Suppression of structural degradation of LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode at 90 °C by AlPO$_4$-nanoparticle coating

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Abstract

This study examined the electrochemical and structural stability of ~1.5 wt.% AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$. The AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ retained ~60% of the original capacity after 50 cycles, compared with the ~30% capacity retention of the bare LiNi$_{0.9}$Co$_{0.1}$O$_2$. The discharge profiles and cyclic voltammograms from 4.5 V at 90 °C for 4 h showed enhanced structural stability. Scanning electron microscopy and X-ray diffraction revealed that the AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ had less degradation than the bare LiNi$_{0.9}$Co$_{0.1}$O$_2$.

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1. Introduction

Layered transition-metal oxides have been studied extensively for use as cathode materials for rechargeable lithium-ion batteries [1]. LiCoO$_2$ has been used as a positive electrode because of the relatively high cell potential and the stable cycling life, even with the high cost and toxicity. LiNiO$_2$ appears to be one candidate as a cathode material, due to the high-specific capacity and low cost. However, this material has poor cycle life and thermal instability.

In an attempt to overcome the problems associated with LiNiO$_2$ and LiCoO$_2$, the solid solution series of lithium nickel-metal oxides, Li(Ni$_{1-x}$M$_x$)$_2$O$_2$ (with M = Co, Mn, Al, Ti, Mg, etc.), have comprised favorable cathode materials for high-energy and high-power lithium-ion batteries [2–8]. However, along with the improvement in the electrochemical properties in Ni-based cathode materials, the thermal stability has been a great concern, and violent reaction of the cathode with the electrolyte needs to be avoided [5–12].

Recently, it was reported that a simple AlPO$_4$-nanoscale coating (~20 nm) on LiCoO$_2$ improved both the thermal stability and the electrochemical performance of LiCoO$_2$ at high voltages [12–14]. This paper reports the effect of a AlPO$_4$-nanoparticle coating on LiNi$_{0.9}$Co$_{0.1}$O$_2$ on the enhanced capacity retention and 90 °C behavior at 4.5 V.

2. Experimental results

Bare LiNi$_{0.9}$Co$_{0.1}$O$_2$ powders were prepared by mixing the appropriate amounts of LiOH·(H$_2$O) and Ni$_{0.9}$Co$_{0.1}$(OH)$_2$, followed by heating in air at 480 °C and 720 °C for 4 h and 13 h, respectively. The AlPO$_4$ nanoparticles (~3 nm) were obtained by dissolving Al(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$HPO$_4$ in distilled water with constant stirring for 30 min [13]. This solution was mixed with
Ni$_{0.9}$Co$_{0.1}$(OH)$_2$ (with an average particle size of $\sim 10 \mu$m), followed by drying at 100 °C for 2 h. The approximately 1.5 wt.% AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ powders were prepared by mixing the appropriate amounts of LiOH $\cdot$(H$_2$O) and AlPO$_4$-coated Ni$_{0.9}$Co$_{0.1}$(OH)$_2$, followed by heating in air at 480 °C and 720 °C for 4 h and 13 h, respectively. Electron-probe micro analysis (EPMA) confirmed the continuous encapsulation of the LiNi$_{0.9}$Co$_{0.1}$O$_2$ particles by an AlPO$_4$ layer.

The cathodes for the test cells consisted of LiNi$_{0.9}$Co$_{0.1}$O$_2$, super P carbon black, and a polyvinylidene fluoride (PVDF) binder in a weight ratio of 94:3:3. The coin-type half cells (Li/LiNi$_{0.9}$Co$_{0.1}$O$_2$) were prepared in an argon-filled glove box, and contained a cathode, a Li-metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF$_6$ in ethylene carbonate/diethyl carbonate (EC/DEC) (50:50 vol.%).

The cycling test of the half cells was carried out between 4.9 V and 2.75 V at 0.1 C rate for the first two cycles, and 1 C (= 300 mA/g) afterwards at 25 °C. After discharging, cyclic voltammogram (CV) of LiNi$_{0.9}$Co$_{0.1}$O$_2$ was performed between 3.4 V and 4.6 V at a sweep rate of 0.1 mV/s. The structural characterization of both the bare and AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathodes was performed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

3. Results and discussion

To test the cycle-life performance, the bare LiNi$_{0.9}$Co$_{0.1}$O$_2$ and AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ coin-type half cells were cycled between 4.9 V and 2.75 V, as shown in Fig. 1. The typical cutoff voltage in the LiNi$_{1-x}$M$_x$O$_2$ system is less than 4.5 V [2–4,6,8,11]. The high cutoff voltage was used in this experiment to increase the capacity, at the expense of the structural degradation due to the reaction with the electrolyte [12–14]. The AlPO$_4$-nanoparticle coating clearly enhanced the capacity retention of the LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode. After 50 cycles, the discharge capacity of the bare LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode deteriorated to $\sim 30\%$ of its original capacity, whereas that of the AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode retained $\sim 60\%$ of its initial capacity.

Fig. 2 shows the discharge profiles from 4.5 V at 90 °C for 4 h. The discharge capacity of the bare and AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ was $\sim 138$ mAh/g and $\sim 182$ mAh/g, respectively (as shown in the inset). The AlPO$_4$-nanoparticle coating could reduce self discharge, by diminishing the surface reaction between the electrolyte and the highly-reactive surface of Li$_x$Ni$_{0.9}$Co$_{0.1}$O$_2$ at 4.5 V. Amine’s group reported that the delithiated LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode surface contained a mixture of organic polycarbonates, LiF or Li$_x$PF$_y$O$_z$-type compounds, due to the high surface reactivity of the cathode materials with the electrolyte [15]. A solid-electrolyte interphase (SEI) layer on the charged
electrodes contained various organic and inorganic electrolyte-decomposition products [15–17]. Cho et al. reported that differential scanning calorimetry (DSC) experiments showed significant heat reduction for the AlPO₄-nanoparticle coating on LiCoO₂ and LiNi₀.₈Co₀.₂O₂, indicating that the critical factor governing the exothermic reaction was the interfacial reaction with the electrolyte and the cathode material [12].

To investigate the rate of phase transitions, the CV of both the bare and AlPO₄-coated LiNi₀.₉Co₀.₁O₂ was performed (Fig. 2). The AlPO₄-coated LiNi₀.₉Co₀.₁O₂ shows clear sets of well-defined peaks compared with the bare cathode. LiNi₁₋ₓCoₓO₂ has hexagonal (and monoclinic) structures at various lithium contents [2–8]. The widths of both the cathodic and anodic peaks were less broadened by the AlPO₄-nanoparticle coating than the bare LiNi₀.₉Co₀.₁O₂. This suggests that the AlPO₄-nanoparticle coating on LiNi₀.₉Co₀.₁O₂ suppresses the degradation of LiNi₀.₉Co₀.₁O₂, because the continuous AlPO₄-nanoparticle coating layer on LiNi₀.₉Co₀.₁O₂ can reduce the side reaction between the cathode and electrolyte at 90 °C.

SEM images of the bare and AlPO₄-coated LiNi₀.₉Co₀.₁O₂ before electrochemical test showed relatively similar grain images (Fig. 3(a)). The bare and AlPO₄-coated LiNi₀.₉Co₀.₁O₂ powders had a Brunauer, Emmett, and Teller (BET) surface area of 0.34 m²/g and 0.38 m²/g, respectively. After 90 °C for 4 h, the BET surface-area measurements were not possible due to the presence of non-active materials (carbon black, binder, and organic salts) on the surface of cathode materials. However, the SEM image of the bare cathode showed degraded surfaces on the grains, while the AlPO₄-coated cathode retained its initial grain morphology (Fig. 3(b)).

After 90 °C storage, the XRD patterns of the bare LiNi₀.₉Co₀.₁O₂ cathode shows more peak broadening compared with the AlPO₄-coated cathode (Fig. 4). Such peak broadening may be associated with microstructural defects or non-uniform distribution of local strains [18,19]. To qualitatively estimate the microstructural defects, Δk (full width at half maximum) was fitted to each peak ((003), (101), (104), and (015)) with the scattering vector k = (4π/λ)sinθ. The peak widths of the bare and AlPO₄-coated LiNi₀.₉Co₀.₁O₂ before charge were similar, Δk = 0.004 ± 0.002 nm⁻¹ and 0.004 ± 0.002 nm⁻¹, respectively. In contrast, after 90 °C for 4 h, the bare and AlPO₄-coated
LiNi_{0.9}Co_{0.1}O_2 showed $\Delta k = 0.21 \pm 0.03$ nm$^{-1}$ and 0.05 $\pm$ 0.01 nm$^{-1}$, respectively. In addition, the AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ exhibited a higher peak-intensity ratio of (003)/(1104) than the bare one (1.83 $\pm$ 0.07 vs. 1.28 $\pm$ 0.09), while the ratio was 2.08 $\pm$ 0.06 vs. 2.14 $\pm$ 0.05 prior to cycling, confirming the enhanced structural stability [20,21]. These results confirm the suppressed microstructural defects and structural degradation in LiNi$_{0.9}$Co$_{0.1}$O$_2$ by AlPO$_4$-nanoparticle coating.

4. Conclusions

Capacity retention and structural stability at 90 °C were enhanced by the AlPO$_4$-nanoparticle coating on LiNi$_{0.9}$Co$_{0.1}$O$_2$. Microstructural analysis indicated an improved structural integrity in the AlPO$_4$-coated LiNi$_{0.9}$Co$_{0.1}$O$_2$ cathode compared with the bare one. This may be attributed to the strong covalency of the PO$_4$ polyanions with Al in AlPO$_4$, which is resistant to the chemical and thermal aggression [22,23]. More studies aimed at identifying the detailed mechanisms of the enhanced electrochemical and thermal performances by the phosphate-coating nanostructures are currently underway.

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References