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$MgAl_2O_4$ spinel-coated $LiCoO_2$ as long-cycling cathode materials

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Abstract

The enhanced cyclability of $LiCoO_2$ coated with $MgAl_2O_4$ is described. A TEM examination of the microstructure of the coated particles revealed that the spinel formed a rather uniform coating over the cathode material. XRD data suggested the presence of substitutional oxides on the surface of the cathode particles. *R*-factor values from XRD studies and galvanostatic cycling studies suggested that a coating level of 1.0 wt.% gave an optimal performance in capacity and cyclability. A commercial sample of $LiCoO_2$ coated with 1.0 wt.% of spinel registered a five-fold improvement in cyclability. The improved cyclability is attributed to a suppression of the cycle-limiting phase transitions that accompany the charge–discharge processes.
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1. Introduction

The capacity fade with cycling of the lithiated cobalt oxide cathode is attributed to an anisotropic volume change, which results in a structural degradation of the host material during repeated cycling [1–3]. The cycling process is accompanied by a hexagonal–monoclinic–hexagonal phase transition [1]. Battery scientists have adopted a two-pronged approach towards enhancing the cyclability of the $LiCoO_2$ cathode. One approach relies on the theoretical studies of Ceder et al. [4], who suggested that the structural characteristics of $LiCoO_2$ could be improved by doping with non-transition metal ions. Although some measure of success can be claimed in this approach, it has been noticed that in some cases the structural stability degraded upon cycling, while in others, any improvement in structural stability was obtained at the expense of the deliverable capacity. The other approach involves coating the cathode particles with a thin layer of oxide materials such as Al_2O_3 [5–8], B_2O_3 [7], MgO [9–11], TiO_2 [7] and ZrO_2 [7]. The enhanced cyclability of the coated cathodes is thought to be due to the formation of substitutional oxides on the cathode surface, which bestow improved structural stability to the core material [9], and/or to a suppression of the cycle-limiting phase transitions associated with the intercalation–deintercalation processes by fracture-tough coating materials [7].

Both Al_2O_3 [5–8] and MgO [9–11] as coating materials have been demonstrated to result in improving the cyclability of $LiCoO_2$. In this paper, we examine the behavior of the mixed spinel oxide, $MgAl_2O_4$, as a coating material. Apart from the fact that the high refractory spinel contains the beneficial Al^{3+} and Mg^{2+} ions, it is mechanically robust and chemically inert.

2. Experimental

A semi-alkoxide sol–gel procedure [12] was adopted for coating commercial $LiCoO_2$ (Coremax Taiwan Corporation) with $MgAl_2O_4$. Coating levels (in wt.%) of $MgAl_2O_4$ used were 0.3, 1.0, 2.0 and 3.0. The $LiCoO_2$ powder was first sonicated for 30 min in an *iso*-propanolic solution of $Mg(NO_3)_2{\cdot}6H_2O$ containing a calculated amount of water. To this mixture, the required amount of Al(sec-OBu)$_3$ in *iso*-

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propanol was added in one stretch with continuous stirring. After 1 h of stirring, the mixture was dried in air at 40 °C, and calcined at 800 °C for 15 min at a heating rate of 1 °C min^{-1} to ensure complete adhesion of the coating material to the core oxide.

An X-ray diffractometer (Siemens D-5000, Mac Science MXP18) was used for structural analysis. Particle morphology and microstructure were examined by scanning electron microscopy (Hitachi model S-3500V) and transmission electron microscopy (JEOL JEM-200FXII), respectively. Depth profiles of aluminum, magnesium, cobalt and oxygen in the coated materials were recorded by ESCA (VG Scientific ESCALAB 250). Details of coin cell assembly are described elsewhere [13]. Lithium metal was used as the anode and a 1 M solution of $LiPF_6$ in EC:DEC (1:1, v/v) was used as the electrolyte. The cells were cycled at 0.1 C rate (with respect to a theoretical capacity of 274 mAh g^{-1}) between 2.75 and 4.40 V in a multi-channel battery tester (Maccor 4000). Phase transitions occurring during the cycling processes were examined by a slow scan cyclic voltammetric experiment run on a Solartron 1287 Electrochemical Interface at a scan rate of 0.1 mV s^{-1} between 3.0 and 4.4 V.

3. Results and discussion

3.1. X-ray diffraction

The diffraction patterns of the bare and the coated $LiCoO_2$ powders conformed to the *R*3*m* symmetry of the core material, suggesting that the coating material existed as a thin film and possibly as a mixed oxide formed by interaction with the core material. Table 1 shows that the lattice constants *a* and *c* of the coated materials are larger than those for the uncoated sample, which suggests that the phases on the surface of the powder are solid solutions formed by the reaction of the coated particles with the core material. We speculate that during the 10-h calcination process, substitutional compounds like $LiAl_yCo_{1-y}O_2$, $LiMg_yCo_{1-y}O_2$ and combinations thereof could have formed on the cathode particle surface. While the replacement of Co^{3+} with the trivalent Al^{3+} is straightforward, the replacement with the divalent Mg^{2+} would require the oxidation of a similar amount of Co^{3+} to Co^{4+} in order to achieve charge balance. The generation of Co^{4+} ions as charge compensators can lead to increased electronic conductivity of the cathode particles [14]. The values of the I_{003}/I_{104} intensity ratios for all the samples (Table 1) were greater than unity, indicating that they had good cation ordering [15]. The good cation ordering is also evident from the well-separated (1 0 8) and (1 1 0) reflections [15,16].

The empirical *R*-factor, defined as the ratio of the intensities of the hexagonal characteristic doublet peaks (0 0 6) and (1 0 2) to the (1 0 1) peak, has been suggested to be an indicator of hexagonal ordering [17,18]. According to Dahn et al. [17,18], the lower the *R*-factor, the better the hexagonal ordering. The values of the *R*-factor were 0.77, 0.75, 0.72, 0.85 and 0.91 for coating levels of 0.0, 0.3, 1.0, 2.0 and 3.0 wt.%, respectively (Table 1).

3.2. Particle morphology and microstructure

SEM images of the bare and coated $LiCoO_2$ particles are shown in Fig. 1. It can be seen that the texture of the surface of the cathode particles distinctly changes after coating. The increasing brightness of the materials observed in these pictures as the coating level increased is associated with the accumulation of charge on the non-conducting coating material as the electron beam impinges on it. It is seen that up to 1.0 wt.%, the coating is uniform. However, at higher coating levels, small, loosely-held agglomerates of the coating material are found glued to the surface, which suggests that at these coating levels, the amount of spinel is more than what is required to form a uniform coating on the cathode powder, and that the excess spinel particles agglomerate into small globules on the surface. Thus, it appears that a coating level of 1.0 wt.% or less would be sufficient to impart a uniform coating on the cathode powder. Fig. 2 shows the TEM image of a 1.0 wt.% spinel-coated $LiCoO_2$ particle. The core cathode particle can be seen to be covered by a loosely-held kernel of the spinel particles, the thickness of which, however, could not be determined from the image.

3.3. ESCA

The spatial distribution of aluminum, magnesium, cobalt and oxygen in the coated samples can be seen from the ESCA depth profiles presented in Fig. 3. The concentration of cobalt can be seen to increase up to a depth of about 10 nm, after which it nearly leveled off. Although the depth profiles show that both aluminum and magnesium penetrated up to about

Table 1
Lattice constants and *R*-factor values of the bare and spinel-coated $LiCoO_2$

Coating level (%)	*a* (Å)	*c* (Å)	*c*/*a*	I_{003}/I_{104}	Unit cell volume (Å^3)	*R*-factor
y = 0.0	2.810	13.938	4.96	1.68	95.3	0.77
y = 0.3	2.815	14.045	4.99	1.81	96.4	0.75
y = 1.0	2.825	14.188	5.02	1.84	98.1	0.72
y = 2.0	2.824	14.175	5.02	1.78	97.9	0.85
y = 3.0	2.817	14.089	5.00	1.64	96.8	0.91

(*y*) wt.% $MgAl_2O_4$ + (100 − *y*) wt.% $LiCoO_2$.

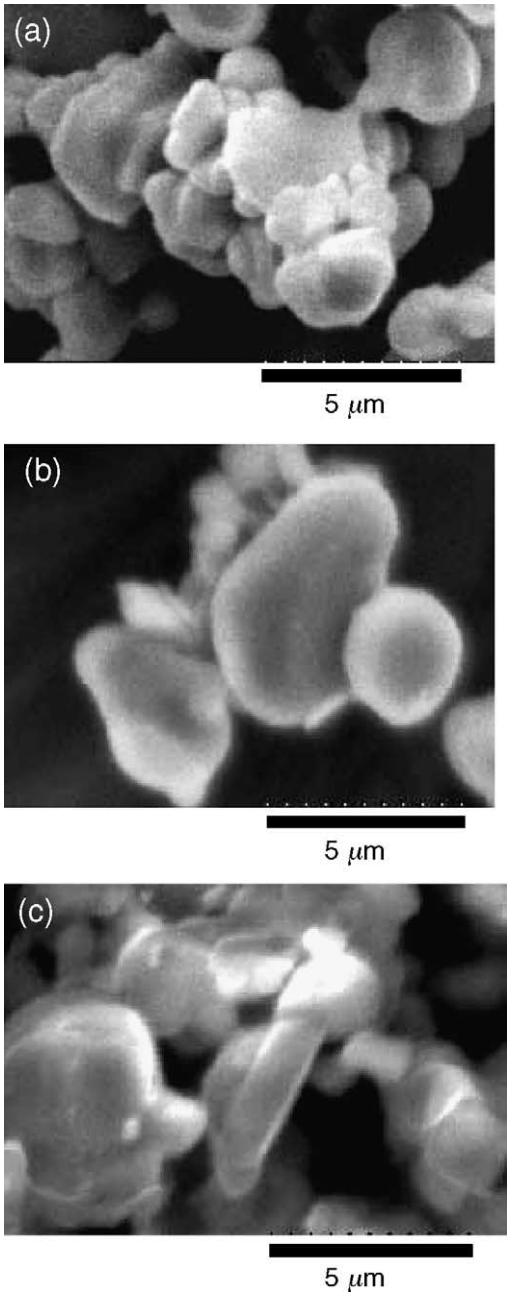

Fig. 1. SEM images of $LiCoO_2$ particles. Coating levels: (a) 0.0; (b) 1.0; (c) 2.0.

70 nm into the bulk of the cathode particle, their concentrations were small. Thus, ESCA data attest our XRD results, which suggested the formation of a substitutional surface oxide.

3.4. Galvanostatic cycling studies

The galvanostatic cycling behavior of the bare $LiCoO_2$ sample was compared with the spinel-coated samples (Fig. 4). The first-cycle discharge capacity of the uncoated $LiCoO_2$ was 167 mAh g^{-1}, while those of the 0.3, 1.0, 2.0 and 3.0 wt.%-coated samples were 160, 164, 112 and

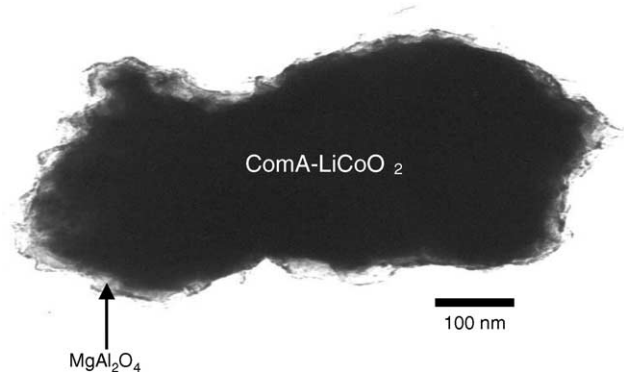

Fig. 2. TEM image of a 1.0 wt.% spinel-coated $LiCoO_2$ particle.

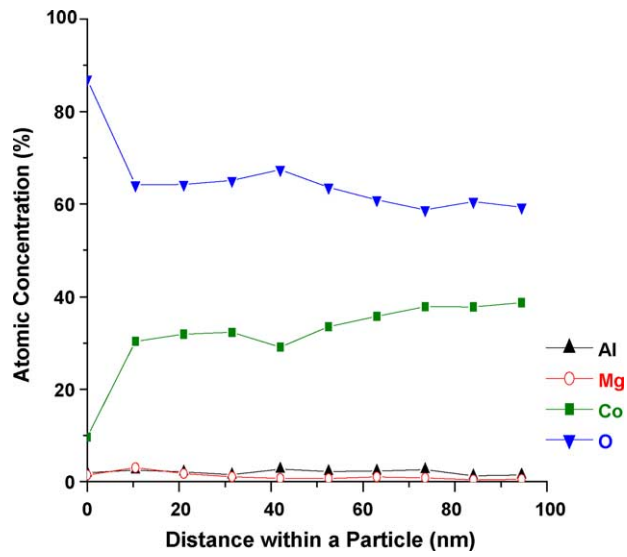

Fig. 3. Depth profiles of aluminum, magnesium, cobalt and oxygen in a 1.0 wt.% spinel-coated $LiCoO_2$ particle.

68 mAh g^{-1}, respectively. The steady decrease in the capacity as the coating level is increased is attributed to the inactive spinel in the electrode. The reduced capacity utilization of the cathode at the higher coating levels (2.0 and

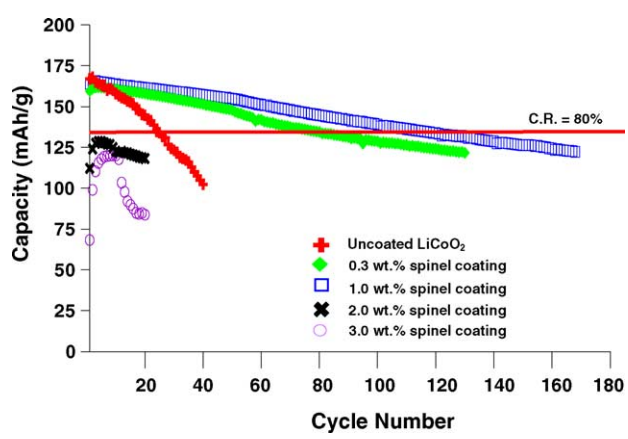

Fig. 4. Comparison of the cycling behavior of the bare and spinel-coated $LiCoO_2$ samples. Charge–discharge: 0.1 C rate between 2.75 and 4.40 V.

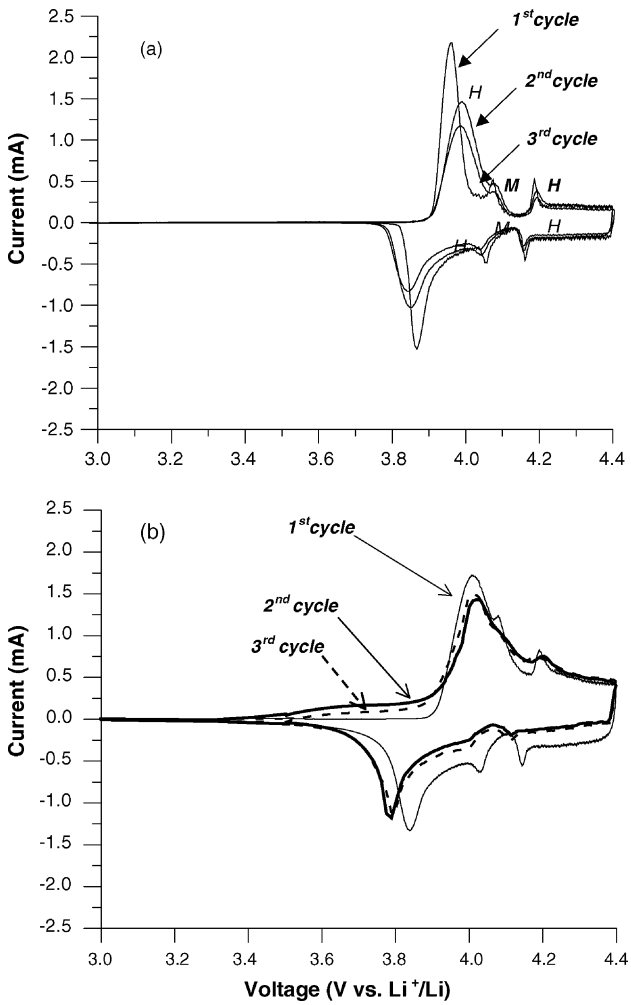

Fig. 5. Cyclic voltammograms of (a) bare $LiCoO_2$ and (b) 1.0 wt.% spinel-coated $LiCoO_2$.

3.0 wt.%) suggests that at these coating levels the coatings are so thick that they impede the diffusion of lithium essential for the electrochemical reactions. Furthermore, the presence of excess coating material between the particles could lower the particle-to-particle electronic conductivity, adversely affecting the efficiencies of the charge and discharge processes.

Cycling studies show that the spinel coating improved the cyclability of the cathode material. For a cut-off value of 80% for the capacity retention, calculated with the first-cycle discharge capacity of the uncoated material as the reference, the number of cycles that the bare $LiCoO_2$ could sustain was 26. The maximum cyclability was achieved with a material coated with 1.0 wt.% spinel (121 cycles, which represents a five-fold improvement in cyclability). An examination of the values of the *R*-factors for the coated and uncoated materials reveals that the materials with the lowest *R*-factor values (and thus, with the best hexagonal ordering of the lattice) gave the highest cyclability. Indeed, the cyclability is seen to be commensurate with the trend in the variation of the *R*-factor.

3.5. Slow scan cyclic voltammetry

Cyclic voltammetry is sensitive to phase transformations occurring during electrochemical reactions [19]. Fig. 5a presents the cyclic voltammograms of the uncoated $LiCoO_2$, while Fig. 5b presents those of the 1.0 wt.% spinel-coated $LiCoO_2$. It can be seen that the peaks due to the phase transitions persisted in every cycle for the uncoated material. However, such peaks seem suppressed beyond the second sweep for the coated sample. It is suggested that any defect in the coating that might have been present initially got repaired as the cycling proceeded. It is inevitable that coated surfaces always have defects such as cracks and pinholes in them. But such defects may form and close with the application of a load or upon thermal cycling. In the case of the coated cathodes, changes in the surface texture resulting from the contraction and expansion of the lattice during the cycling process could have enabled the particles of the coating material to become ingrained in the crevices and cracks on the cathode surface. The more compact kernel that resulted led to a suppression of the phase transitions, enhancing the cyclability of the coated material.

4. Conclusions

A commercial $LiCoO_2$ was coated with $MgAl_2O_4$ by a sol–gel coating process. The slightly larger lattice parameters of the coated materials, as seen from the XRD data, suggested the presence of substitutional compounds of the type $Li_xM_yCo_{1-y}O_2$ (M = Al/Mg) on the surface of the cathode particles. A TEM image of a 1.0 wt.% coated particle indicated that the spinel formed a loosely-held kernel on the cathode particles. ESCA depth profiles gave evidence for the presence of aluminum and magnesium in the bulk of the coated material, suggesting that the cationic species diffused into the bulk of cathode material during the calcination process. Galvanostatic cycling studies showed a five-fold improvement in the cyclabiltiy at a coating level of 1.0 wt.%. At this coating level, the value of the *R*-factor was the lowest, which suggests that cyclability improved with structural ordering.

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