9}F_{0.1} compound.

This unique indication produces the following two possibilities: 1) Only a small portion of the fluorine ion was substituted and the remainder was just an impurity. 2) Even though all the fluorine ions were available for substitution, it has a limited replacement and took part in other reactions.

For case (1), we could not explain the lack of fluorine in the Li_{1.1}Mn₂O_{3.9}F_{0.1} compound because the Li_{1.1}Mn₂O_{3.9}F_{0.1} compound in

**Fig. 4. The plot of specific discharge vs. number of cycles for the Li/1M LiPF₆-EC/DMC/Li_{1.1}Mn₂O₄ and Li_{1.1}Mn₂O_{3.9}F_{0.1} electrodes at high temperature (50 °C).**

this study was not washed or otherwise treated to remove any unreacted compound. However, if we assume that fluorine ions, which were not replaced at the 32e site, worked as another role (in case (2)), we can explain the typical characterization of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{4-y}\text{F}_y$ material as follows: Lithium doped spinel ($\text{Li}_{1.1}\text{Mn}_2\text{O}_4$) in this research exhibited a large C_{32V} region as shown in Fig. 3. As previous report [Lee et al., 2002], we already suggested that LiMn_2O_4 with high degree of oxygen deficiency exhibited a large C_{32V} value, therefore, this value could be an indicator for the oxygen deficiency degree in the LiMn_2O_4 spinel powder. However, the $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ obtained under the same synthetic conditions showed no C_{32V} region in the 4 V region. This means that $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ has no oxygen deficiency in the spinel structure by increasing of the oxygen content as shown in Table 1. Therefore, we suggest that the doped fluorine ions played a role in increasing the oxygen content of $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ by evaporation at high temperature (900 °C) and this resulted in increasing the average Mn oxidation state of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ material. Although the chemical reaction mechanism of $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ by fluorine ions during calcination process does not clear at present, it has a high possibility that the fluorine ions, which was started to dissolve LiF material at 850 °C, might play a role as catalyst to increase oxygen contents.

From the results, we concluded that the amount of doped fluorine in this study had a limitation for substitution in the spinel structure and the excess fluorine ions took part in increasing the oxygen content by evaporating at high temperature. This was the main reason for the unique cycling characterization of the $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ spinel material.

CONCLUSIONS

$\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ materials have been synthesized at 900 °C by using the melt-impregnation method. Although $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ showed severe capacity fading at high temperature, the fluorine-doped spinel ($\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$) compound exhibited excellent cycling performance at both room and high temperatures. We found that the doped fluorine ions increased the oxygen amount in $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ and decreased the C_{32V} region in the charge/discharge curve. This indication increased the average oxidation state of Mn and improved the cycling performance of the $\text{Li}_{1.1}\text{Mn}_2\text{O}_{3.9}\text{F}_{0.1}$ compound.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support by the Chonnam National University.

REFERENCES

- Amatucci, G. and Tarascon, J., *U.S. Patent*, **5**, 674645 (1997).
- Amatucci, G., Pereira, N., Zheng, T. and Tarascon, J., "Failure mechanism and improvement of the elevated temperature cycling of LiMn_2O_4 compounds through the use of the $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_{4-x}\text{F}_x$ solid solution," *J. Electrochem. Soc.*, **148**, A171 (2001).
- Jang, D. H., Shin, Y. J. and Oh, S. M., "Dissolution of spinel oxides and capacity losses in 4 V $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells," *J. Electrochem. Soc.*, **143**, 2204 (1996).
- Lee, Y. S., Hidemitsu, Y., Sun, Y. K. and Yoshio, M., "The effects of lithium and oxygen contents inducing capacity loss of the LiMn_2O_4 obtained at high synthetic temperature," *J. Electroceramics*, **9**, 209 (2002).
- Li, W., McKinnon, W. and Dahn, J., "Lithium intercalation from aqueous solutions," *J. Electrochem. Soc.*, **141**, 2310 (1994).
- Tarascon, J. and Guyomard, D., "High voltage stable liquid electrolytes for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon rocking-chair lithium batteries," *J. Power Sources*, **54**, 92 (1995).
- Tarascon, J. and Martinsville, A., *U.S. Patent*, **5**, 425932 (1995).
- Thackeray, M., David, P., Bruce, P. and Goodenough, J., "Lithium insertion into manganese spinels," *Mat. Res. Bull.*, **18**, 461 (1983).
- Wang, X., Yagi, M., Lee, Y. S., Yoshio, M., Xia, Y. and Sakai, T., "Storage and cycling performance of stoichiometric spinel at elevated temperature," *J. Power Sources*, **97-98**, 427 (2001).
- Xia, Y., Sakai, T., Fujieda, T., Yang, X. Q., Sun, X., Ma, Z. F., McBreen, J. and Yoshio, M., "Correlating capacity fading and structural changes in $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_{4-\delta}$ spinel cathode materials: A systematic study on the effects of Li/Mn ratio and oxygen deficiency," *J. Electrochem. Soc.*, **148**, A723 (2001).
- Xia, Y., Takeshige, H., Noguchi, H. and Yoshio, M., "Studies on an $\text{Li}-\text{Mn}-\text{O}$ spinel system (obtained by melt-impregnation) as a cathode for 4 V lithium batteries part 1. Synthesis and electrochemical behaviour of $\text{Li}_x\text{Mn}_2\text{O}_4$," *J. Power Sources*, **56**, 61 (1995).