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Improved cycling performance of oxygen-stoichiometric spinel $Li_{1+x}Al_yMn_{2-x-y}O_{4+\delta}$ at elevated temperature

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Abstract

$Li_{1+x}Al_yMn_{2-x-y}O_{4\pm\delta}$ spinel cathode materials for lithium-ion batteries have been prepared by two methods, a specific two-step and the conventional one-step solid-state calcination methods. Compared with the conventional method, the new two-step method can guarantee the oxygen stoichiometry in spinel samples as well as reduced surface area. These characters lead to the improvement in cycling performance of spinel cathode even at elevated temperature. Moreover, the increase in doping amount of Al into Mn-spinel contributes to smearing the oxygen deficiency at high calcination temperature (1000 °C). The oxygen stoichiometric spinel samples exhibited greatly improved cycling performance. Further, Mn dissolution from spinel cathodes into the electrolyte was sufficiently suppressed even at elevated temperature of 60 °C. This beneficial influence would be reflected more remarkably in the cycles of lithium-ion full cells (spinel/C).
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Keywords: Al-doped spinels; Cycling performance; Oxygen stoichiometry; Mn dissolution; Lithium-ion batteries

1. Introduction

Spinel type lithium manganese oxides are the most promising cathode materials for lithium ion batteries because they are cheaper, less toxic and more easily prepared than other candidates (lithium nickel oxides and lithium iron orthophosphate). A problem hindering the practical application of Mn spinel is the capacity fading upon cycling in both the spinel/Li and spinel/carbon cells, especially at elevated temperature. Several reasons have been suggested to explain its degraded cycling performance, including structural instability [1–3], Jahn–Teller distortion [4] and Mn dissolution into electrolyte [5–7], etc.

It has been recognized that partial substitution of Mn with other metal cations, such as Li, Co, Ni, Al, Mg, Cr, Fe and so on [9–17], can improve the cycling performance of spinel cathode. However, the capacity fading mechanism of metal-doped spinel remains not clear. Now, we believe that the oxygen stoichiometry of spinel is the most important factor controlling the capacity retention during cycling [2], and metal doping only plays a role in helping the formation of oxygen stoichiometric spinels.

The spinel cathode materials should be prepared at relatively milder temperature of less than 850 °C in order to suppress the formation of oxygen deficiency. Such oxygen stoichiometric spinels prepared by one step calcination have inevitably caused higher specific surface area and low crystallinity. The surfaces of spinel samples possess a certain catalytic activity towards electrolyte oxidation, and then high surface area is likely to trigger the electrolyte oxidation which accompanies dissolution of Mn from spinel. Dissolved Mn ion would destroy SEI film formed on the graphite anode and make the performance of full lithium-ion battery become worse [18]. Especially, such effect becomes more severe at elevated temperature so that ordinary oxygen stoichiometric spinel with high surface area can not be used as cathode material in practical lithium ion batteries.

For the sake of overcoming this problem, many researchers use coating technique [19–23], which would lead to lower rate capability. The spinel cathode materials were prepared at high temperature (>850 °C) in order to decrease the surface area. Such spinels with lower surface area often present oxygen deficiency. Recently, Takahashi et al. [24] reported that annealing at 800 after 1000 °C calcinations can reduce the oxygen defect

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content in the Mg-doped spinel and they showed improved discharge capacity even after the storage at 60 °C. However, we also noticed that a 3.2 V plateau still exits (although very tiny to be perceived) in their modified spinel.

In this paper, we have proposed very simple technique to decrease Mn dissolution and improve cycling performance of spinel cathode materials at elevated temperature. Here, two heating processes are used. High temperature heating in initial step contributes to help the development of crystal growth and leads to decrease in specific surface area. However, resulting intermediate samples belong to oxygen deficient spinel. The oxygen deficiency is repaired in the second step by heating at relatively lower temperature (ca. 600–700 °C) with excess Li salt.

We have synthesized a new spinel with Al-doping and "controlled" oxygen stoichiometry with small specific surface area by above new two-step method. These new materials have shown very low Mn dissolution of 3.2 ppm in electrolyte at 60 °C, and greatly improved cycling performance at elevated temperatures compared to those synthesized by conventional method, especially in the full lithium ion battery (graphite/spinel).

2. Experimental

Various metal-doped Mn-spinels ($LiMn_{1.9}M_{0.1}O_{4-\delta}$; M: Li, Mg, Al, Cr, Co, Fe and Ni; δ: oxygen defect content) were synthesized by a conventional solid state reaction from the mixtures of starting materials, such as LiOH (FMC Co.), Mn_3O_4 (Mitsui Mining Co.), MgO (Ube Co.), Al_2O_3 (Showa Electric Co.), Cr_2O_3 (Koujundo Kagaku Co.), Co_3O_4 (Seido Chemical Co.) Fe_2O_3 (Koujundo Kagaku Co.) and NiO (Seido Chemical Co.). They were fired at 900–1000 °C for 10 h in air, where the rate of the heating/cooling was controlled to be 100 °C/h.

Two series of $Li_{1+x}Al_yMn_{2-x-y}O_{4\pm\delta}$ ($x = 0.05$, $y = 0.05$, 0.10 and 0.15) samples were prepared by two different methods, respectively. The N series samples were prepared by a two-step solid state reaction: (1) in the first step; the mixture of LiOH, Al_2O_3 and Mn_3O_4 (in the mole ratios of 1:0.05:1.95, 1:0.10:0.9 and 1:0.15:0.85 for N–Al005–660, N–Al010–660 and N–Al015–660, respectively) was heated at 500 °C for 5 h and then calcinated at 1000 °C for 10 h to get an intermediate product with small surface area; (2) in the second step; the extra LiOH (0.05 for 1.0 LiOH in the staring material) was added into the intermediate product and then annealed at 660 °C for 10 h to get the final product. Another C series samples designed as C–Al005–*T*, C–Al010–*T* and C–Al015–*T* ("T" is 800, 850, 900, 950 or 1000 corresponding to the calcination temperature), which have almost the same Al content with N–Al005–660, N–Al010–660 and N–Al015–660, were prepared by the conventional one-step method [2]. The chemical composition of as-prepared samples were determined by chemical analysis and listed in Table 1. The details of chemical analysis were described in the previous paper [8].

The structures of the samples were characterized by XRD (Rigaku Rint 1000) using Cu Kα radiation. The specific surface area was measured by the BET method (Micromeritics Flowsorb III). The morphologies of the materials were observed by scanning electron microscopy (SEM).

The Mn dissolution was determined by ICP after two weeks storage of 3 g as-prepared samples in 30 ml of electrolyte solution at 60 °C.

The electrochemical performance of spinel was evaluated using CR2032 coin-type cells. Cathodes were prepared by mixing Mn-spinels with 8 wt.% polyvinylidene fluoride (PVDF) and 4 wt.% acetylene black (AB). The slurry mixture was coated on an Al foil and then pressed. Unless specified otherwise, lithium metal was used as an anode and glass fiber (GA-100) as the separator (Toyo Roshi Kaish Ltd., Japan). The electrolyte was 1 M $LiPF_6$-ethylene carbonate/dimethyl carbonate (EC/DMC, 1:2 by volume) (Ube Industries Ltd., Japan). Cells were galvanostatically charged and discharged with a cut-off voltage range of 3–4.3 V versus Li/Li^+ electrode at room temperature (RT) and 60 °C.

In the lithium ion batteries, the MCMB6-28 anodes were prepared by coating the slurry of 90% MCMB6-28 (Osaka Gas Co. Ltd.) and 10% PVDF (Kureha Co. Ltd.) dissolved in *N*-methyl pyrrolidone (NMP) is coated onto copper foil. An electrochemical test in the voltage region of 3–4.2 V was performed at a constant charge/discharge rate of 0.4 mA/cm^2 at room temperature and 60 °C.

3. Results and discussion

From the previous studies, it was found that oxygen deficiency is always present in extra-heated spinel samples. In the charge–discharge profiles for oxygen-deficient spinel, a 3.2 V discharge plateau usually appears, together with 4.5 V charge–discharge plateaus delivering equivalent capacities. The quantitative relationship between the 3.2 V plateau capacity and oxygen vacancy degree have been already established in Li–Mn–O spinel compounds [25]. Fig. 1 shows the effect of various foreign metals doping on the initial discharge capacity of the 3.2 V plateau ($C_{3.2\,V}$) for $LiMn_{1.9}M_{0.1}O_{4-\delta}$, (M: Mg, Al,

Table 1
Chemical formula of Al-doped spinels

Sample name	Chemical composition	Average Mn valance	Prepared method
C–Al005–1000	$Li_{1.033}Al_{0.049}Mn_{1.918}O_{3.990}$	3.545	One-step method
C–Al010–1000	$Li_{1.035}Al_{0.110}Mn_{1.855}O_{3.994}$	3.570	One-step method
C–Al015–1000	$Li_{1.041}Al_{0.148}Mn_{1.811}O_{3.997}$	3.594	One-step method
N–Al005–660	$Li_{1.035}Al_{0.053}Mn_{1.912}O_{3.993}$	3.552	Two-step method
N–Al010–660	$Li_{1.038}Al_{0.097}Mn_{1.865}O_{3.999}$	3.576	Two-step method
N–Al015–660	$Li_{1.039}Al_{0.146}Mn_{1.815}O_{4.017}$	3.613	Two-step method

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