JOURNALOF

Ceramic Processing Research

# Investigation of Structural Change and Electrochemical Reaction of Spinel-LiMn<sub>2</sub>O<sub>4</sub> by Neutron Diffraction

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The structural change during electrochemical cycling in full-cell system has been investigated by neutron diffraction method and the full-cell consists of spinel-lithium manganese oxide cathode and graphite anode. The structural variation has been monitored by *in-situ* neutron diffraction technique at different state of charges (SOCs), and the obtained data were compared with *ex-situ* powder neutron diffraction patterns. Phase transitions for lithiated/delithiated graphite can clearly explain that the intercalated lithium ions in graphite are not perfectly extracted during a delithiaion process. The content of  $LiC_{12}$  phase increases as an increase in electrochemical cycle numbers, and the lattice parameter of  $LiMn_2O_4$  also decreases due to the reduction of the amounts of Li ions, which can be reversibly intercalated/deintercalated into/from the structure.

Key words: Neutron diffraction, In-situ, LiMn<sub>2</sub>O<sub>4</sub>, Structural change

#### Introduction

Li-ion batteries (LIBs) have been rapidly developed since they were commercialized by Sony electronics in 1991 [1]. Currently, LIBs have been considered as the best energy storage system for small and portable electric devices due to their high power energy density [1]. Since lithium cobalt oxide (LiCoO<sub>2</sub>) with layeredstructure was employed in a commercialized battery, various studies have been performed to overcome the problems arising from its toxicity and cost of the materials [2-4]. In comparison with LiCoO<sub>2</sub>, lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>) with spinel structure is more useful cathode material for lithium battery system due to the fast lithium diffusion kinetics, non-toxicity, low cost, and low oxygen evolution [4-6]. Hence, LiMn<sub>2</sub>O<sub>4</sub> has attracted a considerable attention as one of the most useful candidates of positive electrode in LIBs. Graphite is a most popular anode material due to its structural stability during lithium intercalation/ deintercalation reactions [7]. The lithium ions extracted from the cathode are intercalated into the graphite anode as a form of lithiated graphite compounds (Li<sub>n</sub>C<sub>6</sub>,  $0 \le n \le 1$ ) [8] during a charging process. Recent investigations with a full-cell system have explained the behaviors of the cathode and anode and the relationship between the structural information and electrochemical properties of the system [9-13]. It is important to understand full-cell operation mechanism because the electrode materials should be developed based on the understanding the electrochemical behaviors and failure mechanism of both cathode and anode for a high performance Li-ion battery with long cycle life.

In this study, in-situ neutron diffraction (ND) method was employed to figure out the relationship between the structural change and electrochemical properties of the full-cell system. The full-cell investigated in this study consists of spinel-LiMn<sub>2</sub>O<sub>4</sub> cathode and graphite anode. Only a few works have explained the causes of the deterioration in a LiMn<sub>2</sub>O<sub>4</sub>/gratphie full-cell system [14, 15], even if many studies of LiMn<sub>2</sub>O<sub>4</sub> or graphite have been. H. Berg et. al. [16] studied the partially delithiated LiMn<sub>2</sub>O<sub>4</sub> to explain structural phenomena over 4 V region. J. M. Tarascon [17] reported the structural change before and after electrochemical cycling. However, most of studies were focused on the half-cell system. For more unambiguous understanding of LiMn<sub>2</sub>O<sub>4</sub>/graphite full-cell system, intensive researches should be requested. The insitu neutron diffraction technique is a powerful tool to get more detailed information of structural change of active materials even during electrochemical cycling without cell disassembly [18, 19]. Neutron diffraction analysis is more sensitive than x-ray diffraction because it is based on the neutron interacting with the nucleus of atoms [18, 19]. Moreover, it has higher sensitivity to the light atoms such as Li and O and ability to distinguish isotopes [20, 21] in comparison with x-ray diffraction. In this study, aluminum pouch typed full-cell with Li(Li<sub>0.08</sub>Al<sub>0.08</sub>Mn<sub>1.84</sub>)O<sub>3.99</sub>/graphite was investigated to obtain the structural information at different state of charges (SOCs). In addition, in-situ ND

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patterns were collected after electrochemical cycling of 18650-type commercial LiMn<sub>2</sub>O<sub>4</sub>/graphite full-cell.

### **Experimental**

The aluminum pouch typed full-cells were employed in the measurement of neutron diffraction. The pouch cell consists of commercial LiMn<sub>2</sub>O<sub>4</sub> (provided by Nikki) as the cathode material, artificial graphite (provided by Samsung SDI) as the anode material, poly(vinylidene fluoride) as the binder, and polypropylene (PP) (Celgard membrane) as the separator. The electrolyte is 1.0 M LiPF<sub>6</sub> in mixture of ethylene carbonate, ethylmethyl carbonate, and dimethyl carbonate with additives, lithium tetrafluoroborate (LiBF<sub>4</sub>, 0.50%), fluoroethylene carbonate (FEC, 5.0%), vinylene carbonate (VC, 1.0%). The aluminum and copper foils were used as cathode and anode current collector, respectively. The electrodes and separator were spirally wounded, and then sealed in aluminum pouch with the electrolyte solution. The cell capacity of the LiMn<sub>2</sub>O<sub>4</sub>/graphite full cell was set to 1530 mAh and the capacity ratio of anode to cathode was 1.06. The formation cycles of the fresh cells were done in the range of 2.75 V to 4.20 V at 0.10 C (constant-current mode) and constant-voltage mode until reaching a cut-off current of C/50.

For neutron diffraction measurements, a highresolution powder diffractometer (HRPD) with a Ge(331) single crystal monochromator ( $\lambda = 1.8367$  Å) was used at HANARO in KAERI (Korea Atomic Energy Research Institute). The neutron diffraction data were collected in the range of 0-160 degree. To obtain the neutron diffraction data, the prepared cell was mounted in the *in-situ* neutron diffraction device connected to the WBCS 3000 cycler (Won-A Tech, Korea). The cell was charged with various SOC in the range of 2.75 V to 4.20 V at 1.0 C in constant current mode, and then while neutron diffraction data were collected. The commercial 18650-type cylindrical LiMn<sub>2</sub>O<sub>4</sub>/graphite cells (Zhejiang Xinghai Energy Technique Co, Ltd.) were also investigated with various SOC after electrochemical cycling (10, 300 and 600 cycles) of the cell. The electrochemical cycle tests of the cells were performed at 1.0 C in the constant current mode from 2.90 to 4.20 V using the WBCS 3000 cycler (Won-A Tech, Korea). The obtained data were analyzed by Gaussian peak-fitting method and refined by Rietveld refinement method using the FullProf program (version 2001) with a pseudo-Voigt function.

## **Results and Discussion**

# $\label{eq:linear} Li[Li_{0.08}Mn_{1.84}Al_{0.08}]O_{3.99}/graphite \ pouch \ cell \ after formation \ cycle$

Figure 1(a) shows a series of *in-situ* neutron diffraction data for the aluminum pouch cell as a

Intensity (Arbitrary Units) 4.4 45 46 47 2 θ (degree) 0% 500 (c) 33% SOC 66% SOC 100% 500 Intensity (Arbitrary Units 27 28 29 30 31 32 33 2θ(degree) Fig. 1. (a) In-situ neutron diffraction data of LiMn<sub>2</sub>O<sub>4</sub>/graphite

**Fig. 1.** (a) *In-situ* neutron diffraction data of LiMn<sub>2</sub>O<sub>4</sub>/graphite battery (jelly-roll type Al pouch cell) at SOC 0, 33, 66 and 100%, (b) magnified neutron diffraction data for LiMn<sub>2</sub>O<sub>4</sub> cathode in the range of 43-48 °, and (c) magnified neutron diffraction data for graphite anode in the range of 27-34 ° from Figure 1(a).

function of SOC after the formation cycle. All the peaks are attributed to the components of entire battery such as cathode, anode, current collectors (Cu and Al), binder, electrolyte, carbon black, Al pouch, etc. A significant amount of hydrocarbons from electrolyte, separator, etc. influences the background of neutron diffraction data [22, 23]. The variations of lattice parameter of the cathode (45-47 ° and 94-98 °) and phase transition of the anode (28-33 ° and 95-97 °) are clearly

Intensity (Arbitrary units)

% of SOC

LiMn<sub>2</sub>O

Carbor LiC<sub>12</sub>

LiC,

Cu Al

(b)

180

160

II I II

120

140

1.1

100

2 0 (degree)

ຂ່າ

1

60

40

0% S O C

33% S O C

66% 500

100% 500

20

observed as shown in Figure 1(a). Each phase was investigated by Rietveld refinement using crystallographic information files (CIF) of the major phases such as spinel-LiMn<sub>2</sub>O<sub>4</sub>, graphite, lithiated graphite phases (LiC<sub>12</sub> and LiC<sub>6</sub>), Cu and Al. Figures 1(b) and (c) show the phase transition of LiMn<sub>2</sub>O<sub>4</sub> and graphite as a function of SOC, respectively. During a charging process, lithium ions are extracted from tetrahedral 8a site of LiMn<sub>2</sub>O<sub>4</sub> cathode, and average valence of Mn ions increases. The extraction of lithium ions from LiMn<sub>2</sub>O<sub>4</sub> causes the change in lattice parameter of LiMn<sub>2</sub>O<sub>4</sub> since the concentrations of  $Li^+$  and  $Mn^{3+}$  ions (ionic radius = 0.65 Å [24]) in LiMn<sub>2</sub>O<sub>4</sub> are reduced while the concentration of  $Mn^{4+}$  (ionic radius = 0.53 Å [24]) ion increases. Hence, as shown in Figure 1 (b), all the peaks for LiMn<sub>2</sub>O<sub>4</sub> phase are shifted to higher angle direction as a function of SOC due to the decrease in the lattice parameter. The continuous peak shift indicated that the spinel-LiMn<sub>2</sub>O<sub>4</sub> structure experiences single phase transition during charging/discharging process without any significant structural changes and it is a good agreement with the previous publication [25].

On the other hand, the graphite anode experiences definite phase transition attributed to lithium intercalation. The lithium ions are intercalated into graphene layers of graphite during a charging process and, as a result, lithium-graphite intercalation compounds (Li-GICs) is formed  $(nLi^+ + ne^- + C_6 \leftrightarrow Li_nC_6)$  [26]. The *in-situ* neutron diffraction data of graphite anode unambiguously show the coexistence of several lithiated graphite phases. Figure 1 (c) shows the main scattering feature of graphite assigned to (002) reflection. The several graphite phases are observed at 29.2, 30.6, and 32.1°, which are assigned to LiC<sub>6</sub>, LiC<sub>12</sub>, and graphite, respectively. This peak shifts toward lower scattering angle as an increase in SOC due to the increase in volume of the lithiated graphite phases during the intercalation of lithium ions between the layers of carbon atoms [27]. The phase transition of graphite anode was measured simultaneously with cathode peaks as SOCs during charge, it is possible to understand a mechanism for the electrochemical behavior of an entire cell as lithium reactions between the cathode and anode at the same time. Compared to the graphite anode, the peak intensities of spinel-LiMn<sub>2</sub>O<sub>4</sub> cathode are almost constant during a charging process as shown in Figure 1 (b). It demonstrates the monotonous reaction of cubic spinel structure maintained over the entire composition range (Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub>, 0 < x < 1). However, its lattice parameter and lithium contents in 8a site in spinel are varied as a function of SOC. Based on our results of ex-situ ND analysis of the spinel-LiMn<sub>2</sub>O<sub>4</sub>, the amount of lithium ions in Li1-xMn2O4 varies from 0.35 to 0.96. At fully charged state (100% of SOC) at 4.20 V, all of the lithium ions are not extracted from the structure (Li<sub>0.35</sub>Mn<sub>2</sub>O<sub>4</sub>), which is corresponding to the electrochemically delithiated phase  $\lambda$ -MnO<sub>2</sub> (Li<sub>0.28</sub>Mn<sub>2</sub>O<sub>4</sub>) in the previous report [28]. At 0% of SOC, trace amount of lithium intercalated phase (LiC12) coexisted with delithiated graphite is observed. It means that some of lithium ions do not participate in the reversible electrochemical reaction during a charging/discharging process. The slight reduction of lattice parameter (8.2021 Å) of LiMn<sub>2</sub>O<sub>4</sub> in aluminum pouch cell after the formation cycle, in comparison with that of asprepared LiMn<sub>2</sub>O<sub>4</sub> (8.2066 Å), is another evidence that all of lithium ions are not intercalated into the cathode during a discharging process. N. Sharma et. al [20] proposed that the partial charge and capacity loss can be attributed to the influence of solid-electrolyteinterface (SEI) film formed on the surface of graphite anode after the first cycle. In the long-term cycling tests with the full-cells described in the next section, we did not observe any change of LiC<sub>12</sub> phase in discharge state as shown in Figure 3 (b). It indicates that the coexistence of the  $LiC_{12}$  phase at SOC 0% is mostly influenced from the SEI formation at the first charging process instead of any degradation of graphite anode as cycling. As an increase in cell voltage, the phase transition of graphite anode is revealed by lithiated graphite phases (Li<sub>x</sub>C<sub>6</sub>, 0 < x < 1) in the neutron diffraction data, and the lithium ions should be intercalated into the graphite until most graphite becomes LiC<sub>6</sub> phases which is fully-lithiated graphite phase.

## LiMn<sub>2</sub>O<sub>4</sub>/graphite commercial cell after several cycles

Figure 2 shows electrochemical long-term cycling performance of commercial cylindrical  $\text{LiMn}_2\text{O}_4$ / graphite cell (18650-type) at 1.0 C-rate. It is known that gradual capacity fading is attributed to Mn dissolution and consumption of electrolyte after long cycles [29]. For analysis of this capacity fading mechanism, *in-situ* neutron diffraction data are collected at 2.90 V (0 % of SOC) and 4.20 V (100% of SOC) during each 11th, 301st, and 601st charging. The *in-situ* neutron diffraction data in the discharge state (0 % of SOC) at 2.90 V are plotted in Figure 3(a). The neutron diffraction



Fig. 2. The electrochemical charge-discharge cycling performances of the commercial  $LiMn_2O_4$ /graphite batteries at 1 C-rate.



**Fig. 3.** (a) *In-situ* neutron diffraction data of the commercial LiMn<sub>2</sub>O<sub>4</sub>/graphite batteries at 0% of SOC (2.9 V) after 10, 300 and 600 cycles, (b) magnified neutron diffraction data in the range of 27-32 °, (c) magnified neutron diffraction data for graphite anode in the range of 94- 97 ° from Figure 3(a), (d) relative neutron diffraction intensity of graphite and LiMn<sub>2</sub>O<sub>4</sub> phases.



**Fig. 4.** (a) *In-situ* neutron diffraction data of the commercial  $\text{LiMn}_2\text{O}_4$ /graphite batteries at 100% of SOC (4.2 V) after 10, 300 and 600 cycles, (b) magnified neutron diffraction data in the range of 27-32 °, (c) magnified neutron diffraction data for graphite anode in the range of 94-100 ° from Figure 3(a), (d) relative neutron diffraction intensity of LiC<sub>6</sub> and LiC<sub>12</sub> phases.

data includes Cu and Al peaks for current collectors and large intensity Fe peaks ( $2\theta = 53.8$ , 79.5, 103.1, and 129.5°), and their intensities are not changed during electrochemical charge/discharge cycles. It is difficult to

refine the *in-situ* neutron diffraction patterns due to the significantly low signal-to-noise ratio of the carbon diffraction peaks overlapped with the Fe peak. Hence, the variation of the selected peaks is investigated by

Gaussian peak-fit. Figures 3(b) and (c) show the detailed data of the selected area for active materials, lithiated/delithiated graphite and LiMn<sub>2</sub>O<sub>4</sub>. Figure 3(b) shows the main scattering feature of graphite assigned to (002) reflection and the peak is well maintained without any change in peak intensity and shape even after 600 cycles. It indicates that graphite anode itself is entirely stable during long-term cycling. The variation of LiMn<sub>2</sub>O<sub>4</sub> is shown in Figures 3(c). The feature of LiMn<sub>2</sub>O<sub>4</sub>, assigned to (622) reflection located at  $\sim$  95.8 °, is slightly shifted to higher scattering angle direction and the reduction of its intensity is observed as an increase in the number of cycle. It is demonstrated that the amount of lithium ions participated in a reversible electrochemical reaction is reduced. Moreover, the severe degradation of (622) reflection feature indicates that the crystallinity of spinel-LiMn<sub>2</sub>O<sub>4</sub> structure becomes poor as the number of cycle increases. The relative peak intensity based on (622) reflection of LiMn<sub>2</sub>O<sub>4</sub> and (002) reflection of graphite is plotted in Figure 3 (d). It clearly shows the degradation of LiMn<sub>2</sub>O<sub>4</sub> phase due to Mn dissolution and it causes capacity loss of the cell as the number of electrochemical cycle increases.

The full-range data of the neutron diffraction measured at 4.20 V (100% of SOC) are shown in Figure 4(a). In the charge state, the decrease in the amounts of lithium ions is observed by the peak variation of the lithiated graphite phases (LiC<sub>6</sub> and  $LiC_{12}$ ). As shown in Figures 4(b) and (d), the portion of LiC<sub>12</sub> phase formed during lithiation of graphite increases while the fully lithiated graphite phase (LiC<sub>6</sub>) decreases as an increase in the number of electrochemical cycle. The peak located at 95.1 ° in 4.20 V data indicates LiC<sub>6</sub> assigned to (003) reflection, and a variation of the LiC<sub>6</sub> and LiC<sub>12</sub> (located at 95.9 °) shown in Figure 4(c) is also corresponding to the changes of lithiated graphite phase as a function of electrochemical cycling. After 600 cycles, graphite is mostly transformed into LiC<sub>12</sub>. This indicates that the stage-2 reaction  $(2LiC_{18} + Li$  $3 \leftrightarrow \text{LiC}_{12}$ ) is predominated due to the reduced amounts of lithium ions [26, 30]. For the spinel-LiMn<sub>2</sub>O<sub>4</sub> cathode, the change in the scattering feature is clearly observed at  $\sim 98.3^{\circ}$ . This suggests that the decrease of the (622) peak intensity is attributed to the structural degradation by the deficiency of constituents such as Mn dissolution into the electrolyte [31] and the volume changes [32] as lihitation/delithiation reactions proceeded. The relative peak intensity based on LiC12 and LiC<sub>6</sub> for (002) reflection of graphite is plotted in Figure 4 (d). It clearly shows the amount of Li ions participated in the reversible reaction is reduced because the amount of graphite is not changed as shown in Figure 3(b) and the amount of LiC<sub>6</sub> phase is significantly reduced. To identify the elemental degradation of spinel-LiMn<sub>2</sub>O<sub>4</sub>, the simulated patterns involving elemental deficiencies of Mn and O (Figure 5(a) and (b)) are performed. All the patterns are normalized with Fe peak at 103.1 degree,



Fig. 5. The simulated neutron diffraction patterns as a function of element deficiency of (a) Mn and (b) O in spinel-LiMn<sub>2</sub>O<sub>4</sub> calculated by Fullprof program.

and the changes of the (622) peak showing clear peak degradation at 2.90 and 4.20 V is investigated. The intensity of (622) scattering feature is varied with the amount of Mn (LiMn<sub>y</sub>O<sub>4</sub>, y = 1.5-2) and O (LiMn<sub>2</sub>O<sub>z</sub>, z = 3.5, 3.7, and 4) in the unit cell. As an increase in the deficiencies of Mn and O, the intensity of scattering feature for (622) plane decreases. The peak degradation indicates that the spinel-LiMn<sub>2</sub>O<sub>4</sub> is suffered from structural distortion demonstrating the loss of crystallinity [33].

### Conclusions

In this study, aluminum pouch cells fabricated in a lab and 18650-type commercial cylindrical cells were investigated with *in-situ* neutron diffraction to analyze the relationship between structural change and electrochemical behavior of the cathode and anode and capacity fading as cycling. Spinel-lithium manganese oxide cathode and graphite anode is used for the full-cells. In the *in-situ* measurement, the distinctly changed patterns were measured from phase transition showing stoichiometric lithiated graphite phases ( $\text{LiC}_{12}$  and  $\text{LiC}_6$ ) while no phase changes were found in the spinel-LiMn<sub>2</sub>O<sub>4</sub> cathode material. At 0% of SOC, trace amount of lithiated graphite phase  $(LiC_{12})$  was observed, and it indicates that the graphite anode is not in the fullydelithated state after discharging due to the SEI formation instead of any degradation of graphite. Based on the data measured from the long-term cycled commercial cells, the graphite anode remained its original structure during repeated lihitation/delithiation reactions. On the other hand, the cathode has the lack of structural stability due to the loss of the Mn and O in the spinel structure, which accelerates the capacity fading of full-cell system in LIBs.

# Acknowledgments

This work was supported by Nuclear Research & Development Program through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST)(2010-0018564) The author would like to acknowledge the help from L. Liang (*Sang-A Frontech*).

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