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Complete blocking of Mn^{3+} ion dissolution from a $LiMn_2O_4$ spinel intercalation compound by Co_3O_4 coating

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Complete elimination of Mn^{3+} dissolution from a $LiMn_2O_4$ spinel compound at 60 °C has been achieved by enclosing each particle with a $LiMn_{2-x}Co_xO_4$ solid-solution thin film having a high Co concentration at the surface.

$LiMn_2O_4$ cathode materials have received much attention due to their environmental friendliness and low cost compared to $LiCoO_2$ and $LiNiO_2$. However, their practical applications as Li-ion cells are hindered by structural instability from acidic HF attack on the spinel particles, as a result of the reaction of the $LiPF_6$ salt with residual water in the cell at elevated temperatures.[1–4] This leads to a disproportionation reaction ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$) at the particle surface, resulting in the formation of a defective spinel. The reaction moves progressively inward with increasing exposure to the electrolyte, especially at elevated temperatures. This reduces the intercalation capacity, and therefore should be prevented to ensure long-cycle life for elevated-temperature performance. To reduce such inherent structural degradation, a marginal increase in the overall Mn valence to above +3.5 has been reported.[5–9] However, such methods do not significantly improve the structural stability since a fraction of Mn^{3+} ions still exist in the spinel structure. The most effective way to block Mn dissolution is to completely encapsulate the spinel particles with oxides that are resistant to acidic HF. There have been several attempts to minimize Mn dissolution, but none have blocked the dissolution completely. Such studies even showed a deterioration in cathode-cycle performance compared to unmodified samples or decreased capacity fading during cycling at 55 °C.[10–12]

Here, we report a low-temperature coating method using Co_3O_4, and its effect on the cycling performance at 60 °C in Li/$LiMn_2O_4$ cells. This new approach completely blocks Mn dissolution from the $LiMn_2O_4$ particles.

$LiMn_2O_4$ powder ‘bare sample’ was prepared by firing a stoichiometric mixture of MnO_2 (EMD) and $LiOH{\cdot}H_2O$ at 750 °C for 20 h. The powder, with an average particle size of 13 μm after sieving, was used for coating and for the electrochemical experiments. To coat each particle with the solution of Co_3O_4, cobalt(III) acetate was first dissolved in methanol, then slowly mixed until it reached the appropriate viscosity. The solution was then mixed with the $LiMn_2O_4$ powder in a mole ratio of 10 : 1 (Mn : Co). The coated powder was dried at 150 °C for 1 h, and then fired at 400 °C for 8 h in a dry-air atmosphere. The electrochemical cycling experiments were carried out at 60 °C with coin-type cells (size 2016) containing a $LiMn_2O_4$ spinel electrode, a Li metal anode, a microporous polyethylene separator, and an electrolyte consisting of a 1 M $LiPF_6$ solution in a 1 : 1 EC–DMC mixture (by volume). To fabricate the cathode, the spinel powder was blended with Super-P carbon black (to assist in current collection) and with a polyvinylidene fluoride (PVDF) binder in a mass ratio of 92 : 4 : 4.

X-Ray diffraction (XRD) patterns of the bare- and coated-$LiMn_2O_4$ powders were indexed to cubic spinel ($Fd3m$). The Co_3O_4-coated sample shows no indication of Co_3O_4 or other phases, except for increased peak broadening compared to the bare sample (Fig. 1). This broadening may be due to the formation of a disordered spinel phase throughout the particle, with decreasing Co concentration inward. Raman spectroscopy of the coated sample clearly showed the presence of a Co_3O_4 phase (peak at 693 cm^{-1}), and electron-probe microanalysis

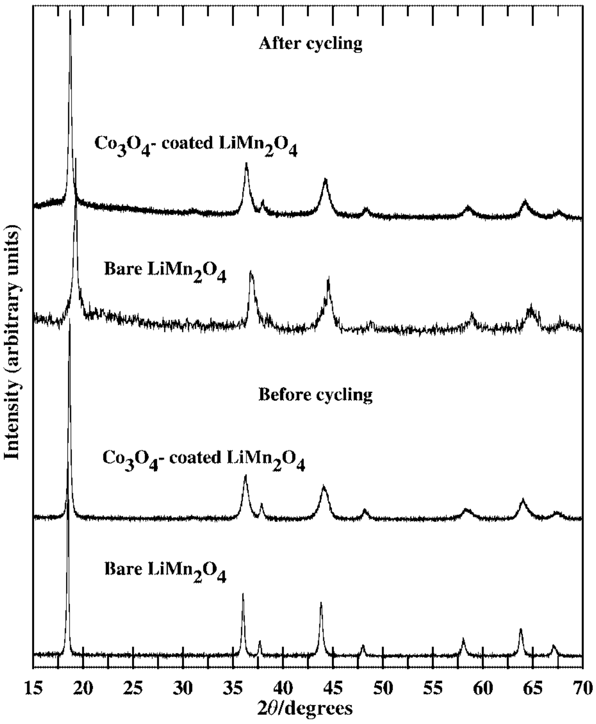

Fig. 1 XRD patterns of bare and Co_3O_4-coated $LiMn_2O_4$ powders before and after cycling.

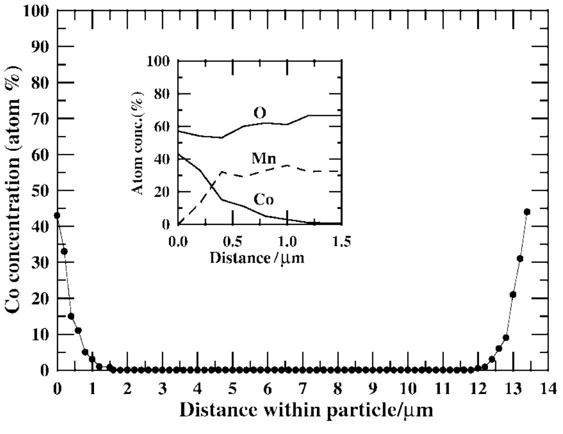

Fig. 2 EPMA of Co concentration across a particle cross-section; the inset corresponds to elemental analysis of the particle within 1.5 μm.

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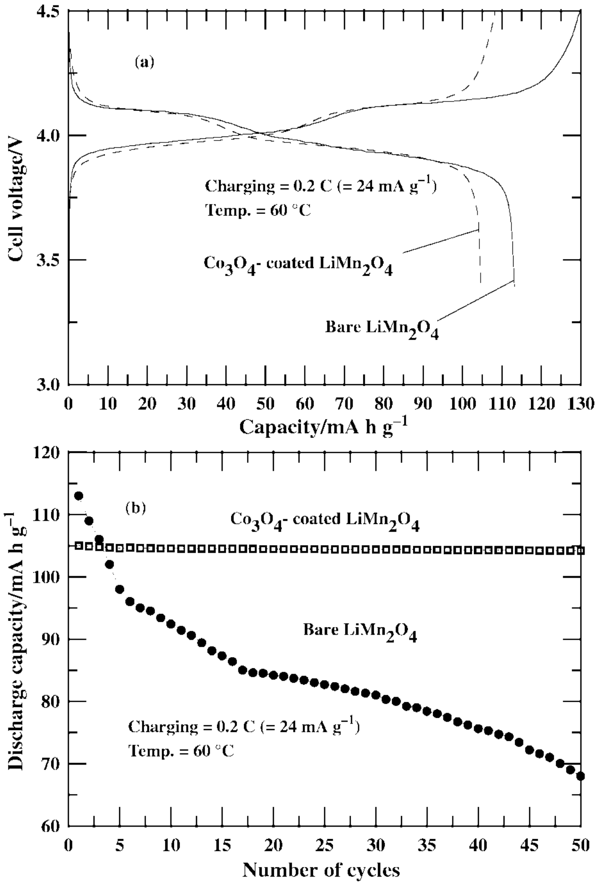

Fig. 3 Plots of (a) voltage profile of bare and Co_3O_4-coated $LiMn_2O_4$ at a charging rate of 0.2 C between 4.5 and 3.4 V, and (b) cycle-life performance of bare and Co_3O_4-coated $LiMn_2O_4$ at a charging rate of 0.2 C between 4.5 and 3.4 V. The coin-type half cells were cycled at 60 °C with a Li-metal anode

(EPMA) of the Co atoms across the particle shows a 43% Co concentration at the surface, as shown in Fig. 2, which is consistent with the Raman data. In addition, Co atoms were mainly distributed within *ca.* 1 μm from the surface, and their concentration sharply decreased further inside the particle. Results indicate the formation of a solid-solution $Li_zMn_{2-x}Co_xO_4$ thin-film phase near the surface by interdiffusion between $LiMn_2O_4$ and Co_3O_4. However, some portion of the unreacted Co_3O_4 resides on the solid solution. It is expected that the coating of each particle with $Li_zMn_{2-x}Co_xO_4$ and Co_3O_4 thin-film coatings, which are resistant to HF attack, can prevent Mn dissolution into the electrolyte.

All spinel compounds with a defective cubic structure have lattice constants smaller than the well-ordered $LiMn_2O_4$ phase, because of the higher concentration of the relatively large Mn^{3+} ion (ionic radii of Mn^{3+} and of Mn^{4+} are, respectively, 0.65 and 0.53 Å).[13] Therefore, from the XRD pattern, all the spinels within the $LiMn_2O_4$–$Li_4Mn_5O_{12}$–λ-MnO_2 tie-line-triangle in the Li–Mn–O phase diagram will have diffraction peaks that lie to higher 2θ values than those of $LiMn_2O_4$. This feature can be seen in the XRD patterns of the spinel electrodes after cycling at 60 °C and after equilibration at 3.4 V for 50 h (Fig. 1). They show a shift in the spinel peaks to higher 2θ values (a = 8.122 ± 0.003 Å), accompanied by peak broadening (the lattice constant of the bare sample before cycling is 8.234 ± 0.005 Å). This shows that the starting $LiMn_2O_4$ spinel becomes defective during cycling at 60 °C. However, the coated sample does not show any peak shift (a = 8.178 ± 0.005 Å) or peak broadening after cycling.

The cycling behavior of bare- and coated-$LiMn_2O_4$ materials was tested in coin-type half-cells using Li metal as the anode between 4.5 and 3.3 V at a rate of 0.2 C (= 24 mA g^{-1}) at 60 °C. Fig. 3 shows the initial voltage profiles of the samples. The discharge capacity of the coated sample was 105 mA h g^{-1}, while that of the bare sample was 113 mA h g^{-1}. The decreased irreversible capacity upon coating, 3 mA h g^{-1} *vs.* 17 mA h g^{-1} in the bare sample, is significant. Furthermore, there is negligible capacity loss in the coated sample over 50 cycles, while that of the bare sample shows a 41% loss. It is believed that surface encapsulation by both Co_3O_4 and $Li_zMn_{2-x}Co_xO_4$ prevents Mn dissolution from HF attack at 60 °C.

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