Preparation of $Li_{1+y-x}Zn_xMn_{2-y}O_4$ Spinel as a Cathode Material for Li^+-batteries

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$Li_{1+y-x}Zn_xMn_{2-y}O_4$ spinel has been synthesized using LiOH, $Zn(NO_3)_2$, and MnO_2. The substitution of Zn^{2+} for Li^+ in the tetrahedral 8a site of spinel was successfully achieved by adjustment of the synthetic conditions, such as atmosphere and cooling rate. The performance of 8a site Zn-doped spinel was investigated in the terms of initial capacity and polarization.

The increasingly widespread application of portable electronic technology has spurred a high demand for light-weight, high-energy, high-power, and long-life rechargeable batteries. Recently, great attention has been focused on $LiMn_2O_4$ spinel, the 4V-cathode material for lithium-ion batteries because of nontoxicity and low cost. However, the spinel $LiMn_2O_4$ always suffers from a severe capacity loss at elevated temperature, which drawback will preclude its wider use for practical batteries. This phenomenon may partly be ascribed to Jahn–Teller distortion, which results in the structure fatigue and even de-integrations within $LiMn_2O_4$ particles.[1] One effective way to ameliorate Jahn–Teller distortion is to elevate Mn oxidation state by cation doping with suitable metal ions.[2–5] The doped cation can occupy either the octahedral 16d or tetrahedral 8a sites of the spinel structure, in both cases the foreign metal ions can influence greatly the performance of spinel. For example, in the case of Cr-doped spinel, the improved stability was attributed to Cr substitution at 16d site.[6,7]

Zn doping is of interest in the viewpoint of its preference for the tetrahedral sites. Some groups have attempted to correlate the substitution of foreign metal ions to 8a sites of spinel for the improvement of cycleability in the terms of retarding Mn dissolution.[8,9] In turn, Zn^{2+} occupation of 8a site can force some Li^+ migrating from 8a sites to 16d sites and thus make the situation more complex. Cation ordering sometime takes place in 16d site, causing a symmetry reduction of the spinel from space group $Fd3m$ to $P4_332$ (same as $P4_132$).[10] Moreover, $ZnMn_2O_4$ is a potentially possible impurity in the Zn-doped spinel products. All the multiple factors make the correct evaluation of Zn-doped spinel a heavy task.

We have tried to synthesize Zn-doped spinel by elaboration of the experimental conditions. Here, we report how to prepare the pure 8a site-Zn-substituted spinel. Its performance as a cathode material for lithium-ion battery is also shown.

The mixture of LiOH, $Zn(NO_3)_2$, and MnO_2 powders was pre-calcined at 470 °C for 20 h in air, post-calcined at temperatures range from 600 to 800 °C for 20 h in air or oxygen atmosphere, and then the furnace was cooled or quenched by liquid nitrogen. The powder X-ray diffraction (XRD) using Cu Kα radiation was employed to identify the crystal structure of the samples. Rietveld program (RIETAN) was applied for refining the XRD profiles. Li and Zn contents were determined by atomic absorption spectroscopy and spectrophotometry using PAN, respectively. Total heavy-metal content was determined by the complexometry. The details of electrochemical cell and the fabrication procedure of the electrode were the same as those described previously.[11] The electrolyte was 1 mol/dm^3 $LiPF_6$-ethylene carbonate/dimethyl carbonate (1:2 by volume). The current density was 0.4 mA/cm^2 with the cut-off voltages of 3.5 and 4.5 V.

The preparation conditions for Zn-doped spinel should be controlled very strictly, which at least include the following aspects, the relative atomic ratio of metal ions, the heating history, and the atmosphere. Figure 1 demonstrates the XRD patterns of the various samples. In Figure 1a, the effect of cooling method could be observed. The sample obtained by slow cooling can be mainly indexed as the space group $P4_132$ besides weak impurity peaks of $ZnMn_2O_4$, which implies cation ordering occurs in the 16d sites during slow cooling. In the contrast, rapid cooling generates typical XRD pattern of $Fd3m$ symmetry, the diffraction peaks of (220) and (422) are indicative of the occupation of 8a sites by Zn^{2+} ion. Then, it appears that cation ordering in 16d sites is thermodynamically preferred, while the $Fd3m$ symmetry of Zn-doped spinel could be "frozen" from high temperatures drastically through rapid cooling. So rapid cooling method such as liquid nitrogen quench is valuable for the preparation

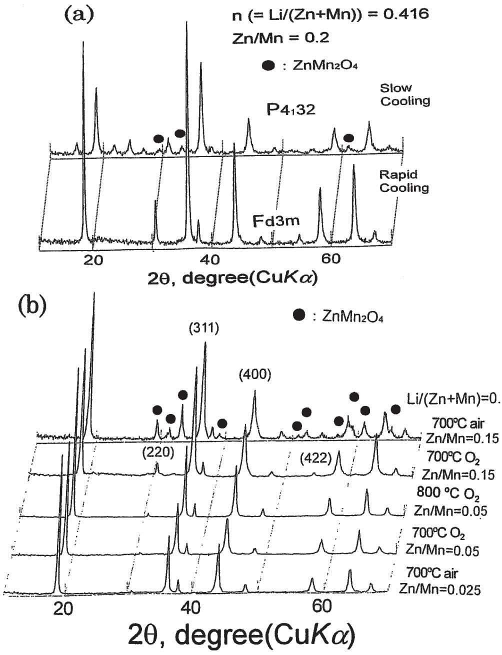

Figure 1. XRD patterns of Zn-doped spinel samples prepared at different conditions; (a) Li/(Zn + Mn) = 0.416, Zn/Mn = 0.2, slow and quick cooling methods; (b) Li/(Zn + Mn) = 0.5, Zn/Mn = 0.025, 0.05, or 0.15, in air or O_2.

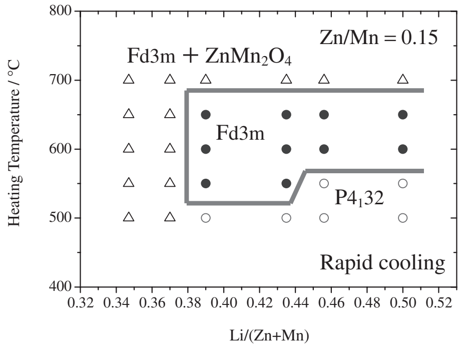

Figure 2. Phase diagram of Li–Zn–Mn–O (Zn/Mn = 0.15) calcined in air and rapidly cooled.

of Zn-doped spinel with *Fd*3*m*. Figure 1b shows the effect of atmosphere (oxygen or air) for the rapid-cooled samples. For the samples containing higher Zn contents (say, Zn/Mn = 0.15), $ZnMn_2O_4$ formed under air could be precluded under oxygen atmosphere. At lower Zn content, the signs of $ZnMn_2O_4$ could hardly be identified. Although (220) and (422) peaks become weak in such a case, the high peak intensity ratio of (311)/(400) is a fingerprint of Zn residence at 8a sites.

Figure 2 shows the phase diagram of Li–Zn–Mn–O (Zn/Mn = 0.15) calcined in air and rapidly cooled. It can be seen that $ZnMn_2O_4$ is stable at temperatures higher than 700 °C in air and in low Li/(Zn + Mn) ratio. The solid-line circled region illustrates the suitable conditions to get 8a site-Zn-doped spinel at the doping level of Zn/Mn = 0.15.

Figure 3 demonstrates Zn occupancy in 8a site and corresponding Li occupancy in 16d site. Those are determined by Rietveld refinement for the samples prepared at 700 and 800 °C, respectively. For Zn occupancy in 8a sites, both groups of points fall in the theoretical solid line deduced by assuming all Zn resides in 8a site. The selective occupancy of Zn in 8a site can thus be verified. However, if the ratio of Li/(Zn + Mn) is lower than 0.5, Li occupancy in 16d site is less than half of the occupancy value of Zn in the 8a site. Consequently, Mn^{3+} content rises up in the Zn-doped spinel, enlarging the capacity.

Figure 4 shows the initial charge-discharge profiles of the representative $Li_{1+y-x}Zn_xMn_{2-y}O_4$ spinel samples. The theoretical capacity of $LiZn_{0.096}Mn_{1.904}O_4$ (Zn/Mn = 0.05) is about 119.6 mAh/g.[12] Nevertheless, some samples with reduced Li contents (Li/(Zn + Mn) = 0.43 or 0.45, 800 °C) deliver the capacities of 120–127 mAh/g. Ideal spinel formula for $n = 0.43$ and 0.45 would be written as $[Li_{0.900}Zn_{0.100}]_{8a}[Mn_{1.998}Li_{0.002}]_{16d}O_4$ and $[Li_{0.901}Zn_{0.099}]_{8a}[Mn_{1.970}Li_{0.030}]_{16d}O_4$, respectively (*n* stands for the atomic ratio of Li/(Zn + Mn)). The calculated capacities limited by 8a site Li^+ content are 129–131 mAh/g. Experimental data agree well with the above capacity. These results and Li MAS NMR study for $LiZn_{0.1}Mn_{1.9}O_4$[13] support the selective occupation of Zn in 8a site of spinel structure. The polarization between the charge and discharge curves is about 0.2 V, comparable to that for $LiMn_2O_4$. This phenomenon means that 10% occupation of Zn in 8a site doesn't influence Li^+ diffusion rates remarkably.

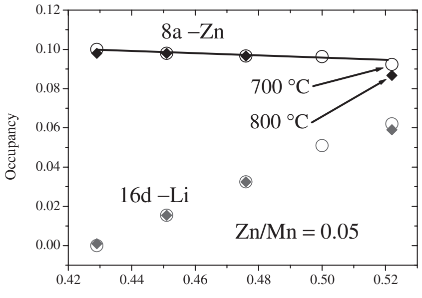

Figure 3. Occupancy of Zn in the tetrahedral site and the corresponding Li occupancy in the octahedral site as a function of the atomic ratio of Li/(Zn + Mn)(700 and 800 °C, Zn/Mn = 0.05, 0.429 < Li/(Zn + Mn) < 0.523).

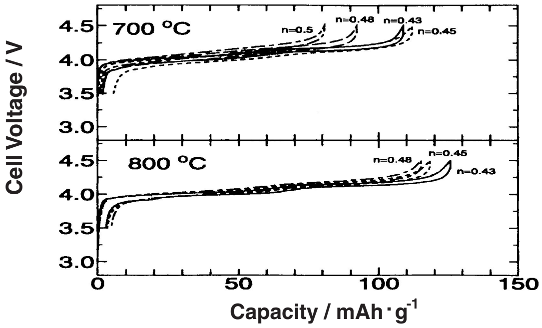

Figure 4. Initial charge–discharge profiles of the representative $Li_{1+y-x}Zn_xMn_{2-y}O_4$ spinel samples(Zn/Mn = 0.05, n = Li/(Zn + Mn)).

In conclusion, the preparation for Zn-doped Li–Mn–O spinel was studied in detail. Zn substitution for Li in the tetrahedral 8a site has been fulfilled. 8a site-Zn-doped spinel shows satisfactory performance in the terms of high initial capacity and relative low polarization between charge and discharge curves.

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