Effect of Al₂O₃-Coated α-LiMnO₂ Cathodes Prepared at Various Temperatures on the 55°C Cycling Behavior

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Abstract: The electrochemical cycling behavior of Al₂O₃-coated orthorhombic LiMnO₂ (α-LiMnO₂) cathodes prepared at various temperatures (150–700°C) is investigated. The cathodes prepared at 400°C exhibit the best cycling performance, maintaining a maximum capacity of bare α-LiMnO₂, with a minimal capacity loss. However, an increase in cycling temperature reduces the initial capacity and maximum capacity to 150 mAh/g and 75 mAh/g, respectively, between 4.4 and 2.5 V after 100 cycles. Mn dissolution in LiMn₂O₄ spinel was the origin of elevated HF, which drastically increases the dissolution of Mn at 55°C cycling. In order to improve the structural stability of the α-LiMnO₂ cathode during 55°C cycling, a partial substitution of Mn with Al in Li₅Mnₓ₋₅AlₓO₂ was studied by Chiang et al. In this article, we report the effect of electrochemical cycling on α-LiMnO₂ cathode materials that were prepared with a sol-gel coating of Al₂O₃ and subsequent heat-treatments at various temperatures ranging from 150 to 700°C. This sol-gel coating provides a means of controlling the specific capacity depending on the heat-treatment conditions.

Experimental: α-LiMnO₂ powders were prepared using stoichiometric amounts of LiOH·H₂O and MnO₂ (1.05:1 mol ratio) and heating at 800°C for 24 h under N₂ or Ar atmospheres. An excess amount of Li (0.05 mol) was used to compensate for the loss of Li during firing. To coat Al₂O₃ on the α-LiMnO₂ powder surface (with an average particle size of 13 μm), aluminum ethylhexanodiolisopropoxide Al(OOC₂H₅)₃(OCH₂)₂Al was first dissolved in 2-propanol, followed by continuous stirring for 20 h at 21°C. The powders were then mixed with the coating solution such that the total amount of the coating solution corresponded to 15 wt % of the α-LiMnO₂ powders used. Metal alkoxides of Al(OR)₃ were first hydrolyzed into Al(OR)₃(OH) by a reaction with H₂O in the atmosphere. Subsequently, the Al-OH groups in the hydrolyzed alkoxides Al(OR)₃(OH) were polycondensed into Al-O groups to form (OR)₃Al-O-Al(OR)₃ within the coating layer. Finally, the Al-OR
groups reacted with the o-LiMnO₂ surface-OH groups, resulting in a good adhesion of the Al₂O₃ gel to the o-LiMnO₂ particle surface. During firing, the Al alkoxide gel on the o-LiMnO₂ surface-O-Al(OR)₃ was first decomposed into amorphous Al₂O₃ and then crystallized. After drying the o-LiMnO₂ powders coated with the aluminum alkoxide gel at 150°C for 10 h, the batches were then fired at 400, 500, 600, and 700°C, respectively, for 10 h in a dried air atmosphere.

For electrochemical testing, cathode slurry was prepared by mixing the oxide powders, carbon black (Super P), and poly(vinylidene) fluoride (PVDF) in the weight ratio of 92:4:4. When the slurry reached an appropriate viscosity, it was coated on an aluminum foil using a minicoater, and the N-methylpyrrolidone was completely evaporated at 150°C for 1 h in a dried air atmosphere. And the cell was remade replacing the cycled Li-metal anode with fresh Li. These remade cells showed similar capacity within 170 mAh/g, comparable to those of the matching original cells after 50 cycles. This confirmed that the capacity fading of the original cell after cycling was due to the cathode. XRD patterns were taken after 50 cycles using the electrodes that were prepared as follows: the cycling tests were stopped at the end of discharge at 2 V and held at this voltage for 20 h. The cells were then disassembled carefully in a glove box to remove the cathode. The sample cathode was subsequently washed with DMC to remove the LiPF₆, followed by drying in a vacuum oven at 80°C for 24 h. An electron probe microanalysis (EPMA, JXA-8900R, JEOL) was used to measure the Al concentration profile from a cross-sectioned particle, and Auger electron spectroscopy (AES) with sputtering was used for the concentration profile in the vicinity of the particle surface.

Results and Discussion

The XRD patterns of the Al₂O₃-coated o-LiMnO₂ samples prepared at 150, 400, 500, 600, and 700°C are shown in Fig. 1. A small concentration of Li₂MnO₃ phase was observed in the coated LiMnO₂ specimen prepared at 150°C, which is similar to the case of bare o-LiMnO₂, but it disappeared at 400°C. The formation of the Li₂MnO₃ phase was due to a reaction with oxygen in the atmosphere. Since this phase disappeared after heat-treatment at 400°C, Li₂MnO₃ was probably distributed mainly at the surface, thus decomposing to LiAlO₂ and LiMnO₂ (Fig. 1). However, the LiAlO₂ phase disappeared after heat-treatment at 700°C (Fig. 1). In addition, the splitting of (130) diffraction peak is interesting, increasing with heat-treatment temperature. A full-width-at-half-maximum (FWHM) of the (011) peak from bare and 400°C samples, which is indicative of the degree of stacking faults between the Mn and Li sites, was approximately Δ(2θ) = 0.096° (after correcting with the instrumental resolution function), corresponding to <1% stacking faults. However, this width is wider than that of o-LiMnO₂ (0.015°) reported by Jang et al. indicating the formation of a more disordered orthorhombic structure.
Although the XRD patterns do not show evidence of Al₂O₃ or LiMn₁₋ₓAlₓO₂ formation from a reaction between the Al₂O₃ gel and o-LiMnO₂, LiAlO₂ formation as a minor peak indicates that the Al₂O₃ gel solution reacted with the o-LiMnO₂ at the surface. In order to further investigate the distribution of Al atoms throughout the particle after coating, EPMA was used to map its distribution, as shown in Fig. 2. Coated samples prepared at 150, 400, and 500°C show that Al atoms are distributed within the ~1μm region. However, heat-treatments at higher temperatures (600 and 700°C) lead to a deeper diffusion of Al atoms into the particle. This is consistent with AES of samples prepared at 150 and 400°C, showing the formation of a LiMn₁₋ₓAlₓO₂ solid solution in the vicinity of the surface (an inset in Fig. 2). A sputtering rate of 260 Å/min obtained from standard SiO₂ is assumed to have the same sputtering rate in the present sample.

The different distribution of Al atoms in the surface region clearly affects lattice constants of the orthorhombic phase, a, b, and c. The lattice constant a decreases up to 500°C, while b and c increase up to 500°C (Fig. 3). However, the lattice constants, b and c, decrease at 600 and 700°C. The increasing lattice constants, b and c, up to 500°C is probably due to the discretely higher Al concentration at the surface than in the bulk. However, the trend at 600 and 700°C is believed to be due to deeper diffusion of Al atoms into the particle. A similar behavior was also observed in SnO₂-coated LiCoO₂. Such a different Al distribution also influences the cycling behavior of coated electrodes, showing large capacity variation depending on the heat-treatment temperature. The discharge capacities of the coated electrodes prepared at 400 and 500°C are 170 and 167 mAh/g, respectively, between 4.5 and 2 V at a rate of 0.2 C (36 mA/g) after six cycles. However, those prepared at 600 and 700°C show a rapid decrease to 100 and 95 mAh/g, respectively (Fig. 4a). Note that capacities of the coated samples prepared at 400 and 500°C are similar to that of bare o-LiMnO₂. Such a rapid capacity decrease in samples prepared at 600 and 700°C is due to the uniform formation of the solid solution, o-LiMn₁₋ₓAlₓO₂, across the particle. A higher capacity in the coated LiMnO₂ prepared at lower temperatures may be due to the formation of a thin solid solution at.
the particle surface. In addition, capacity retention of the coated electrodes appears to deteriorate with increasing heat-treatment temperatures, showing 2, 6, 30, and 33% losses of discharge capacities after 50 cycles. This again shows that the capacity retention is effective with a thin coating of $\text{LiMn}_{0.95}\text{Al}_{0.05}\text{O}_2$ on the LiMnO$_2$ powders. However, capacity retention of the coated sample prepared at 700°C, in which LiMn$_{0.95}$Al$_{0.05}$O$_2$ was formed uniformly across the particle, is much worse than that of the homogeneous $\text{o-LiAl}_{100-x}\text{Mn}_{100+x}\text{O}_2$, which shows only a 3% capacity loss after 50 cycles.$^4$ Such a difference may be due to the different C rates used. Chiang et al.$^4$ used charge and discharge current rates of 150 and 75 mA/g, which are five and two times, respectively, faster than this study (36 mA/g for charge and discharge). Slower C rate tests at an elevated temperature caused higher capacity fading in the LiMnO$_2$ spinels.$^{31}$ At room-temperature cycling of the uncoated and coated electrodes, no capacity fading was observed after 50 cycles.

Structural studies were conducted on cycled electrodes discharged to 2 V after 50 cycles, as shown in Fig. 5. The XRD patterns clearly show that the major crystalline phases exhibit an overall cubic symmetry, irrelevant of the Al concentration. Note that the amount of monoclinic and Li$_2$MnO$_3$ phases increased with higher heat-treatment temperatures. Hence, coated electrodes prepared at 600 and 700°C consist of a majority of cubic, with a minor concentration of Li$_2$MnO$_3$ and monoclinic phases. On the other hand, coated LiMnO$_2$ specimens prepared at 400°C have only cubic phase after 50 cycles. The formation of the monoclinic phase gets reduced as the Al atoms remain at the particle surface, indicating that

$\sim 1$ µm thin coating of LiMn$_{0.95}$Al$_{0.05}$O$_2$ at the surface effectively suppresses the formation of the cycling-induced monoclinic phase. The formation of the Li$_2$MnO$_3$ phase was reported to be caused mainly by Mn dissolution from the Li$_2$Mn$_2$O$_4$ tetragonal spinel (space group $I4_1/amd$).$^{17}$ In order to study Mn dissolution from the bare and coated electrodes, half-cells were floated at the end of the 4 and 3 V plateaus (3.95 and 2.5 V, respectively) at constant-voltage modes for 20 h. (During six cycles, the cells were cycled at charge and discharge rates of 0.01 C.) The electrodes were then dissembled from the half-cells in the glove box, and kept in tightly sealed vials containing constant amounts of the electrolytes at 55°C for 15 days. The 4 and 3 V plateaus correspond to 0 < $x$ < 1 and 1 < $x$ < 2, respectively, in Li$_x$Mn$_{2-x}$O$_4$, where the Li atoms insert at the 8a tetrahedral sites and the 16c octahedral sites, respectively. Inductively coupled plasma (ICP) mass spectroscopy of the electrodes shows a distinct difference upon heat-treatment temperatures, as shown in Fig. 6. Mn dissolution in the electrodes floated at 2.5 V rapidly increases, compared to those floated at 3.95 V.

Furthermore, Mn dissolution proceeds much faster in the cathodes prepared at 600 and 700°C, than those prepared at 400 and 500°C. These results indicate that not only is Li$_2$Mn$_2$O$_4$ more structurally unstable than Li$_2$MnO$_3$ in an acidic electrolyte, but also the uniform (deep) formation of a solid solution across the particle is not effective in preventing Mn dissolution from the particle.

This argument is also supported by examining the capacities on the two voltage plateaus with cycling. While the coated samples prepared at 400°C show almost no capacity decreases at both the 4 and 3 V plateaus, those prepared at 700°C show a significant 3 V capacity decrease, thus showing 7 mAh/g after 50 cycles (Fig. 7a and b). However, the 4 V capacity loss was 34% (from 45 to 30 mAh/g), indicating that the Li$_2$Mn$_2$O$_4$ phase was transformed to defect-type spinels. The formation of these spinels cannot be identified by XRD because the diffraction peaks of those phases are superimposed on each other. Nonetheless, the degree of peak broadening indicates the formation of such defect spinels (Fig. 5). The results show that tetragonal Li$_2$Mn$_2$O$_4$ spinel is converted to rock salt Li$_2$MnO$_3$ during cycling. However, this contradicts the observation that o-LiMn$_2$O$_2$ appears to have no capacity fading over the 4 and 3 V plateaus during room-temperature cycling, while the XRD patterns of the cycled electrode clearly show increased peak broadening.$^5$ This can be attributed to the small crystallite size and increased lattice strain, but not to Mn dissolution.
On the other hand, peak broadening in the coated samples prepared at 400 and 500°C can be attributed to other reasons, since both ICP analysis and the capacity-evolution plot at the 4 and 3 V plateaus indicate that Mn dissolution from the LiMn$_2$O$_4$ and Li$_2$MnO$_3$ is not likely to occur. Instead, such broadening may be associated with the small crystallite size and/or lattice strain. To confirm this, XRD peak widths $\Delta k \sim \text{FWHM}$ were fit for each peak with the scattering vector $k = (4\pi\lambda \sin \theta)$ (Fig. 8). A resolution function ($\Delta k_{\text{resol}} = 0.0046 \text{ Å}^{-1}$) was subtracted after fitting each diffraction peak to consider the instrumental broadening effect in diffraction. As shown in Fig. 8, $\Delta k$ has increased from $\Delta k = 0.0065 \pm 0.0021 \text{ Å}^{-1}$ (averaged from (010) up to (112) peaks) before cycling to $\Delta k = 0.0328 \pm 0.0204 \text{ Å}^{-1}$ (averaged from (111) up to (440) peaks) after cycling in electrodes at 400°C, indicating that the small crystallite size (on the order of a few hundred angstroms) and/or lattice strains were developed during cycling. Similar trends are observed in the coated sample prepared at 500°C. Further studies are currently underway to separately identify the broadening mechanisms of the low-index peaks, (111) and (311), and high-index peaks, (222), (400), and (440).

Conclusions

Al$_2$O$_3$-coated LiMnO$_2$, prepared at 400°C for 10 h, exhibited both the least capacity loss and Mn dissolution compared to those prepared at 500, 600, and 700°C. A higher concentration of Al atoms at the surface than in the bulk apparently stabilizes the cubic LiMn$_2$O$_4$ and tetragonal Li$_2$MnO$_3$ lattices during cycling. However, when Al atoms diffused more deeply (uniformly) into the particle (LiMn$_{1-x}$Al$_x$O$_2$), capacity retention deteriorates. The increased degree of peak broadening after cycling in the coated cathodes prepared at lower temperatures was associated with the formation of nanosize crystallites and/or lattice strains, while peak broadening in those cathodes prepared at higher temperatures originated from Mn dissolution.

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