Comparative studies between oxygen-deficient LiMn$_2$O$_4$ and Al-doped LiMn$_2$O$_4$

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Abstract

Lithium-rich and Al-doped spinel materials with good capacity retention when cycled at high temperature have been synthesized. These materials have been studied in comparison with oxygen-deficient spinel using X-ray diffraction at room temperature (RT, 25 °C) and low temperature (LT, −30 °C). The XRD spectra at LT and RT showed that Al-doped spinel materials have superior structural stability against oxygen loss during heat treatment at 660 °C under Ar atmosphere. The in situ XRD spectra collected during cycling at high temperature (HT, 55 °C) showed that Al-doped spinel materials had better cycle performances and it was closely related to the structural stability against oxygen loss during charge–discharge cycling.
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Keywords: LiMn$_2$O$_4$; Capacity fading; Al-substitution; Phase transition; In situ X-ray diffraction

1. Introduction

Recently, using lithium ion batteries as power source for electric vehicles (EV) or hybrid electric vehicles (HEV) has been discussed and studied widely both in academic and in industrial communities. One of the major barriers of this application is the high cost of lithium ion batteries. The low cost and environmental friendly nature makes the LiMn$_2$O$_4$ spinel type materials a good candidate to replace the LiCoO$_2$ type materials which is widely used in small batteries. Three types of phase diagrams have been proposed for LiMn$_2$O$_4$ type spinel materials charging through the 4.0 and 4.2 V plateaus. According to Ohzuku [1], the stoichiometric spinel has two cubic phases and one two-phase coexistence region in this voltage range (two-phase model). Xia and Yoshio [2] had demonstrated that by making the sample lithium rich, the two-phase coexistence regions are suppressed and the struc-

ture change takes place in a continuous fashion (pseudo-one-phase model). Derived from the synchrotron based in situ X-ray diffraction studies, Yang et al. [3] reported a new two-phase coexistence region and proposed a three-phase model (cubic I, II, and III) in this voltage range for lithium-rich spinel materials. Xia et al. [4] also published their work about the effects of oxygen deficiency in LiMn$_2$O$_4$ type spinel materials. In that paper, by altering the lithium and oxygen contents, the results for the one-phase, two-phase, and three-phase models were all reproduced. Recently, Yoshio et al. [5] reported that the oxygen stoichiometry is the most important factor controlling the capacity retention during cycling, especially at high temperature. The capacity fading at high temperature is the main obstacle preventing the LiMn$_2$O$_4$ type materials from mass commercial use as a cathode material in lithium ion batteries [6–9]. Therefore, investigating the relationship between the structural changes and the capacity retention during cycling for spinel materials is very important. In this paper, as a part of a series of on going studies, we report our findings on the relationship between the structural

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changes and the capacity retention by comparing the structural stabilities between oxygen content varied $LiMn_2O_4$ and Al-doped $LiMn_2O_4$.

2. Experimental

The lithium-rich spinel materials and Al-doped spinel materials were prepared by Saga University and TOSOH Corporation. The details of sample preparation have been described elsewhere [10,11]. The oxygen-deficient spinel materials were prepared through heat treatment of commercial available compound $Li_{1.07}Mn_{1.93}O_4$ as a starting material [12]. The samples were annealed at 660 °C under Ar atmosphere with various time durations in order to obtain different concentrations of oxygen vacancies. The samples are labeled according to the starting material and annealing time, i.e. Fxh for commercial spinel sample, TLixh for TOSOH Li-rich sample, and TAlxh for TOSOH Al-doped sample, annealed for x hours. Cathodes were prepared by slurring the active material powder with 10% poly-vinylidene fluoride (PVDF, KynarFlex 2801, Atochem), and 10% acetylene black (w/w) in an n-methyl pyrrolidone (NMP) solvent, then coating the mixture onto Al foil. The cathodes were incorporated into cells with a Li foil negative electrode, a Celgard separator and a 1 M $LiPF_6$ electrolyte in a 1:1 ethyl carbonate (EC): dimethyl carbonate (DMC) solvent (LP 30 from EM Industries Inc.). For in situ XRD spectra collected on beam line and X18A at National Synchrotron Light Source (NSLS), a radiation wavelength of $\lambda = 1.195$ Å was chosen, while a wavelength of $\lambda = 0.7048$ Å was used for additional spectra collected on X7A, where a position sensitive detector (PSD) was used. All the XRD spectra collected are recalculated and presented with $\lambda = 1.54$ Å, which is the wavelength of conventional lab XRD with Cu Kα radiation, for easy comparison with other data.

3. Results and discussion

In the previous report [12], the XRD spectra of various oxygen-content spinel materials at low temperature (LT, -30 °C) were reported. The XRD peaks originating from the low-temperature phase were observed, and it became more pronounced as the population of oxygen vacancies increased. From these results it could be summarized that the longer the heat treatments time at 660 °C under Ar atmosphere, the higher the concentration of the oxygen vacancies. This high concentration of oxygen vacancies is one of the major sources for the deterioration of the structural stability of spinel materials. Therefore, we can say that the oxygen deficiency is one of the key factors that may contribute to the structural instability and in turn capacity fading.

To improve the structural stability of the spinel materials, various attempts have been made and among those are Al-doping and Li enrichment. Saga University and TOSOH
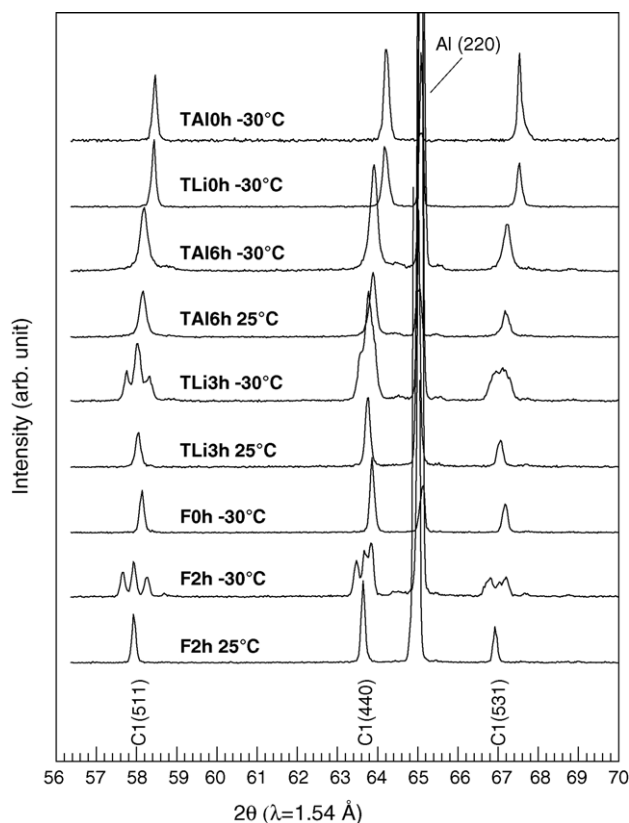

Fig. 1. XRD patterns of stoichiometric, oxygen-deficient, lithium-excess, and Al-doped spinel materials at room temperature (25 °C) and low temperature (-30 °C).

Corporation have successfully prepared Li-rich spinel $Li_{1.11}Mn_{1.89}O_4$ and Al-doped spinel, $Li_{1.07}Al_{0.15}Mn_{1.78}O_4$ with significantly improved cycling characteristics. The XRD spectra for commercial spinel, Li-rich spinel, and Al-doped spinel samples annealed for different time durations at 660 °C under Ar atmosphere are plotted in Fig. 1. Since the cubic structure of the spinel materials is the well-known space group *Fd3m*, only three Bragg peaks (5 1 1), (4 4 0), and (5 3 1) were recorded for each 2θ scan. F2h sample shows typical cubic *Fd3m* phases at room temperature (RT, 25 °C). Peaks representing low-temperature phase flanking the original cubic structure peaks were observed at low temperature. This low temperature structure formation is believed to be a result of oxygen vacancies created in the spinel structure during annealing under Ar atmosphere [12]. This was further confirmed by the spectrum collected on F0h sample. This spectrum does not show any peaks representing low-temperature phase at low temperature. Because F0h had not undergone the annealing under Ar atmosphere, no additional oxygen vacancies had been introduced into the structure. Therefore, no low-temperature structure was observed. TLi3h samples show similar behavior with F2h samples. It shows typical *Fd3m* phase peaks at RT but low-temperature phase peaks flank the original peaks at LT. Again, when no annealing was done on the Li rich sample, i.e. TLi0h, it did not show any low-temperature phase peaks at LT. Li enrichment
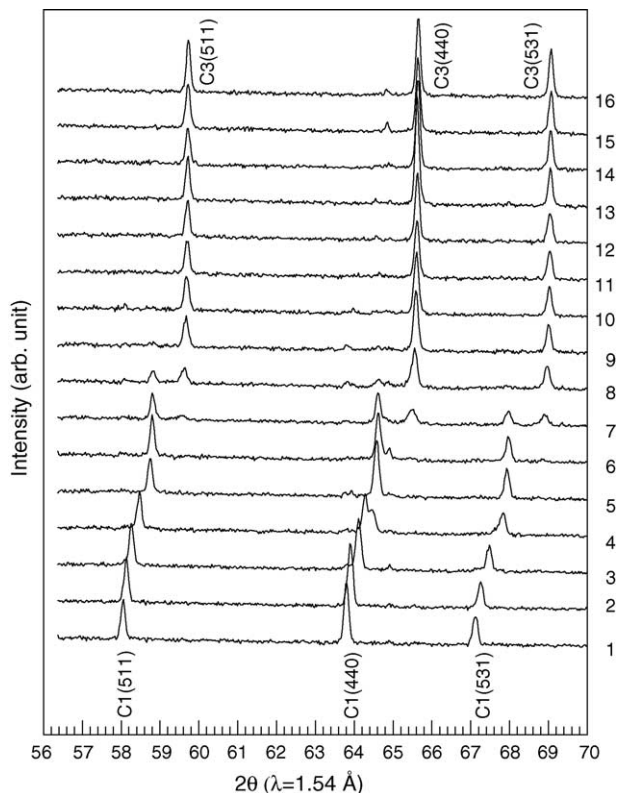
Fig. 2. In situ XRD patterns for F2h sample during first charging up to 5.0 V at 55 °C cycled at C/9 rate.

Fig. 3. In situ XRD patterns for F0h sample during first discharging down to 0.5 V at 55 °C cycled at C/9 rate.

does not seem to be effective in improving structural stability related to oxygen vacancies. TAl0h sample does not show any low-temperature phase peaks at LT, which can be predicted easily, because it had not undergone annealing under Ar atmosphere and no oxygen vacancies was introduced into the spinel structure. However, Al-doped spinel samples show totally different behavior with commercial spinel or Li-rich spinel samples after annealing under Ar atmosphere. TAl6h at both RT and LT does not show any low-temperature phase peaks although it has undergone the longest annealing time among the samples shown in Fig. 1. If this long annealing time were applied to the conventional spinel, it would have created the highest concentration of oxygen vacancies. However, for the Al-doped sample prepared by Saga University and TOSOH, the concentration of oxygen vacancies is even much lower than those conventional spinel heat treated for shorter time. From these results, we would like to point out that Al-doped spinel materials provided by Saga University and TOSOH show superior structural stability against oxygen loss during annealing in Ar atmosphere.

In order to understand the evaluation of structural changes during cycling at high temperature (55 °C), comparative studies among F0h, F2h, and TAl0h were carried out. Fig. 2 shows in situ XRD patterns of F2h sample during first charging up to 5.0 V at C/9 rate. From the spectra, two two-phase coexistence regions on both the 4.0 and 4.2 V plateaus can be clearly identified, in agreement with the three-cubic model
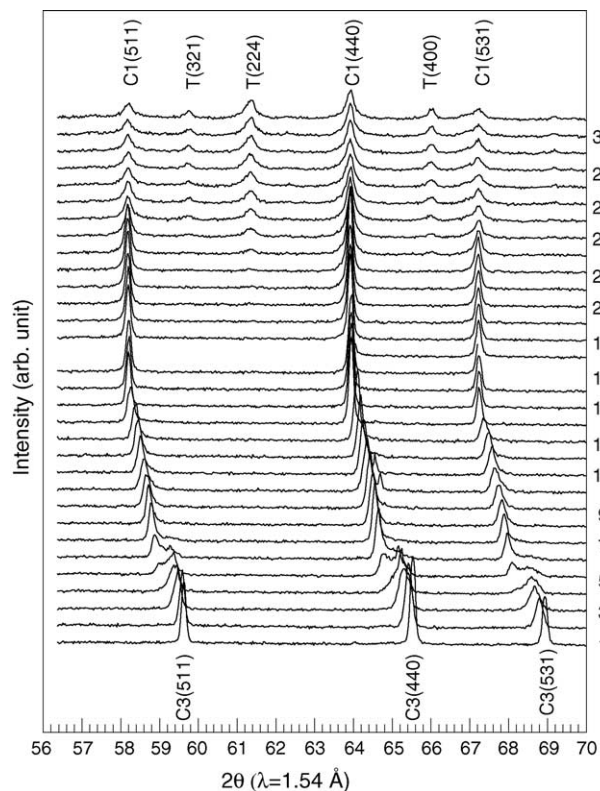
proposed by Yang et al. [3], which indicates that this sample is an oxygen-deficient spinel material [4]. In situ XRD patterns of F0h sample during first discharging down to 0.5 V at C/9 are shown in Fig. 3. It is observed that the structure underwent a series of phase transitions from cubic III to cubic I via cubic II similar to those of F2h in Fig. 2. This indicates that F0h sample itself is also somewhat oxygen-deficient [4] even without the heat treatment. It is very likely that the structural change during electrochemical cycling is far more sensitive to the oxygen vacancies than those during temperature change. One should also notice that the peaks originating from the tetragonal phase is clearly observed at the potential around 0.5 V.

On the other hand, Al-doped sample show much stabilized structural change. Fig. 4 shows in situ XRD spectra of TAl0h during charging up to 4.8 V and discharging down to 0.3 V at C/9 rate. It is clearly observed from Fig. 4(a) and (b) that all three peaks move to higher and lower angles in a continuous fashion during charging and discharging, respectively. Further, even though the sample was discharged to lower depth of the potential than F0h was, i.e. to 0.3 V, the formation of the tetragonal phases was significantly suppressed. At scan 21 and 22 of Fig. 4(b), it seems that there is a little hump (marked with arrow) originating from tetragonal phase, but it is very small compared to that of F0h and is not clear enough to distinguish.
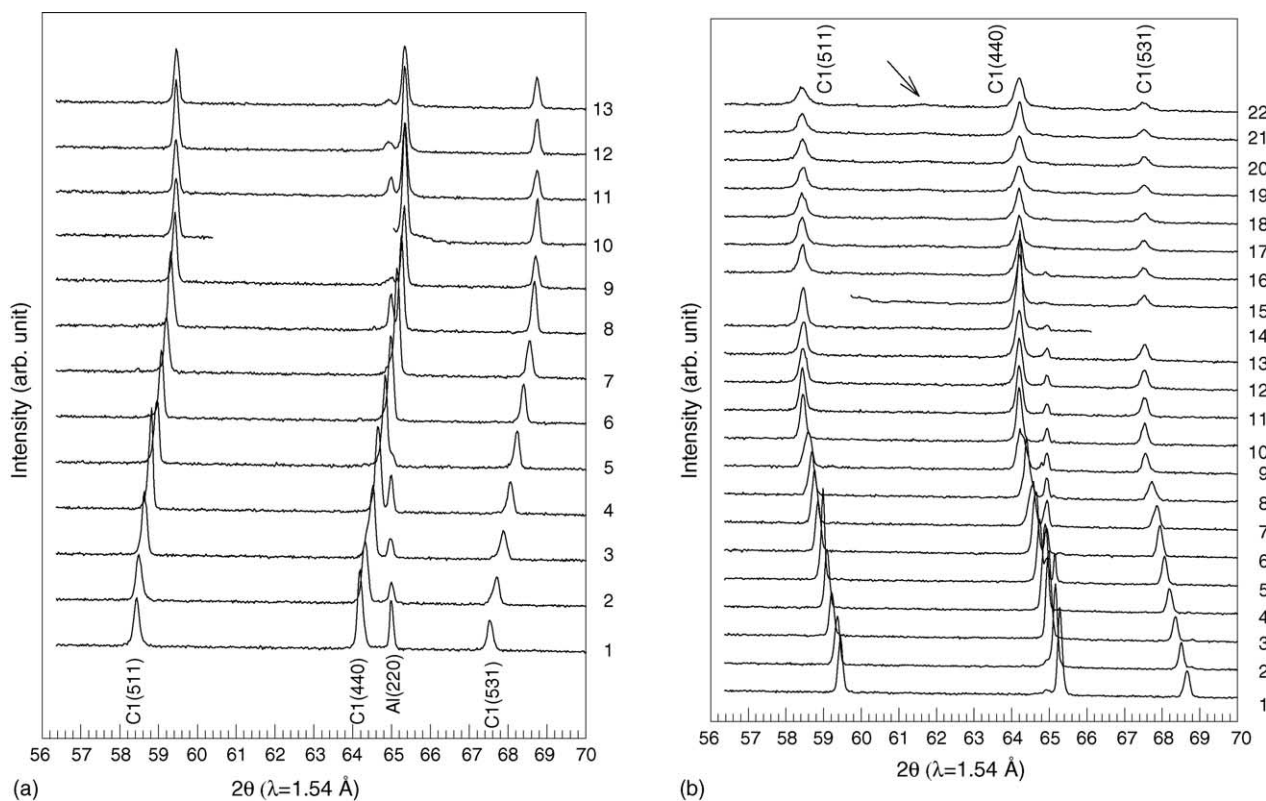
Fig. 4. In situ XRD patterns for TAl0h sample during first (a) charging up to 4.8 V and (b) discharging down to 0.3 V at 55 °C cycled at C/9 rate.

In the previous report [4], the relationship between capacity fading and structural changes had been reported. In that report, the samples which underwent a three-cubic model structure change showed the poorest cycle performance with big capacity fading at both 4.0 and 4.2 V plateau, while the samples experiencing the pseudo one-phase model showing the best cycling performance. Therefore, it can be predicted that TAl0h would show better cycling performance than F0h or F2h do, which had been demonstrated by Okada et al. [11]. Figs. 5 and 6 show in situ XRD spectra of F2h and TAl0h collected during 31st charging up to 4.8 V at C/9 rate, respectively. It is clearly shown that most of the peaks for F2h in Fig. 5 do not move as the charging goes on, which indicates that the majority part of the active materials have become inactive. Also, significant intensities of the peaks arising from the tetragonal phase are observed, the formation of which is one of the well-known causes for the capacity fading in spinel materials. On the other hand, the XRD spectra of TAl0h in Fig. 6 show peak shifting during charging. Although some residues of the cubic I and cubic II phases are observed at the end of charge, the peaks originating from the tetragonal phase are hardly observable. From these results, it is believed that Al-doping significantly improves the high-temperature cycle performance of spinel materials. This is in big part due to the improved stability against oxygen loss, which is confirmed by the in situ XRD spectra shown in Fig. 7. The sample TAl6h was discharged down to 0.3 V at C/9 rate at 55 °C. Even though the sample was annealed at 660 °C under
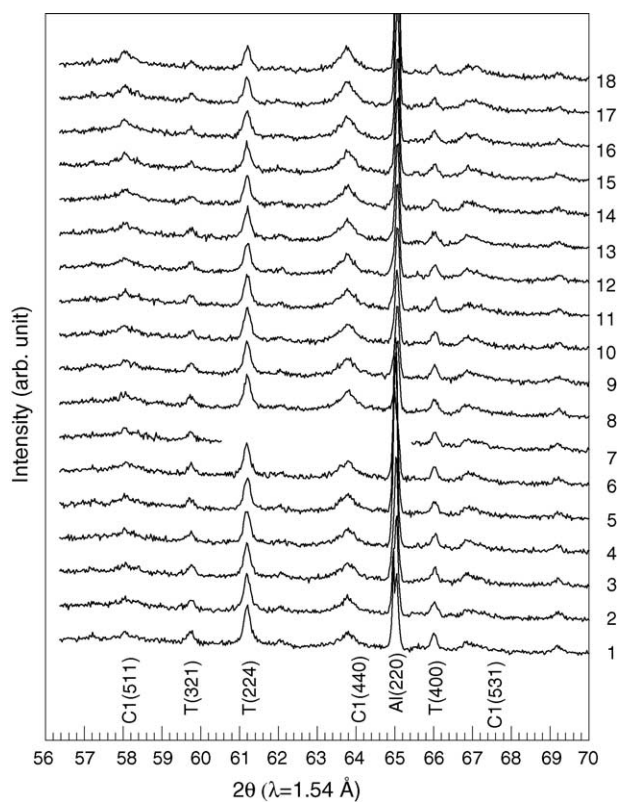

Fig. 5. In situ XRD patterns for F2h samples during 31st charging up to 4.8 V at 55 °C cycled at C/9 rate.
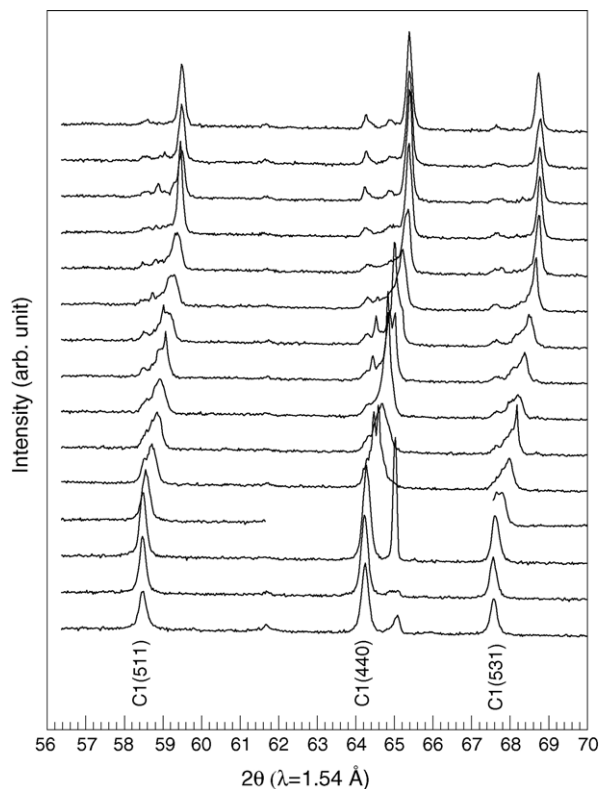
Fig. 6. In situ XRD patterns for TAl0h samples during 31st charging up to 4.8 V at 55 °C cycled at C/9 rate.
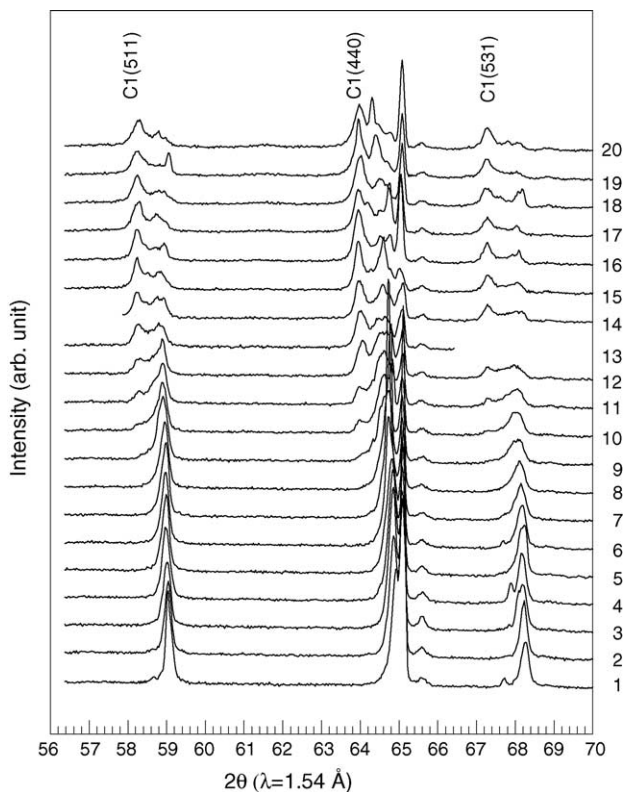

Fig. 7. In situ XRD patterns for TAl6h samples during first discharging down to 0.3 V at 55 °C cycled at C/9 rate.

Ar atmosphere for 6 h, the XRD spectra is closer to two-phase model and do not show the peaks originating from tetragonal phase at the end of discharge. This is an interesting result compared to that of F0h. This again confirms the superior resistance to oxygen loss in consistency with the results shown in Fig. 1. From the result shown in the present study, we can conclude that Al-doping improves the structural stability of spinel materials against oxygen loss, and also improves the cycle performance at high temperature.

4. Conclusions

In this paper, we made comparative studies between oxygen-content-varied spinel materials and Al-doped spinel materials. Oxygen-deficient spinel materials prepared by heat treatment at 660 °C under Ar atmosphere showed tetragonal phase peaks flanking the original cubic peaks at −30 °C in the XRD spectra, while Al-doped spinel materials which were heat treated under Ar atmosphere did not. Further, the in situ XRD spectra at 55 °C revealed the reasons that why Al-doped spinel materials have better cycle performances than the conventional spinel materials. Another in situ XRD spectra collected during discharge of Al-doped spinel material heat treated under Ar atmosphere for 6 h showed the behavior of two-phase model resembling those of oxygen stoichiometric spinel materials. On the other hand, those of undoped samples showed three-cubic model structure changes indicating oxygen deficiency in their structure. From these results, it is concluded that Al-doped sample showed better structural stability against oxygen loss and less distinctive structural changes during cycling at high temperature (55 °C), which contributed to the cycle performances.

References

[1] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc. 137 (1990) 769.
[2] Y. Xia, M. Yoshio, J. Electrochem. Soc. 143 (1996) 825.
[3] X.Q. Yang, X. Sun, S.J. Lee, J. McBreen, S. Mukerjee, M.L. Daroux, X.K. Xing, Electrochem. Solid-State Lett. 2 (1999) 157.

[4] Y. Xia, T. Sakai, T. Fujieda, X.Q. Yang, X. Sun, J. McBreen, M. Yoshio, J. Electrochem. Soc. 148 (2001) A723.

[5] M. Yoshio, X. Wang, H. Nakamura, Proceedings of 203rd ECS Meeting, Abstract number 1147, 2003.

[6] D.H. Jang, Y.J. Shin, S.M. Oh, J. Electrochem. Soc. 143 (1996) 2204.

[7] M.M. Thackeray, Y. Shao-Horn, A.J. Kahaian, K.D. Kelper, E. Skinner, J.T. Vaughey, S.A. Hackney, Electrochem. Solid-State Lett. 1 (1998) 7.

[8] K.Y. Chung, K.-B. Kim, J. Electrochem. Soc. 149 (2002) A79.

[9] K.Y. Chung, W.-S. Yoon, K.-B. Kim, X.-Q. Yang, S.M. Oh, J. Electrochem. Soc. 151 (2004) A484.

[10] M. Yoshio, X. Wang, H. Nakamura, H. Noguchi, B. Deng, Proceedings of 203rd ECS Meeting (N1 Symposium), vol. 2003–20, Paris, France, 2003, pp. 513–519.

[11] M. Okada, N. Suzuki, K. Yamamoto, T. Shoji, T. Mouri, M. Yoshio, Proceedings of 200 ECS Meeting (2001 Joint International Meeting), Abstract number 278 (2001).

[12] X.Q. Yang, X. Sun, M. Balasubramanian, J. McBreen, Y. Xia, T. Sakai, M. Yoshio, Electrochem. Solid-State Lett. 4 (2001) A117.