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Short communication

Correlation between local strain and cycle-life performance of AlPO$_4$-coated LiCoO$_2$ cathodes

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Abstract

AlPO$_4$-coated LiCoO$_2$ cathodes display improved cycle-life performance compared with bare LiCoO$_2$. This is attributed to suppression of cobalt dissolution from the cathodes by the AlPO$_4$-nanoparticle coating. Dissolution of cobalt during cycling with a charge cut-off voltage of 4.6 V leads to structural degradation, and induces a non-uniform distribution of local strain in the cathodes. The strain in coated samples is significantly reduced after 50 cycles, and is correlated with the enhanced cycle-life performance.
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1. Introduction

LiCoO$_2$ has a hexagonal α-NaFeO$_2$ layered structure ($R\bar{3}m$), which is based on a close-packed network of oxygen atoms with alternating Li and Co planes. This material is used as a cathode material in commercial Li-ion batteries due to its excellent electrochemical properties. It has been reported, however, that LiCoO$_2$ experiences serious capacity loss during cycling above 4.3 V [1,2]. This behaviour results from electrolyte decomposition [3], structural degradation of cathode [4,5], and Co dissolution [6]. During de-lithiation of Li$_x$CoO$_2$, the c-axis expands up to ∼2.6% at $x \cong 0.5$ (∼4.2 V vs. Li). In addition, the phase changes at ∼4.5 V with ∼3% contraction [7]. The structural changes with lithium concentration correlate with the observed electrochemical performance. Amatucci et al. [6,7] have suggested that the phase change at ∼4.5 V is sufficiently large to cause mechanical stresses among the grains. This electrochemical grinding coupled with Co dissolution and structural degradation by lithiation/de-lithiation, results in capacity loss. Even with ∼1 wt.% Co loss in LiCoO$_2$, the capacity retention significantly decreases to only ∼10% after 25 cycles [6].

Recently, Cho et al. [8] have suggested that an AlPO$_4$-nanoparticle coating on the LiCoO$_2$ surface improves the thermal stability and electrochemical performance of LiCoO$_2$ cathodes at high voltages (≥4.3 V). High-resolution transmission electron microscopy (TEM) confirmed that the nanoscale layer (∼15 nm) was coated homogeneously over the LiCoO$_2$ surface, and consisted of randomly oriented AlPO$_4$ nanoparticles with an average diameter of ∼3 nm. In this communication, it is shown that capacity fading of LiCoO$_2$ cathode material during cycling with a charge cut-off voltage of 4.6 V is correlated with a non-uniform distribution of local strain induced by repeating lithiation/de-lithiation and Co dissolution. The AlPO$_4$-nanoparticle coating provides a fundamental solution for capacity fading and thermal instability at a high charge cut-off voltage.

2. Experimental

Al(NO$_3$)$_3$·9H$_2$O (3 g) and (NH$_4$)$_2$HPO$_4$ (1 g) were dissolved in distilled water until a white suspension of AlPO$_4$ nanoparticles was obtained. LiCoO$_2$ powders (with an average particle size of ∼10 μm) were then slowly added to the coating solution and mixed until the final viscosity of the slurry reached ∼100 P. The weight ratio of AlPO$_4$ and LiCoO$_2$ was 1:99. Subsequently, the slurry was poured into a tray, dried in an oven for 6 h at 130 °C, and annealed at 400, 600, or 700 °C for 5 h in a furnace. The

electrolyte used was 1 M LiPF$_6$ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC: 30/30/40 vol.%). Cycling tests of the coin-type half cells (Li as an anode) were performed between 4.6 and 3 V with 0.1 C for the first and second cycles, 0.2 C for the third cycle, 0.5 C for the fourth cycle, and 1 C for the subsequent cycles (1 C = 140 mA g^{-1}). Co dissolution from the bare and coated LiCoO$_2$ cathodes was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The electrolytes for measuring Co dissolution were obtained from the cycled cells using the centrifugal separation method. The local strain was characterised by X-ray diffraction (XRD) (M18XHF-SRC, MAC Science) using Cu $K\alpha$ radiation.

3. Results and discussion

The cycle-life performance of the bare and AlPO$_4$-coated LiCoO$_2$ cathodes is shown in Fig. 1 (a). The coated sample annealed at 400 °C has a lower initial discharge capacity than

even the bare sample. As the annealing temperature is increased, a solid-state electrolyte layer may easily be formed [9]. Because of the insulating nature of AlPO$_4$, the nanoscale ($\sim$15 nm) coating layer needs to be in the optimum condition [5,8,9]. The initial discharge capacity of the samples annealed at 600 or 700 °C is higher than that obtained from a sample with 400 °C annealing. Nevertheless, the coated cathode annealed at 400 °C still exhibits a capacity retention after cycling which is superior to the bare counterpart with a 4.6 V charge (Fig. 1 (b)). Moreover, Co dissolution from the coated cathodes after 50 cycles is reduced significantly compared with the bare sample. Based on these results, the capacity retention may correlate with suppression of Co dissolution by the AlPO$_4$-nanoparticle coating layer. Co dissolution accompanies a non-uniform distribution of local strain as a result of structural degradation, such as point defects, non-stoichiometry, dislocations, stacking faults, etc. Therefore, this study has attempted to correlate the cycle-life performance with the local strain in the cathode material.

Representative XRD patterns of bare and coated cathodes after 50 cycles with a charge cut-off voltage of 4.6 V as shown in Fig. 2. To investigate the structural changes after cycling, five peaks ((0 0 3), (1 0 1), (1 0 4), (0 1 5) and (0 1 8)) were fitted from the patterns. Peak-broadening may be associated with either the microstructural defects or a non-uniform distribution of local strain [10,11]. Peak widths Δk (full width at half maximum) were fitted for each peak with a scattering vector $k = (4\pi/\lambda)\sin\theta$ using a double-peak Lorentzian function for $K\alpha_1$ and $K\alpha_2$. The effective grain size estimated from the intercept at $k = 0$ does not show any systematic changes due to the large error range in the fitting process. To remove the instrumental-broadening effect in the diffraction patterns, a resolution function has been obtained from the diffraction of Si crystals.
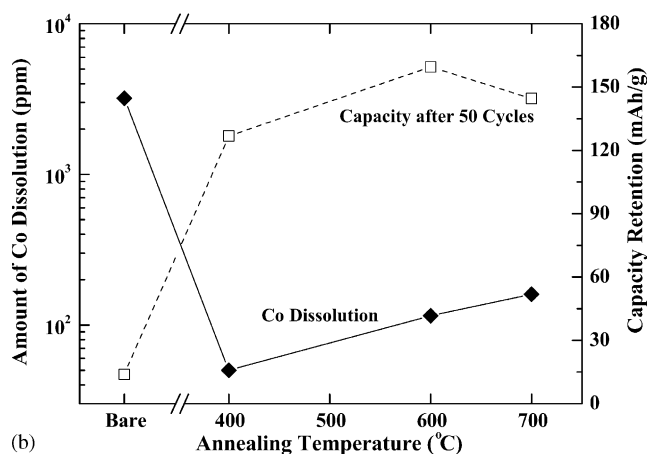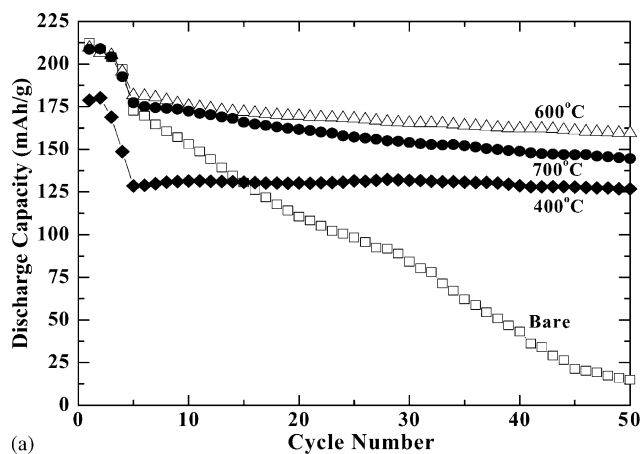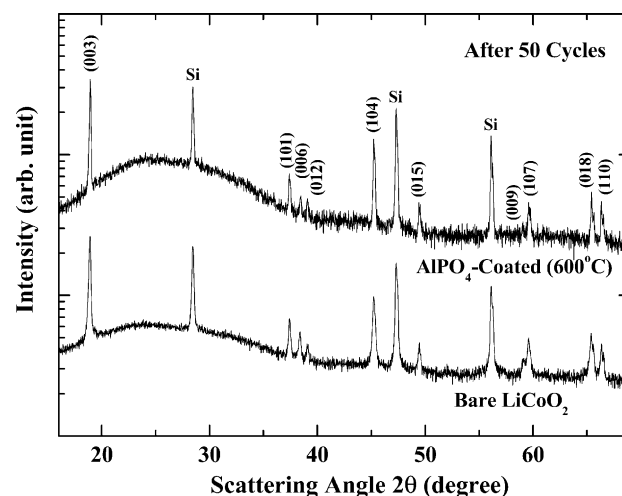

Fig. 1. Plots of: (a) cycle-life performance in coin-type half cells (Li as an anode) using bare and AlPO$_4$-coated LiCoO$_2$ up to 50 cycles between 4.6 and 3 V; (b) amounts of Co dissolution and capacity retention as a function of annealing temperature.

Fig. 2. Representative XRD patterns of the bare and AlPO$_4$-coated (annealed at 600 °C) LiCoO$_2$ cathodes after 50 cycles with a 4.6 V cut-off voltage.
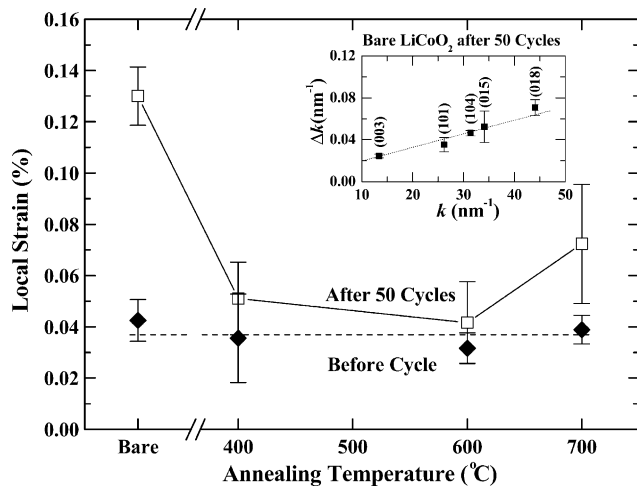
Fig. 3. Plots of local strain before and after cycling as a function of annealing temperature. Inset shows Δk vs. k plot for bare $LiCoO_2$ after 50 cycles with 4.6 V cut-off voltage; the slope of the linear-fitted function (dotted line) describes non-uniform distribution of local strain in the sample.

The relationship between Δk and k can be described as follows:

$$\Delta k = \frac{\Delta d}{d}k + K\frac{2\pi}{D} \tag{1}$$

where $\Delta d/d$ is the non-uniform distribution of local strain in the cathode, and D is the effective grain size suggested by Scherrer, with a shape factor K of approximately 1 [12]. The local strain in the cathodes before and after cycling with a charge cut-off voltage of 4.6 V as a function of the annealing temperature, is shown in Fig. 3. The inset is a representative Δk vs. k plot in the bare sample measured at 3 V after 50 cycles. The local strain in the cathodes can be estimated from the slope of a Δk vs. k plot after subtraction of the resolution function ($\Delta k_{res} = 0.076 - 0.00033k$ (nm^{-1})). All the cathodes before cycling have a similar local strain of ~0.04%. The local strain in the bare sample after 50 cycles increases approximately by a factor of 3. By contrast, the strain in the coated samples is effectively prevented after cycling even with a charge cut-off voltage of 4.6 V. The analysis of local strain in Fig. 3 clearly demonstrates that the AlPO$_4$-nanoparticle coating effectively suppresses the structural degradation caused by Co dissolution, and thereby prevents capacity fading of the cathode during cycling even at such a high charge cut-off voltage of 4.6 V.

4. Conclusion

In conclusion, an AlPO$_4$-nanoparticle coating of LiCoO$_2$ induces an enhanced cycle-life performance and suppresses Co dissolution from cathodes, compared with a bare counterpart. Analysis of local strain by the Scherrer equation shows that the AlPO$_4$-nanoparticle coating on the LiCoO$_2$ surface effectively suppresses any non-uniform distribution of local strain in the coated samples. Therefore, the AlPO$_4$ coating makes it possible to improve the cycle-life performance in the cathodes even at a charge cut-off voltage of 4.6 V. Further studies are needed, however, to systematically correlate the electrochemical properties with the more detailed microstructure of the LiCoO$_2$ cathode and the nanoscale-coating layer.

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