Available online at www.sciencedirect.com
ScienceDirect
Current Applied Physics 7 (2007) 172–175
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

Suppression of structural degradation of $LiNi_{0.9}Co_{0.1}O_2$ cathode at 90 °C by $AlPO_4$-nanoparticle coating

Donggi Ahn [a], Joon-Gon Lee [a], Jin Sun Lee [a], Jisuk Kim [b], Jaephil Cho [b], Byungwoo Park [a,*]

[a] *School of Materials Science and Engineering, and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Republic of Korea*
[b] *Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Republic of Korea*

Received 13 October 2005; accepted 6 February 2006
Available online 27 July 2006

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 $LiNi_{0.9}Co_{0.1}O_2$.

PACS: 82.47.Aa

Keywords: $AlPO_4$-nanoparticle; Coating; $LiNi_{0.9}Co_{0.1}O_2$

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, $Li(Ni_{1-x}M_x)O_2$ (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 $LiOH \cdot (H_2O)$ 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 $Al(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2HPO_4$ in distilled water with constant stirring for 30 min [13]. This solution was mixed with

* Corresponding author. Tel.: +82 2 880 8319; fax: +82 2 885 9671.
E-mail address: byungwoo@snu.ac.kr (B. Park).

1567-1739/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2006.02.014

$Ni_{0.9}Co_{0.1}(OH)_2$ (with an average particle size of ~10 μm), 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 $LiOH \cdot (H_2O)$ 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. For the 90 °C storage test, the bare $LiNi_{0.9}Co_{0.1}O_2$ samples and the $AlPO_4$-coated samples were charged to 4.5 V at a rate of 0.1 C and held there until the current decreased to 10%. These samples were heated to 90 °C for 4 h, followed by cooling to 30 °C, and discharged to 2.75 V at 0.1 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 $LiNi_{1-x}M_xO_2$ 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 ~30% of its original capacity, whereas that of the $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ cathode retained ~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 ~138 mAh/g and ~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 $Li_xNi_{0.9}Co_{0.1}O_2$ at 4.5 V. Amine's group reported that the delithiated $LiNi_{0.8}Co_{0.2}O_2$ cathode surface contained a mixture of organic polycarbonates, LiF or $Li_xPF_yO_z$-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

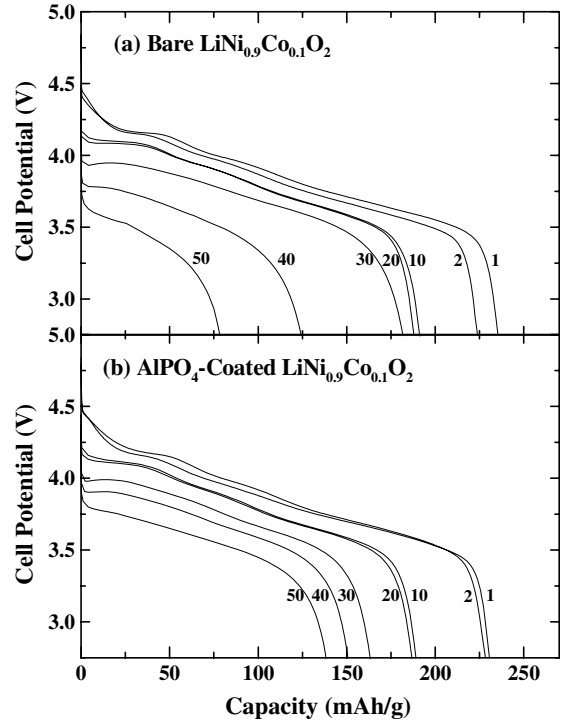

Fig. 1. Discharge profiles of (a) bare and (b) $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ powders between 4.9 V and 2.75 V. The cells were cycled at 0.1 C for the first two cycles, followed by 1 C (= 300 mA/g) thereafter.

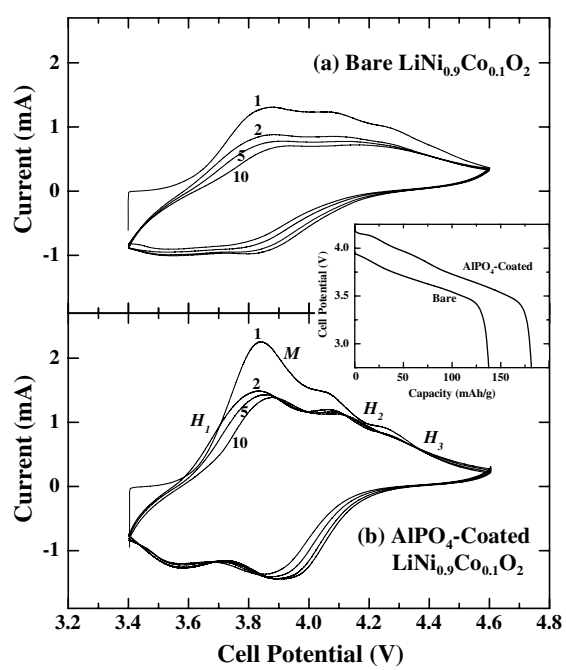

Fig. 2. Cyclic voltammogram after 90 °C storage of (a) bare and (b) $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ cathodes. After 90 °C for 4 h at 4.5 V, the cells were cooled to 30 °C and discharged to 2.75 V at 0.1 C. The inset shows the discharge profiles before CV.

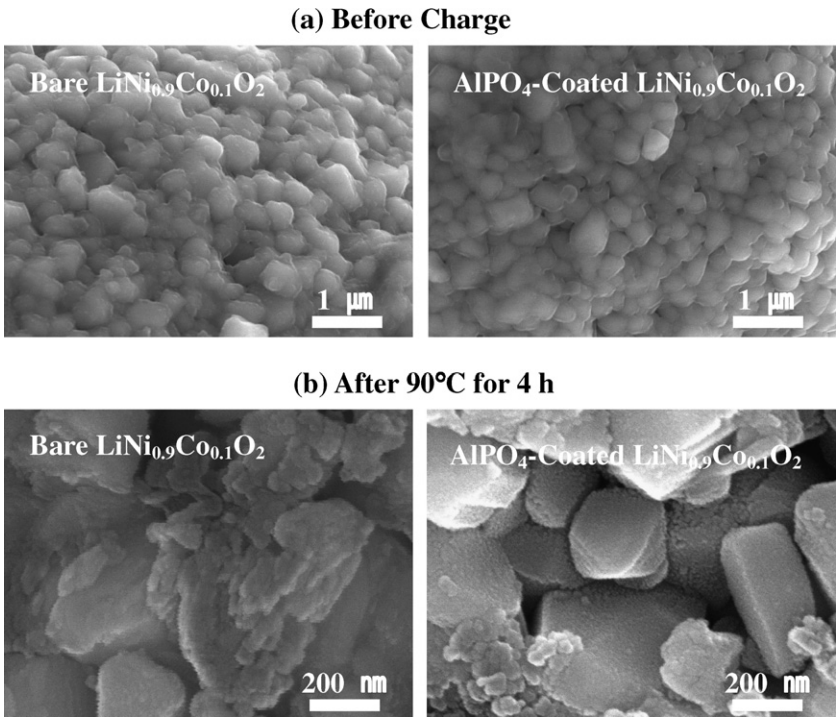

Fig. 3. SEM images of the bare and $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ particles: (a) before charge and (b) after 90 °C for 4 h at 4.5 V (and discharged to 2.75 V).

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 $AlPO_4$-nanoparticle coating on $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$, 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 $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ was performed (Fig. 2). The $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ shows clear sets of well-defined peaks compared with the bare cathode. $LiNi_{1-x}Co_xO_2$ 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 $AlPO_4$-nanoparticle coating than the bare $LiNi_{0.9}Co_{0.1}O_2$. This suggests that the $AlPO_4$-nanoparticle coating on $LiNi_{0.9}Co_{0.1}O_2$ suppresses the degradation of $LiNi_{0.9}Co_{0.1}O_2$, because the continuous $AlPO_4$-nanoparticle coating layer on $LiNi_{0.9}Co_{0.1}O_2$ can reduce the side reaction between the cathode and electrolyte at 90 °C.

SEM images of the bare and $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ before electrochemical test showed relatively similar grain images (Fig. 3(a)). The bare and $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ powders had a Brunauer, Emmett, and Teller (BET) surface area of 0.34 m^2/g and 0.38 m^2/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 $AlPO_4$-coated cathode retained its initial grain morphology (Fig. 3(b)).

After 90 °C storage, the XRD patterns of the bare $LiNi_{0.9}Co_{0.1}O_2$ cathode shows more peak broadening compared with the $AlPO_4$-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 $k = (4\pi/\lambda)\sin\theta$. The peak widths of the bare and $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ before charge were similar, $\Delta k = 0.004 \pm 0.002\ nm^{-1}$ and $0.004 \pm 0.002\ nm^{-1}$, respectively. In contrast, after 90 °C for 4 h, the bare and $AlPO_4$-coated

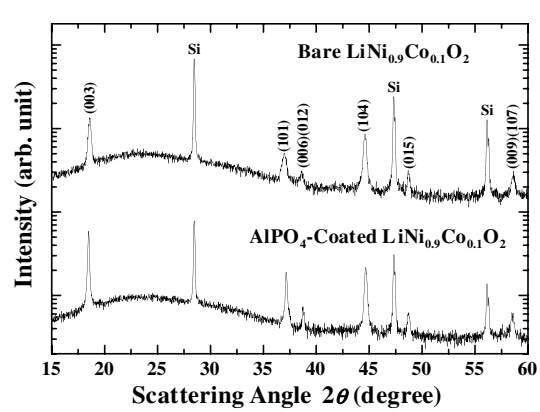

Fig. 4. XRD patterns of the bare and $AlPO_4$-coated $LiNi_{0.9}Co_{0.1}O_2$ cathode after 90 °C for 4 h at 4.5 V (and discharged to 2.75 V).

$LiNi_{0.9}Co_{0.1}O_2$ 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)/(104) than the bare one (1.83 ± 0.07 vs. 1.28 ± 0.09), while the ratio was 2.08 ± 0.06 vs. 2.14 ± 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.

Acknowledgements

This work was supported by the ERC program of MOST/KOSEF (R11-2002-102-00000-0), and by the Basic Research Program (R01-2004-000-10173-0) of KOSEF.

References

[1] J.M. Tarascon, M. Armand, Nature 414 (2001) 361.
[2] C. Delmas, I. Saadoune, Solid State Ionics 53–56 (1992) 370.
[3] T. Ohzuku, A. Ueda, M. Kouguchi, J. Electrochem. Soc. 142 (1995) 4033.
[4] M. Okada, K.-I. Takahashi, T. Mouri, J. Power Sources 68 (1997) 545.
[5] S. Venkatraman, Y. Shin, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A9.
[6] H. Arai, S. Okada, Y. Sakurai, J.-I. Yamaki, J. Electrochem. Soc. 144 (1997) 3117.
[7] Y. Gao, M.V. Yakovleva, W.B. Ebner, Electrochem. Solid-State Lett. 1 (1998) 117.
[8] J. Cho, H.S. Jung, Y.C. Park, G.B. Kim, H.S. Lim, J. Electrochem. Soc. 147 (2000) 15.
[9] M. Guilmard, L. Croguennec, C. Delmas, Chem. Mater. 15 (2003) 4484.
[10] A.M. Kannan, A. Manthiram, J. Electrochem. Soc. 150 (2003) A349.
[11] Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A200.
[12] J. Cho, H. Kim, B. Park, J. Electrochem. Soc. 151 (2004) A1707.
[13] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, B. Park, Angew. Chem. Int. Ed. 42 (2003) 1618.
[14] J. Cho, J.-G. Lee, B. Kim, B. Park, Chem. Mater. 15 (2003) 3190.
[15] A.M. Andersson, D.P. Abraham, R. Haasch, S. Mack, J. Liu, K. Amine, J. Electrochem. Soc. 149 (2002) A1358.
[16] M. Balasubramanian, H.S. Lee, X. Sun, X.Q. Yang, A.R. Moodenbaugh, J. McBreen, D.A. Fischer, Z. Fu, Electrochem. Solid-State Lett. 5 (2002) A22.
[17] S.C. Levy, P. Bro, Battery Hazards and Accident Prevention, Plenum Press, New York, 1994.
[18] Y. Kim, J. Oh, T.-G. Kim, B. Park, Appl. Phys. Lett. 78 (2001) 2363.
[19] B. Kim, J.-G. Lee, M. Choi, J. Cho, B. Park, J. Power Sources 126 (2004) 190.
[20] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, Electrochim. Acta 38 (1993) 1159.
[21] R.V. Chebiam, F. Prado, Y. Xia, A. Manthiram, J. Electrochem. Soc. 148 (2001) A49.
[22] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[23] S. Okada, S. Sawa, M. Egashira, J.-I. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, A. Yoshino, J. Power Sources 97–98 (2001) 430.