Improved Cycleability of Oxygen Stoichiometric $Li_{1+x}Mg_yMn_{2-x-y}O_{4+\delta}$ at Elevated Temperature

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A new type of oxygen stoichiometric Mg-doped $LiMn_2O_4$ spinels with improved crystallinity and decreased surface area was prepared by a special "two-step" method. These materials exhibited greatly improved cycleabilty (ca. 1.5% capacity loss after 50 cycles) and reduced Mn dissolution at elevated temperature than conventional Mg-doped materials.

As an alternative material for $LiCoO_2$ now widely used in commercial Li-ion batteries, $LiMn_2O_4$ spinels have been investigated intensively for its merits of low cost, low toxicity, and excellent safety performance.[1–5] Although many published papers had reported that 4 V $LiMn_2O_4$ cathodes will suffer capacity fading upon cycling especially at elevated temperatures (above 40 °C), capacity decline was observed mostly for spinel samples with oxygen deficiency. We have reported the different electrochemical performance of Mn spinels depending on the Li/Mn ratio and average valence of Mn cation,[1] and we defined $(Li, Mn)_3O_{4+\delta}$ based on chemical analysis of each component as oxygen rich spinel taking the total metal cations as 3. With respect to the total oxygen anions located in 32e site, the oxygen rich spinel can be rewritten with $[Li]_{8a}[Li_xMn_{2-x-\delta}\square_\delta]_{16d}[O_4]_{32e}$ (□ denotes vacancies). So we call the oxygen rich spinels as oxygen stoichiometric or metal defect spinels with metal cation vacancies. For spinels with $(Li, Me, Mn)_3O_{4+\delta}$ or $(Li, Me, Mn)_3O_{4-\delta}$ (Me denotes other metal cation doped), we define them as oxygen rich or oxygen defect spinel respectively. Recently it was recognized that the main reason for the capacity loss is the oxygen deficiency.[2] The cycleabilty of Mn spinels would be improved after the oxygen deficiency was removed, and it can be improved by partial substitution of Mn with other metal cations such as Li[1,2] and Mg[6] mainly for the improved oxygen stoichiometry after doping if synthesized at lower than 850 °C. It should be emphasized that the doped spinels tend to become oxygen deficient if the sintering temperature was raised over 900 °C even though Li or other metal cation is doped. The problem for conventional materials is the large Mn dissolution at elevated temperature, about 70 ppm if synthesized below 850 °C. It was reported that dissolved Mn cations could be deposited on the lithiated graphite and then induce capacity loss of graphite anodes during cycling or storage.[4] In this paper, a new type of oxygen stoichiometric Mg-doped spinels with low solubility of Mn cations was prepared by a special "two-step" method for the first time. They exhibited greatly improved cycleability and reduced Mn dissolution than other Mg-doped spinels prepared by conventional "one-step" method.

The new type materials Mg010-N ($Li_{1.036}Mg_{0.10}Mn_{1.864}O_{4.021}$ from chemical analysis, the same case for other materials except for specification), and Mg075-N ($Li_{1.034}Mg_{0.080}Mn_{1.886}O_{4.010}$) were synthesized by a "two-step" solid state reaction: in the first step, a mixture of LiOH, MgO, and MnO_2 (in mole ratio of 1:0.1:1.9 for Mg010-N and 1:0.075:1.925 for Mg075-N) was heated at 470 °C for 5 h to obtain a precursor, then it was calcinated at above 900 °C for 10 h to get an intermediate product; in the second step, the intermediate was mixed and ground with extra LiOH (0.05 for 1 LiOH in the initial mixture) and then annealed at 600–800 °C to get the final product. For comparison, material Mg010-C800 ($Li_{1.035}Mg_{0.093}Mn_{1.873}O_{3.999}$) with almost the same metal doping content as Mg010-N was prepared with conventional "one-step" method[2] by calcination at 800 °C. Other materials Mg010-T with general formula of $LiMg_{0.10}Mn_{1.90}O_4$ (calculated from the initial mixture of LiOH, MgO, and MnO_2), were also prepared by the one-step method. "T" equals to 800, 850, 900, 950, or 1000 corresponding to the calcination temperature. The total content and average valence of Mn cation were determined by potential titration[7] and Mg determined by EDTA titration. The Li content was analyzed by ICP with internal standard method with coefficient of deviation less than 0.2%.[8] The deviation coefficients for other metal analysis are much better, and thus the third decimal of the results is reliable.

Electrochemical characterization for the Mg-doped materials 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 or 0.4 mA/cm^2 respectively with coin cells.[9] The electrolyte with 1 M $LiPF_6$ in EC/DMC (1/2 in volume) was supplied by Ube Industries Ltd. Mn dissolution content of the as-prepared materials after storage for several weeks at 60 °C was determined by ICP spectroscopy.[9]

It have been well-recognized that calcination temperature is of great importance to the characteristics of Mn system spinels, such as oxygen defect and particle size. Up to now, lots of research work have been devoted to the oxygen deficiency in the spinels, and it could be identified by the charge/discharge profiles or analyzed by chemical analysis.[10,11] The initial two charge/discharge curves for the cathodes of Mg010-800, Mg010-1000, and Mg010-N were shown in Figure 1. No evident extra plateau at around 3.2 V correlated with oxygen defi-

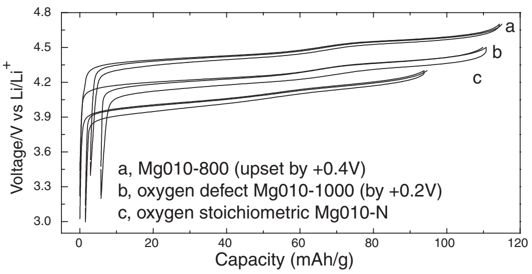

Figure 1. Initial two cycles for the Mg010-800, Mg010-1000, and Mg010-N cathodes (0.1 mA/cm^2 at room temperature).

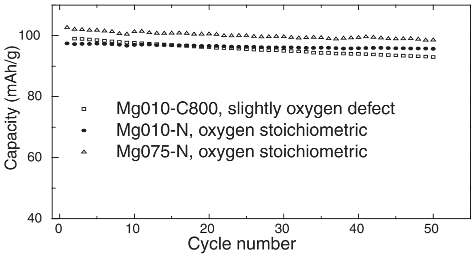

Figure 2. Cycle performance of Mg010-C800, Mg010-N, and Mg075-N cathodes at 60 °C ($0.4\,\mathrm{mA/cm^2}$).

ciency was observed for Mg010-800 (by calcination at 800 °C), this indicates nearly no oxygen defect. After increasing the calcination temperature to 1000 °C, a small extra plateau appeared for Mg010-1000. The extra plateau would disappear for Mg010-N after annealing at 600 °C in the two-step procedure. This means that annealing with extra LiOH at 600 °C can compensate the oxygen deficiency originated from calcination at 1000 °C to obtain oxygen stoichiometric spinels. It could be imagined that the extra LiOH played a very important role in the annealing process. The oxygen defect intermediate Mg010-1000 ($\mathrm{Li}_{1.005}\mathrm{Mg}_{0.097}\mathrm{Mn}_{1.898}\mathrm{O}_{3.995}$) could absorb some oxygen and lithium to be oxidized/recrystallized into oxygen stoichiometric Mg010-N. Therefore, a new type of Mg-doped spinels with oxygen stoichiometry can be prepared. All the Mg-doped spinels in this paper were characterized by powder XRD to be of single cubic phase and ($Fd\,\bar{3}m$) space group.

Figure 2 shows the elevated temperature cycle performance of Mg010-C800 ($\mathrm{Li}_{1.035}\mathrm{Mg}_{0.093}\mathrm{Mn}_{1.873}\mathrm{O}_{3.999}$, prepared by conventional method at 800 °C), and the new type materials Mg010-N and Mg075-N. Average capacity retention ratio[9] for Mg010-C800 is about 99.87%/cycle during cycling at 60 °C, which is much better than undoped spinels,[1] and it was improved greatly to ca. 99.97%/cycle (very close to 100%, the ideal value) for Mg010-N. The initial capacity for Mg010-N is about 97 mAh/g, and it could be increased to ca. 103 mAh/g for Mg075-N (ca. 99.93%/cycle) by reducing the Mg doping content. The two materials Mg010-C800 and Mg010-N have almost the same Mg or metal doping content but different oxygen content because of different synthesis procedure. The analyzed oxygen content for Mg010-C800 is 3.999 (very slight oxygen defect), and it is 4.021 for Mg010-N (4.010 for Mg075-N). Mg010-N can be expressed as oxygen stoichiometric $[\mathrm{Li}]_{8a}[\mathrm{Li}_{0.031}\mathrm{Mg}_{0.10}\mathrm{Mn}_{1.854}\ {}_{0.015}]_{16d}[\mathrm{O}_4]_{32e}$ from the view point of structure. So the main reason for the significantly improved cycleabilty at elevated temperature is the oxygen content of Mg-doped spinels.[2] Another reason for the improved cycleability should be noted here is the improved crystallinity. It was found that the $I_{\max}$/fwhm of the (111) peak, a useful index for XRD peak sharpness or powder crystallinity, is 2146/0.22 and 2441/0.18 for Mg010-C800 and Mg010-N respectively (fwhm represents full width at half I_p maximum). This should be ascribed to the first-step calcination or crystallization at "ultra-high" temperature (ca. 1000 °C).

Besides the improved cycleability, reduced Mn dissolution is also necessary for the application of spinel cathodes in Li-ion batteries at elevated temperatures (together with graphite anodes).[4] The measured Mn dissolution content is about 20 ppm for Mg010-C800 after two weeks storage at 60 °C, and it was reduced significantly to ca. 3 ppm for Mg010-N and Mg075-N. It is much larger for undoped $\mathrm{LiMn_2O_4}$ by conventional method (about 100 ppm). One reason for the reduced Mn dissolution is the improved crystallinity of our new type materials.[3] Another reason is the decreased specific surface area. The average particle size for Mg010-C800 was about 0.4 μm and it was enlarged to ca. 4 μm for Mg010-N as shown in Figure 3. The measured BET surface area was ca. 3.0 and ca. $0.5\,\mathrm{m^2/g}$ for Mg010-C800 and Mg010-N, respectively. Therefore, the reduced Mn dissolution could be expected after the material surface area or contact area between the spinel particles and the organic electrolyte was decreased.[3]

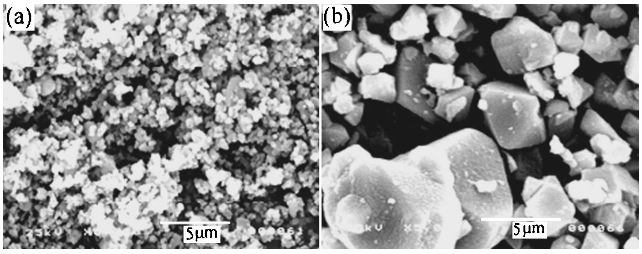

Figure 3. The SEM images for Mg010-C800 (a) and Mg010-N (b).

In conclusion, a new type of oxygen stoichiometric Mg-doped spinels showing greatly improved cycleability and reduced Mn dissolution at elevated temperatures was prepared through a two-step method. The new kind materials with reversible capacity of 100–110 mAh/g are promising to satisfy the requirements of Li-ion batteries for long-term application.

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