Short communication

Capacity fading with oxygen loss for manganese spinels upon cycling at elevated temperatures

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ABSTRACT

The nominal $LiMn_2O_4$ and Li-doped spinels with different oxygen stoichiometry were prepared and investigated for capacity fading upon cycling at elevated temperatures. The discharge plateau at 3.2 V originating from oxygen defects in manganese spinels is observed to grow very quickly to nearly a maximum scale in initial 15 cycles at 60 °C. Meanwhile, the majority of capacity fading is lost. Therefore, the quick capacity fading in the initial stage is associated with the increase of oxygen deficiencies or oxygen loss upon cycling. It is proposed that the oxygen loss is originated from the decomposition of instable spinel phases that containing little Li cations on the 8a sites ($[\square_1]_{8a}[Mn_{2-x}]_{16d}[O_{4-\delta}\square_\delta]_{32e}$, etc.), which are formed upon charging to the upper voltage limit. This phenomenon is much severe for nominal $LiMn_2O_4$ spinels with oxygen deficiencies. After partial substitution of Mn with Li, part of the Li cations on the 8a sites will be retained upon charging to the upper voltage limit. Thereafter, the cycling performance can be improved for the stabilized spinel phases formed upon charging.

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1. Introduction

The manganese spinels are important alternative materials for $LiCoO_2$ especially in the large-scale Li-ion batteries, because of the advantages such as low cost, low toxicity and superior performance in the overcharged states. In the past years, lots of research work had been devoted to the development of $LiMn_2O_4$ spinels for commercial application, and most are intensified on the capacity fading upon cycling [1–13]. The reasons such as the Jahn–Teller distortion [1], Mn dissolution [4,5], two-phase coexistence [6], oxygen defect [7–10] and so on have been proposed to be responsible for the capacity fading upon cycling. After partial substitution of Mn with other meal cations (Li, Mg, Co, etc.), the cycling stability can be significantly improved especially at room temperature [2]. However, the capacity fading at elevated temperatures >50 °C is still too high for practical applications [11–13]. And the efforts to develop spinel materials with satisfactory cycling performance and to further understand the capacity-fading mechanism at elevated temperatures have attracted much attention.

It had been reported by Xia et al. that the manganese spinels with oxygen deficiencies ($[Li]_{8a}[Me_xMn_{2-x}]_{16d}[O_{4-\delta}]_{32e}$) demonstrate poor cycling stability at room temperature, although they are doped with Li cations [8]. And they proposed that oxygen deficiencies could result in the capacity fading in the 4.1 V plateau region (together with phase transitions between the cubic I and II spinels). Sun et al. [14] observed that Li-doping could reduce the lattice constant gap between adjacent cubic phases upon lithium intercalation/deintercalation by synchrotron-based in situ XRD. And we believe that this effect is beneficial to the improvement of cycling performance because of reduced mechanical grinding from phase transitions. After the oxygen deficiencies are removed and partial Mn is replaced by other cations, the cycling stability can be greatly improved especially at elevated temperatures [12,15]. In order to further understand the capacity-fading mechanism of manganese spinels upon cycling at elevated temperatures, the charge/discharge behavior and the variation of structural composition of spinel materials upon cycling at 60 °C were investigated. The majority of capacity fading is observed to lose quickly in the initial 15 cycles together with the increase of oxygen defect, especially for the oxygen deficient spinels. The increase of oxygen defect is ascribed mainly to the decomposition of instable spinel phases formed upon charging to the upper voltage limit.

2. Experimental

A Li-doped spinel designated as Li010-N600 was prepared by a two-step method: first sintering the mixture of LiOH and MnO_2 in the mole ratio of 1:2 at 1000 °C to obtain an intermediate, and then

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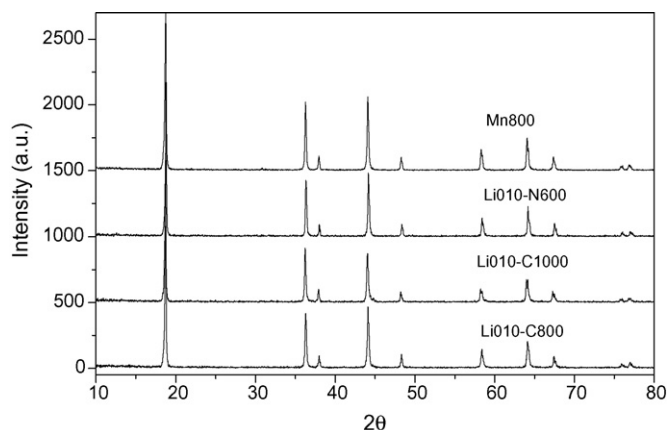E-mail address: bdeng21@yahoo.com.cn (B. Deng).

Fig. 1. The XRD patterns for Mn800, Li010-C800, Li010-C1000 and Li010-N600.

annealing it at 600 °C with the addition of LiOH (0.10 for 1.0 LiOH in the starting mixture) to control oxygen stoichiometry. Other spinels designated as Mn800, Li010-C800 and Li010-C1000 were prepared by conventional method from the starting mixtures of LiOH and MnO_2, with molar ration of 1.0/2.0 for Mn800, and 1.1/2.0 for Li010-C800 and Li010-C1000, respectively. Mn800 and Li010-C800 were prepared by only calcination at 800 °C, and Li010-C1000 was prepared by first calcination at 1000 °C and then annealing at 600 °C. Please note that the Li-doping content of Li010-C800 and Li010-C1000 is almost the same as that of Li010-N600 by adding enough LiOH in the starting mixture. The electrochemical performance of these materials was examined with coin cells. Pellet-type cathodes were prepared and assembled with a metal lithium anode to make half-cells of CR2032 type [10,12]. Then electrochemical characterization was performed in the voltage region of 3.0–4.3 V or 3.5–4.3 V at a constant charge/discharge rate of 0.1 mA cm^{-2} or 0.4 mA cm^{-2}, respectively. The electrolyte used in this paper is 1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7, v/v).

All the as-prepared materials were characterized by Rigaku Rint1000 X-ray diffractometer with Cu Kα radiation. The chemical composition and Mn dissolution were determined by chemical analysis [10,12]. The total content and average valence of Mn cation were determined by potential titration and the Li content was analyzed by ICP with internal standard method. The chemical formulae of the materials are obtained based on the chemical analysis data and electroneutrality principle, and they are expressed in a general formula (Li, Mn)$_3$O$_{4\pm\delta}$. To measure the Mn dissolution content, 3 g of the as-prepared materials were immersed in 30 ml electrolyte solution, and the material powders were filtered after storage for several weeks at 60 °C in a constant temperature box. The Mn content in the filtered electrolyte was determined by ICP spectroscopy.

3. Results and discussion

The manganese spinels Mn800, Li010-C800, Li010-C1000 and Li010-N600 were examined by XRD for phase purity. The XRD patterns in Fig. 1 show that all these materials are single-phase spinels of the ($Fd\bar{3}m$) space group. The chemical compositions of the as-
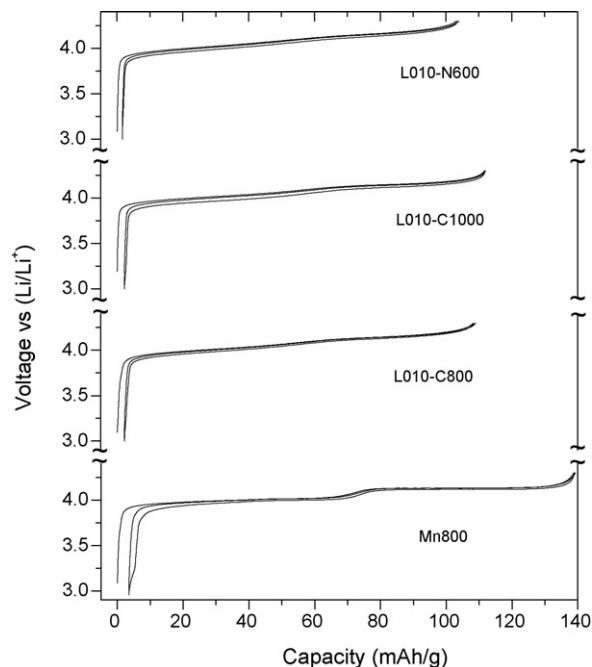

Fig. 2. The initial two cycles of Mn800, Li010-C800, Li010-C1000 and Li010-N600 at ambient temperature (0.1 mA cm^{-2}).

prepared materials were analyzed and are summarized in Table 1. The LiMn$_2$O$_4$ spinels belong to the ($Fd\bar{3}m$) group with Li ions located on the tetrahedral 8a sites, manganese cations and oxygen anions on the octahedral 16d and 32e sites, respectively. Therefore, Mn800 (Li$_{1.010}$Mn$_{1.990}$O$_{3.988}$) is an oxygen-deficient spinel and it can be rewritten as [Li]$_{8a}$[Li$_{0.010}$Mn$_{1.990}$]$_{16d}$[O$_{3.988}$□$_{0.012}$]$_{32e}$ in the terms of site assignments [12]. After doping with Li, the oxygen non-stoichiometry in the spinel materials can be suppressed. The Li010-C800 is nearly a spinel with oxygen stoichiometry, and it could be rewritten as [Li]$_{8a}$[Li$_{0.099}$Mn$_{1.901}$]$_{16d}$[O$_{3.998}$□$_{0.002}$]$_{32e}$. More oxygen deficiencies are detected in Li010-C1000 ([Li]$_{8a}$[Li$_{0.090}$Mn$_{1.910}$]$_{16d}$[O$_{3.991}$□$_{0.009}$]$_{32e}$), because it was once calcinated at 1000 °C (much higher than 800 °C for Li010-C800). Li010-N600 is a special spinel with no oxygen deficiency present on the 32e sites but with vacancies on the 16d sites ([Li]$_{8a}$[Li$_{0.087}$Mn$_{1.894}$□$_{0.019}$]$_{16d}$[O$_4$]$_{32e}$), although it has nearly the same Li-doping content as Li010-C800 and Li010-C1000. Please note that two different formulae are used while referring to a spinel material throughout this text, one based on the general formula (Li, Mn)$_3$O$_{4\pm\delta}$ and another denoting the site assignments.

The oxygen stoichiometry can also be identified by the extra discharge plateau around 3.2 V appearing in the charge/discharge profiles for manganese spinels [7–11]. The charge/discharge curves of Mn800, Li010-C800, Li010-C1000 and Li0100-N600 at an ambient temperature are shown in Fig. 2. As seen for Mn800 (nominal LiMn$_2$O$_4$ spinel), a large extra plateau appeared at 3.2 V indicating that the oxygen defect is very severe. After doping with Li, the extra plateau becomes very small for Li010-C800 and Li010-C1000 demonstrating that the oxygen defect is significantly suppressed.

Table 1
Physiochemical properties of the spinel samples in the present paper

| Sample name	Chemical formula	Structural composition in terms of site assignments [12]	Mn dissolution
Mn800	Li$_{1.010}$Mn$_{1.990}$O$_{3.988}$	[Li]$_{8a}$[Li$_{0.010}$Mn$_{1.990}$]$_{16d}$[O$_{3.988}$□$_{0.012}$]$_{32e}$	ca. 100 ppm
Li010-C800	Li$_{1.099}$Mn$_{1.901}$O$_{3.998}$	[Li]$_{8a}$[Li$_{0.099}$Mn$_{1.901}$]$_{16d}$[O$_{3.998}$□$_{0.002}$]$_{32e}$	ca. 20 ppm
Li010-C1000	Li$_{1.090}$Mn$_{1.910}$O$_{3.991}$	[Li]$_{8a}$[Li$_{0.090}$Mn$_{1.910}$]$_{16d}$[O$_{3.991}$□$_{0.009}$]$_{32e}$	ca. 3 ppm
Li010-N600	Li$_{1.094}$Mn$_{1.906}$O$_{4.025}$	[Li]$_{8a}$[Li$_{0.087}$Mn$_{1.894}$□$_{0.019}$]$_{16d}$[O$_4$]$_{32e}$	ca. 3 ppm
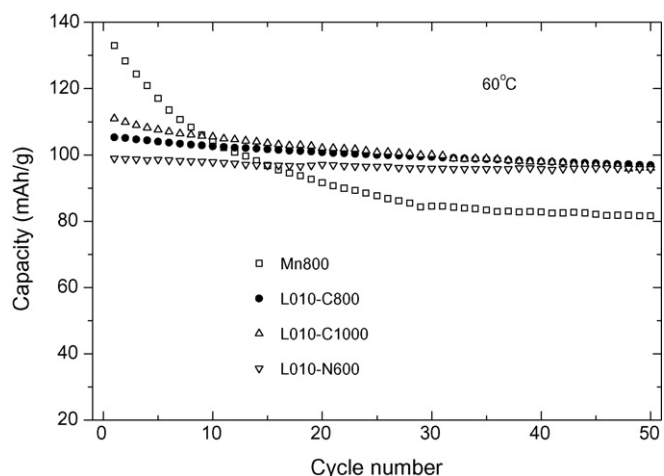
Fig. 3. The cycling performance of Mn800, Li010-C800, Li010-C1000 and Li010-N600 at 60 °C (0.4 mA cm⁻²).

And no extra plateau is observed for Li010-N600, meaning that no oxygen deficiency is present. Therefore, the electrochemical profiles correlating with oxygen stoichiometry are consistent with the chemical analysis results in Table 1. As described in the experimental, the Li-doping content for Li010-N600, Li010-C800 and Li010-C1000 is almost the same, but their thermal treating history is much different. So it can be concluded that not only the Li-doping but also the thermal process will influence the final chemical compositions of manganese spinels, especially the oxygen stoichiometry.

In order to understand the cycling performance at elevated temperatures, the spinels Mn800, Li010-C800, Li010-C1000 and Li0100-N600 were investigated at 60 °C. As seen from Fig. 3, the capacity fading at 60 °C is very severe for Mn800 and only 61% of the discharged capacity in the first cycle is available after 50 cycles. After Li-doping, the cycling performance is improved greatly and the capacity retention ratio after 50 cycles is improved to ca. 92.1%, 86.5% and 96.8% for Li010-C800, Li010-C1000 and Li010-N600, respectively. And the differing cycling performance for these Li-doped spinels can be mainly ascribed to the variation of oxygen stoichiometry [12,15]. Furthermore, it is noticeable in Fig. 3 that the majority of capacity fading was lost quickly in the initial 15 cycles, especially for Mn800. After about 15 cycles, the capacity fading became relatively stabilized in the following cycles. This phenomenon indicates that significant structural and chemical changes may occur for these spinels in the initial 15 cycles. To explore possible variations, the electrochemical charge/discharge profiles of Mn-800, Li010-C800, Li010-C1000 and Li010-N600 cathodes were investigated after being cycled at 60 °C. The profiles in Fig. 4 were examined at 0.1 mA cm⁻² (room temperature) after the cathodes were galvanostatically cycled at 0.4 mA cm⁻² (60 °C) between 3.5 V and 4.3 V for 15, 30, or 60 cycles, respectively, and the initial two cycles of the fresh cathodes at 0.1 mA cm⁻² are also shown for comparison.

Fig. 4(a) shows the charge/discharge curves of Mn800 at 0.1 mA cm⁻². The extra plateau around 3.2 V is very evident in the initial two cycles, and it is enlarged significantly in 15 cycles. After 15 cycles, the 3.2 V plateau is nearly stabilized upon cycling in the subsequent cycles. The variation of the 3.2 V plateau indicates that the oxygen defects in Mn800 may be increased to a maximum scale in initial 15 cycles, and then it becomes nearly stabilized. In addition, the boundary of the 4.0 V and 4.2 V plateau regions can be clearly observed in the initial two cycles (Fig. 4(a)). After 15 cycles, the boundary becomes unclear and the charge/discharge

profiles are similar to that of Li-doped spinels such as Li010-C800 and Li010-C1000. These phenomena can tell us that the chemical composition of Mn-800 spinel is changed upon cycling: Mn-800 is inclined to lose oxygen upon cycling and transformed to a Li-rich spinel material at the same time. The Li-rich spinel material is assumed to be stable upon cycling at elevated temperatures and the capacity-fading rate becomes very slow in the subsequent cycles. In other words, doping with Li can improve the cycling stability as confirmed by the performance of Li-doped manganese spinels (Fig. 3). Fig. 4(b)–(d) shows the charge/discharge curves of Li010-C800, Li010-C1000, and Li010-N600 at 0.1 mA cm⁻². It can be seen that the variation tendency of the 3.2 V plateau upon cycling is similar to that of Mn800, although the variation gap in 15 cycles is reduced. Meanwhile, the majority of capacity fading is lost quickly in the initial 15 cycles as shown in Fig. 3. Therefore, the growth of the 3.2 V discharge plateau or the loss of oxygen is suggested to be responsible for the quick capacity fading. In addition, the increase of the 3.2 V plateau is the largest for Li010-C1000 while the least for Li010-N600, although the Li-doping content in Li010-C800, Li010-C1000 and Li010-N600 is almost the same. From Table 1, we know that the oxygen defect of Li010-C1000 is the severest among the three Li-doped spinels, and no oxygen defect present in Li010-N600. Therefore, it can be inferred that the more oxygen defects in manganese spinels, the greater increase of the 3.2 V plateau, and the more capacity loss in the initial 15 cycles. Accordingly, differing cycle performance is observed for the Li-doped spinels with different oxygen stoichiometry.

The oxygen loss observed mainly in the initial 15 cycles indicates the variation of structural and chemical composition for manganese spinels. As for Mn800, it could be inferred from Fig. 4(a) that Mn800 is transformed from a nominal $LiMn_2O_4$ spinel to a Li-rich spinel in the initial 15 cycles. At the same time, oxygen defect is increased together with decreased oxidation state of Mn cations. This phenomenon implies that manganese oxides with oxidation state higher than the average value may leave the bulk phase upon cycling at 60 °C. In other words, it is possible that part of λ-MnO_2 phase formed at fully charged state of Mn800 might become electrochemically inactive. If so, some impurities of manganese oxides without activity will be detected after 50 cycles. The XRD examinations on Mn-800, Li010-N600 and Li010-C800 cathodes were carried out after 50 cycles (0.4 mA cm⁻² at 60 °C) and the results are shown in Fig. 5. The coin cells after 50 cycles were dissembled and the cathodes (in pellet) in fully discharged state were washed with DMC in the glove box. And then the pellets were examined by X-ray diffractometer. As seen from Fig. 5, two extra diffraction peaks at about 38.2° and 44.5° are observed for Mn800 and Li010-C800 except for the typical peaks of spinel phase, but not observed for Li010-N600. It is obvious that these peaks do not belong to λ-MnO_2 phase (spinel structure), and they are assumed to come from the decomposition product of instable spinel phases like λ-MnO_2. Other researchers had reported the instability of spinel phases that formed upon charging manganese spinels to 4.3 V or higher voltage limit. Gao and Dahn had found that charging to higher voltages above 4.3 V can lead to the increase of the 3.2 V plateau for Li-doped spinels [7]. Wang et al. observed that the increase of oxygen defect would become much milder for nominal spinels like Mn800 if decreasing the upper voltage limit from 4.3 V to 4.1 V, which is far from the fully charged states [10]. Based on the charged capacity, spinel phases containing little Li cations on the 8a sites ($[\square_1]_{8a}[Li_{0.010}Mn_{1.990}]_{16d}[O_{3.988}\square_{0.012}]_{32e}$, etc.) are formed at 4.3 V for nominal spinels like Mn800 [16]. On the contrary, spinel phases with partial Li cations being retained on the 8a sites will be formed upon charging to voltages below 4.3 V ($[\square_{1-x}Li_x]_{8a}[Li_{0.010}Mn_{1.990}]_{16d}[O_{3.988}\square_{0.012}]_{32e}$). And only spinel phases with much residual Li present on the 8a
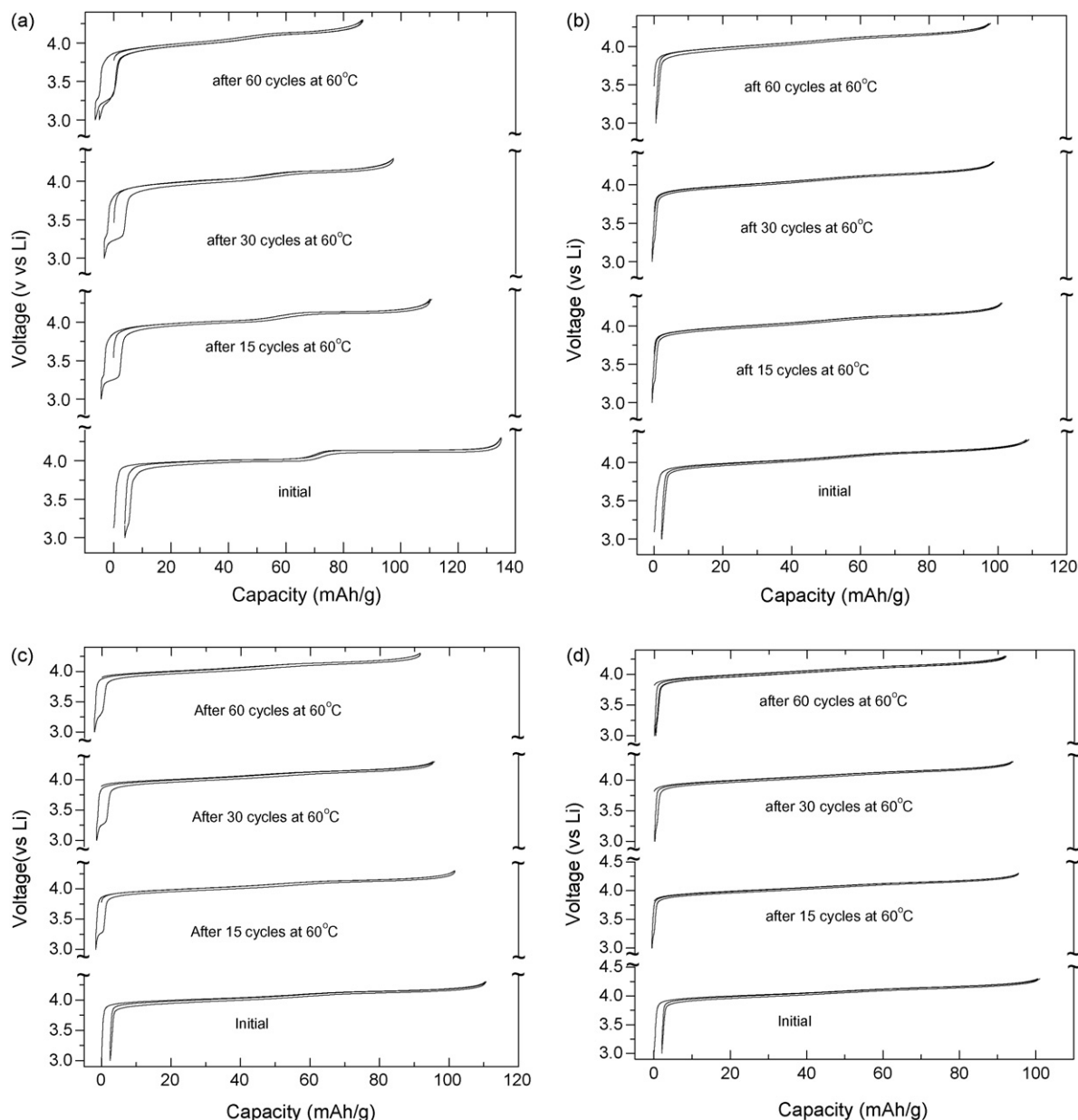
Fig. 4. The charge/discharge profiles for Mn800 (a), Li010-C800 (b), Li010-C1000 (c) and Li010-N600 (d) at 0.1 mA cm^{-2} (ambient temperature), before and after different cycles at 60 °C (0.4 mA cm^{-2}).

sites can be formed for Li-doped spinels upon charging to 4.3 V. For instance, the charged capacity is ca. 110 mAh g^{-1} upon charging to 4.3 V for Li010-C800 (see Fig. 2), and about 80% of the Li cations on the 8a sites will be extracted out compared to 100% extraction for ca. 140 mAh g^{-1}. It is well believed that the presence of Li cations on the 8a sites should be beneficial to the structural stability. And the improved stability is supported by the reduced sharpness of the extra peaks from decomposition products of Li010-C800 cathodes compared to that of Mn800 (Fig. 5). Therefore, the spinel phases that containing little Li cations on the 8a sites (like $[\square_1]_{8a}[Mn_{2-x}]_{16d}[O_{4-\delta}\square_\delta]_{32e}$) are instable compared to other spinel phases with much Li cations retained on the 8a sites in the charged states.

Fig. 5 also shows that the peak broadening and sharpness decreasing are significant for Mn800 because of decreased crystallinity after 50 cycles at 60 °C [17]. But they are not evident for Li010-C800 and Li010-N600. It is believed that the oxygen loss

from the bulk phase can damage the structural integrity of spinel phases and then lead to the decrease of crystallinity. To further understand the variation of structural composition upon cycling, spinels expressed by a general formula $(Li, Mn)_3O_{4\pm\delta}$ are located in the $LiMn_2O_{4-\delta}$–$Li_2Mn_4O_9$–$Li_4Mn_5O_{12}$ tie triangle (Fig. 6) [15], which is a cubic section obtained from the Li–Mn–O phase diagram proposed by Thackeray et al. [18]. Based on the Li/Mn ratio and average oxidation state of Mn, oxygen deficient spinels like Mn800 are located in the ACD area (for spinels with vacancies on the 32e sites). Oxygen rich spinels $(O/(Li + Mn) > 4/3)$ like Li010-N600 are located in the ACB area (for spinels with no vacancy on the 32e sites but vacancies on the 16d sites). Other spinels with oxygen stoichiometry are located on the AC line (for spinels with no vacancies on both the 16d and 32e sites). Li010-C800 and Li010-C1000 are located nearby the AC line according to their chemical compositions. From the discussions on the composition variation in the former paragraphs, it can be inferred that the structural compo-
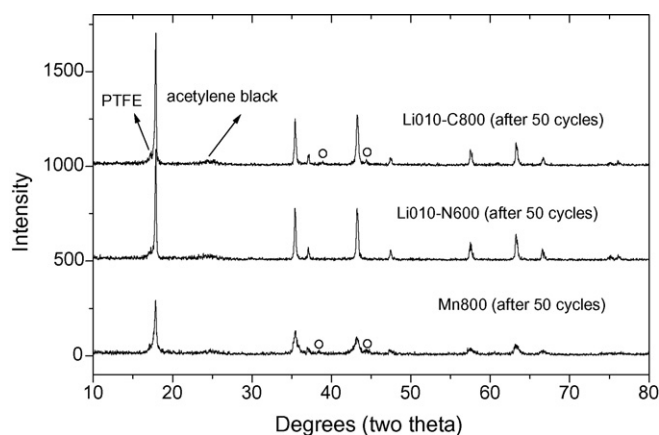
Fig. 5. The XRD patterns for the cathodes of Mn-800, Li010-N600 and Li010-C800 after 50 cycles (0.4 mA cm^{-2} at 60 °C).
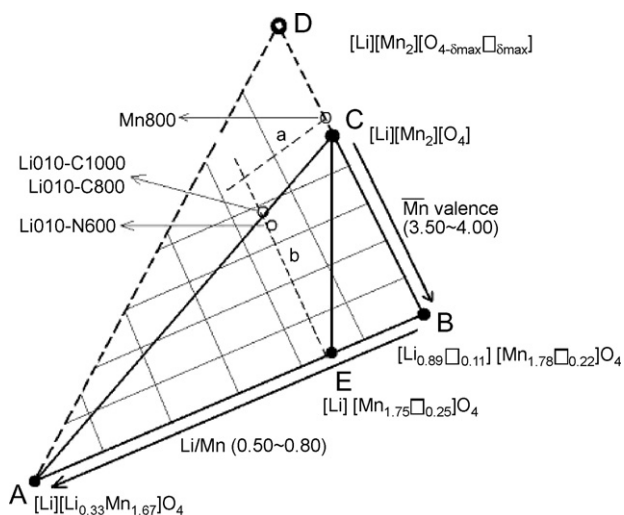

Fig. 6. The cubic section of Li–Mn–O phase diagram.

sition of Mn800 varies in the direction of "a" line (dashed) upon cycling, and that of the Li-doped spinels varies in the direction of "b" line across AC. From the viewpoint of structural composition, structure reconstructions will occur together with oxygen loss upon cycling. Mn800 is transformed from a nominal spinel (without Li cations on 16d sites) to a Li-rich spinel (with Li cations on the 16d sites). In contrast, Li010-N600 is transformed from a spinel with vacancies on 16d sites but no vacancy on 32e sites (in ACB) to a spinel phase with vacancies on 32e sites but no vacancy on 16d sites (in ACD) after 50 cycles. The phase transformation of Li010-N600 is assumed to be able to weaken or buffer the damage to structural integrity from oxygen loss. This kind of buffer effect cannot occur for Li010-C800 and Li010-C1000 because only oxygen is lost from the 32e sites in the initial cycles. The greatly improved structural stability of oxygen-rich spinels is supported by nearly no XRD peaks from decomposition products being observed for Li010-N600 (Fig. 5). Therefore, further improved cycling stability is observed for

Li010-N600 compared to that of Li010-C1000 and Li010-C800 in the initial cycles (see Fig. 3).

The Mn dissolution may be considered as another reason for the oxygen loss, because it is very popular for manganese spinels. Wang et al. had observed that the Mn dissolution after storage in electrolytes at 60 °C would reduce the oxygen deficiencies in the spinels like Mn800 [10]. The Mn dissolution of the spinels investigated in this paper was determined after storage at 60 °C for 2 weeks, and summarized in Table 1. It is about 100 ppm and 20 ppm for Mn800 and Li010-C800, respectively, but the increase of oxygen defect for Mn800 is much severer than that of Li010-C800 (see Fig. 4). In addition, the increase of oxygen defect for Li010-C800 is severer than that of Li010-N600 although the Mn dissolution of Li010-N600 is reduced greatly to ca. 3 ppm. Therefore, the main reason for the increased oxygen deficiencies or oxygen loss should be ascribed to the decomposition of instable spinel phases that formed upon charging to the upper voltage limit in the initial cycles.

4. Conclusions

It is observed that the majority of capacity fading for manganese spinels is lost in the initial 15 cycles together with oxygen loss upon cycling at 60 °C. The oxygen loss upon cycling is proposed to originate from the decomposition of instable spinel phases formed upon charging to the upper voltage limit. For instance, spinel phases that containing little Li cations present on the 8a sites ($[\square_1]_{8a}[Li_{0.010}Mn_{1.990}]_{16d}[O_{3.988}\square_{0.012}]_{32e}$, etc.) will be formed for nominal LiMn$_2$O$_4$ spinels like Mn800 at 4.3 V. After Li-doping, spinel phases with partial Li cations retained on the 8a sites are formed upon charging to 4.3 V. Therefore, the structural stability upon cycling can be improved, and the capacity loss in the initial cycles can be reduced. In addition, oxygen rich spinels like Li010-N600 are suggested to have a kind of buffer effect to the damage to structure integrity from oxygen loss upon cycling, and then the structural stability and cycling performance can be further improved.

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