BNL-113647-2017-JA

**Electronic Structural Studies on the Improved
Thermal Stability of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ by
 ZrO_2 Coating for Lithium Ion Batteries**

**Ji-Young Kim, Sang Hoon Kim, Dong Hyun Kim, Dieky Susanto,
Se Young Kim, Won-Young Chang, Byung Won Cho, Won-Sub Yoon,
Seong Min Bak, Xiao Qing Yang, Kyung Wan Nam, and Kyung Yoon Chung**

Submitted to Journal of Applied Electrochemistry

March 2017

Chemistry Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC)
USDOE Office of Energy Efficiency
and Renewable Energy (EERE)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Electronic Structural Studies on the Improved Thermal Stability of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ by ZrO_2 Coating for Lithium Ion Batteries

Ji-Young Kim¹, Sang Hoon Kim¹, Dong Hyun Kim¹, Dieky Susanto¹, Se Young Kim¹, Won-Young Chang¹, Byung Won Cho¹, Won-Sub Yoon², Seong Min Bak³, Xiao Qing Yang³, Kyung Wan Nam^{4,*} and Kyung Yoon Chung^{1,*}

¹Center for Energy Convergence Research, Korea Institute of Science and Technology, Hwarangno 14-gil, Seongbuk-gu, Seoul 136-791, Republic of Korea.

Fax: 82-2-958-5229; Tel: 82-2-958-5228; E-mail: kychung@kist.re.kr (co-corresponding author)

²Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea.

³Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973 USA.

⁴Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea.

[Tel:82-2-2260-4978](tel:82-2-2260-4978); E-mail:knam@dongguk.edu (co-corresponding author)

Abstract

The electronic structures of bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode systems were investigated using a combination of time-resolved X-ray diffraction and soft X-ray absorption spectroscopy (XAS) techniques. The ZrO_2 coating on the surface of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ was effective in elevating the onset temperature of the dissociation of charged $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, which will enhance the safety of Li-ion cells. Soft XAS spectra of the Ni $\text{L}_{\text{II,III}}$ -edge in the partial electron yield mode were obtained, which showed that the enhanced electrochemical properties and thermal stability of the cathode materials by ZrO_2 coating can be attributed to the suppression of unwanted Ni oxidation state changes at the surface.

Keywords: $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, ZrO_2 coating, thermal stability, soft X-ray absorption spectroscopy (XAS), Batteries

1. Introduction

Lithium ion batteries (LIBs) have been extensively investigated and widely used in energy devices and storage systems.[1] In these applications, LiCoO_2 has been studied as a representative cathode material.[2] However, the increasing price of cobalt and environmental concerns have spurred interest in the development of alternative non-toxic cathode materials with higher capacity, lower cost, and better safety characteristics.[3,4] LiNiO_2 is also a promising candidate as a cathode active material due to its low cost and high specific capacity.[5] However, the layered LiNiO_2 structure suffers from problems with low reproducibility, short lifetime, and low stability at high temperature.

$\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ offers improved electrochemical and thermal stabilities compared to LiNiO_2 because of its stabilized layered structure acquired through the substitution of Al and Co for Ni sites, which results in the reduction of the a-axis.[6] $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ has demonstrated some promising advantages in high energy density applications such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EV).[4]

However, the significant capacity fading of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ remains an issue that must be resolved prior to commercialization.[7] In addition, cathode materials with high Ni content have reportedly become thermally unstable due to the reactive and unstable Ni^{4+} ions in the delithiated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ materials. [8]

Previous studies have shown that the electrochemical properties of cathode materials can be improved significantly by coating with metal oxides and metal fluorides such as SiO_2 , TiO_2 , ZrO_2 , and AlF_3 . [9–16] Among the various types of coatings, those based on ZrO_2 have been reported to effectively improve the capacity retention of cathode materials during high voltage cycling. [9,10] Our group also reported structural studies on the effects of a ZrO_2 coating on LiCoO_2 cathode materials using an in situ X-ray diffraction (XRD) technique employing a synchrotron X-ray source. [10, 11, 16] Based on these investigations, we related the improvement in capacity retention upon coating to the preservation of the variation range of the lattice parameters. In other words, the larger the variation range of the lattice parameters, the larger the capacity. [17] This phenomenon seems to be related to the protection of the surface of the LiCoO_2 particles and the reduction of electrolyte decomposition at higher voltages. [11] Thus, a ZrO_2 coating may be a very effective way to prevent detrimental reactions at the surfaces of the cathode particles. However, previous

reported studies have focused on the effects of ZrO_2 coatings on electrochemical performance. We believe that the ZrO_2 coating may also affect the safety characteristics of a cathode material, especially its thermal stability, which is a very important requirement for cathode materials.

In this study, the surface and bulk structures in electrochemically Li-ion de-intercalated bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode systems were investigated using a combination of soft X-ray absorption spectroscopy (XAS) and in situ XRD in order to understand the thermal degradation mechanism of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode. Soft XAS using synchrotron radiation is a powerful technique for investigating the electronic structures of electrode materials for LIBs. [17–19] Spectra can be obtained in both the electron yield (EY) and fluorescence yield (FY) modes, where the EY mode is surface sensitive (within $\sim 50 \text{ \AA}$) and the FY mode detects the bulk electronic structure. [20, 21] Thus, we applied soft XAS in the EY mode to investigate the electronic structural changes at the surface of bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes. To determine the structural changes in the bulk, we applied the in situ XRD technique. Using this combination of techniques, a more complete understanding of the thermal degradation mechanism of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes could be achieved.

2. Experimental

2.1. Synthesis of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$

For the synthesis of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, stoichiometric amounts of LiNO_3 (Aldrich, 99%), $\text{Ni}(\text{NO}_3)_2$ (Aldrich, 99%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 98%), and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, 98%) were dissolved in ethanol under magnetic stirring. To this solution, a saturated aqueous solution of citric acid was slowly added under magnetic stirring as a chelating agent. In a rotary evaporator at 250 rpm, the solution was evaporated at 60°C for 12 h and then dried at 90°C for 12 h. Calcination was performed at a rate of $5^\circ\text{C}/\text{min}$ to 850°C in a tube furnace operating under an air atmosphere for 15 h, and then left to cool to room temperature.

2.2. ZrO_2 coating on $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$

For the ZrO_2 coating at the surface of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, 0.09 g zirconium acetylacetonate was dissolved in ethanol followed by immersing the prepared $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ powders (2 g) into the solution. Then, the solution was continuously

stirred for 12 h at 90°C, accompanied by the slow evaporation of solvent. The obtained ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ powders were heated at 800°C for 6 h in air. The amount of zirconium acetylacetonate powders was calculated such that the final product contains 1.0 wt.% of ZrO₂.

2.3. Characterization

Powder X-ray diffraction measurements were performed with a Rigaku X-ray diffractometer using monochromatic Cu K α radiation at 40 kV and 100 mA. The diffraction data were collected at a scan speed of 2° min⁻¹ over a 2 θ range from 10 to 90°. A high-resolution transmission electron microscopy (HRTEM) system (HRTEM, Tecnai G2, FEI Company) with an energy-dispersive X-ray spectroscopy (EDS) attachment and elemental mapping function (Inca Energy, Oxford) was used to investigate the elements present on the surface and in the bulk of the synthesized cathode materials.

For electrode fabrication, the active materials were mixed with acetylene black and polyvinylidene fluoride in N-methylpyrrolidone in a weight ratio of 90:6:4. The slurry was mixed for 30 min using a mortar and pestle, coated onto Al foil using a doctor blade, and dried at 80°C in an oven for 24 h. The electrodes were assembled in an argon-filled glove box (<0.1 ppm O₂ and H₂O, MBRAUN, MB200B) using Li metal as the counter electrode in a 2032 coin-cell configuration (Hohsen Corp., Japan). An electrolyte composed of 1 M LiPF₆ in ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC) = 1:1:1 by volume was used. The cells were stored for 6 h to ensure complete impregnation of the electrodes and separators with the electrolyte. Charge-discharge tests were conducted using a multichannel battery tester (Model 4000, Maccor Inc.) in the potential range 3.0–4.35 V.

For the time-resolved XRD studies, a similar setup was used for the preparation of a charged sample, Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O₂, with $x = 0.33$ (2/3 lithium extraction). [8, 22, 23] The cell was transferred to a glove box for disassembly. The charged cathode material was scraped off from the electrode and transferred into either a 0.3 or 0.5 mm quartz capillary, which was sealed after wetting with a drop of excess electrolyte. [8] The capillary was mounted in the thermal stage of the diffractometer and XRD spectra were recorded as a set of circles on a mar345 image plate detector (Marresearch GmbH, Germany) in the transmission mode. The beamlines used were the X7B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) and the 1D and 5A at the Pohang Accelerator Laboratory (PAL). Soft XAS measurements were performed at the National Institute of

Standards and Technology (NIST) beamline U7A located at the NSLS. For the in situ soft X-ray study, a purpose-built thermally controlled sample holder was used. The charged electrodes mounted onto the holder were heated inside a vacuum chamber at the desired temperature and the corresponding soft XAS spectra were measured. The soft X-rays entered the vacuum chamber and impinged the sample at an angle of 45° . The partial electron yield (PEY) soft XAS spectra were simultaneously collected by PEY-detectors that were placed at 90° to the incoming X-rays. The beam was 1 mm in diameter. The estimated incident X-ray energy resolution was ~ 0.2 eV. The PEY data were recorded using a channel electron multiplier detector with the entrance grid bias set to -150 V. The PEY signal was normalized using the incident beam intensity obtained from the photoemission yield of a clean Au grid, to eliminate the effects of beam fluctuations and monochromator absorption features. All spectra were processed using standard pre- and post-edge normalization methods, as described in previously published work. [18, 24, 25] The pre-edge jump was subtracted to zero, followed by post-edge normalization, which consisted of dividing the pre-edge normalized spectra by the edge jump intensity obtained far above the Ni L-edge. The pre- and post-edge normalizations were performed using the Athena program. [26]

3. Results and discussion

Figure 1. X-ray diffraction patterns of (a) bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and (b) ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$

The X-ray diffraction patterns of bare and ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ are compared in Fig. 1. Both patterns show well-defined layered structures based on the hexagonal structure with space group R-3m. The absence of detectable impurity phases indicates the quality of the Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ powders. Both patterns for the bare and ZrO₂-coated samples are identical, implying that the coating process does not affect the bulk structure. The peaks originating from the ZrO₂ may not be observable because the coating layer constitutes less than 1.0 wt%. [27]

Figure 2. Low (A) and high magnification (a) HRTEM images for ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂, and the corresponding EDS elemental mappings of O (b), Zr (c), Ni (d), Co (e), and Al (f)

Figures 2(A) and (a) present the low and high magnification HRTEM images of the ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂. Figure 2(A) clearly shows a rough coating layer of ZrO₂ nanoparticles (~50–200 nm in diameter) on the Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ surface. **The particles do not cover the whole surface of Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂.** The nominal concentration of the ZrO₂ coating layer was 1.0 wt%. According to a previous report [18] and our preliminary experiments, the 1.0 wt% ZrO₂ coating had the highest impact on capacity-retention improvement. Coating at higher concentrations resulted in overpotentials in the cathode materials, whereas lower concentrations showed negligible effects.

EDS measurements were performed to confirm the presence of the ZrO₂-coating layer. In Figs. 2(b)–(f), the EDS mapping images show that O, Al, Ni, and Co were well dispersed within the particles, except Zr. The Zr was only present at the surface of the

particles and not in the bulk, indicating that the ZrO_2 nanoparticles cover the surfaces of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ particles.

Although the ZrO_2 particles do not cover the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ powders densely and completely, the large number of nanosized ZrO_2 particles attached tightly on the surface of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ powders would greatly reduce the surface area exposed to the electrolyte during charge/discharge cycling. [28]

Figure 3. (a) Initial charge-discharge curves of bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes at a current density of 0.2 C between 3.0 and 4.35 V and (b) rate performances of both electrodes

To investigate the electrochemical performance, the cell tests using cathodes of bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes were conducted. Figure 3 (a) displays the initial charge-discharge curves of bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes. The cut-off voltages were 3.00 and 4.35 V, and the current density was 0.2 C. The initial capacity of ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes were 168.4 and 153.6 mAhg^{-1} , respectively. This result is in good agreement with previous reports. [12, 13] The cycle performances of the bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes at various current rates are presented in Figure 3 (b). In the previous reports, the discharge capacity decreased with increasing current rates due to the limited lithium diffusion and electronic conduction. The behavior of bare electrode is similar to the coated electrodes in terms of stability, whereas the coated electrodes demonstrate slightly lower capacities due to the insulating property of ZrO_2 coating at a rate of 0.2 C. In contrast, a fast decay in capacity was observed in the bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode. Stable

electrochemical performance in terms of rate capability and cycleability has been demonstrated at various cycling rates on the coated electrodes.

The data in Fig. 3 reveal that the ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode exhibits superior cycling performance compared to the bare electrode. The ZrO_2 coating layer seems to improve the structural stability and suppress the chemical instability of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathode material, thus resulting in the improved capacity retention.[29] A more detailed discussion will be given later using the collected in situ XRD, TR-XRD, and soft-XAS data.

Figure 4. TR-XRD patterns of bare and ZrO_2 -coated $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes.

There are many literature reports on electrochemical performance improvement by ZrO_2 coating. However, due to its high nickel content, the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode is subject to thermal instability which leads to changes in its crystal structure with increasing temperature. [22] Accordingly, we considered the thermal stabilities of the bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes. In this study, to investigate structural changes in both samples during thermal decomposition, time-resolved (TR)-XRD analysis was performed. Figure 4 presents a series of TR-XRD patterns of charged samples of bare and ZrO_2 -coated $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathode materials collected during heating from 25 to 450°C. Two-thirds of the lithium ions were extracted from the samples, resulting in the $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ composition. The XRD patterns of the bare and ZrO_2 -coated partially de-intercalated

materials at room temperature revealed layered structures (space group: R-3m). For the bare $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, the phase transition from the layered to the disordered spinel structure (space group: Fd3m) started at ca. 219°C, as indicated by the coalescence of the $(108)_\text{R}$ and $(110)_\text{R}$ peaks in the layered structure. [30–32] This disordered spinel phase was gradually transformed to the rock-salt phase as the temperature increased from 353 to 450°C, as is evident from the decrease in the intensities of the spinel $(311)_\text{S}$ and $(511)_\text{S}$ peaks. [22] At the end of heating at 450°C, the main peaks were indexed as the cubic rock-salt phase (space group: Fm3m), with minor peaks corresponding to residual disordered spinel phase. [22] In contrast, the onset temperature for the thermal phase transition of ZrO_2 -coated $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ was 244°C. Additionally, the transition from the disordered spinel phase to the rock-salt phase did not occur in the ZrO_2 -coated material. A significant improvement in the thermal stability of the charged $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ was achieved by coating the surface with ZrO_2 .

In our previous study, we observed two O_2 release peaks that occurred at 240 and 320°C during each phase transition. [22] Generally, the O_2 released from the charged cathode is very reactive and, thus, can seriously affect the safety of LIBs. The second transition from the disordered spinel phase to the rock-salt phase more seriously affects the stability of $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ because a larger amount of O_2 gas is released during this transition than the first. The results reveal that the ZrO_2 coating on the surface of the $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ is effective in retarding the phase transition of the charged $\text{Li}_{0.33}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and would thus result in improved LIB safety. To investigate the effects of the ZrO_2 coating on the structural changes of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes during charging, and their relationship to the capacity retention, a synchrotron-based in situ XRD technique was used.

Figure 5. The first charge curves of the bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes at a current density of 0.1 C

Figure 5 shows the first charge curves of the (a) bare and (b) ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes collected during the experiment. An upper voltage limit was not set in order to monitor the full structural variation during charging. The samples were charged at a rate of 0.1 C and the experiment was terminated by a 12 h time limit. The scan numbers for the XRD experiment are marked on the charge curve. During charging, 361 XRD pattern scans were collected.

The charge curves show that the bare sample could only reach a maximum of 5.2 V, whereas the ZrO_2 -coated sample peaked at 5.4 V. In our previous report, we showed that a ZrO_2 coating was effective in improving the capacity retention of LiCoO_2 cathode materials during cycling with a high voltage limit window. [10, 16] This was attributed to the ZrO_2 -coating layer's ability to sluggish kinetics of reaction and to protect the surface of the cathode particles from side reactions with the electrolyte. Similarly, the reason that the ZrO_2 -coated sample can reach a higher voltage in the present case is very likely due to the same protective ability. It seems that the bare sample experiences more severe side reactions with the electrolyte, thus preventing charge accumulation in the cathode material and resulting in a sluggish increase in the

Figure 6. In situ XRD patterns of (a) bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and (b) ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes during first charge.

voltage of the electrode.

The in situ XRD patterns collected during the first charges of the cells using the bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes are plotted in Fig. 6. The scan numbers marked beside the patterns correspond to the numbers marked on the first charge curves in Fig. 5. The structural changes that occur in $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ during the first charging have been previously studied. [4] The peaks in the XRD spectra can be indexed to a hexagonal phase similar to that previously indexed for LiNiO_2 . [4, 28] During charging, there are negligible differences in the structural variations between the bare and ZrO_2 -coated samples. Both samples follow the same

Figure 7. Normalized Ni $L_{II,III}$ -edge XAS spectra of bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathode materials during heating using PEY mode

structural variation progression over a similar potential range, as shown in previous reports, indicating that the ZrO_2 -coating layer does not affect the bulk structural variation during the charging of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$. [4]

An investigation of the local structures of transition metal oxides in cathode materials using soft XAS was reported earlier. [23] In that report, we applied soft XAS simultaneously at the Ni L-edges in both the FY and PEY modes, to investigate changes in the electronic structure of the bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode during heating. The Ni L-edges XAS spectrum of bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ in the FY mode

indicated that the Ni ions in the bulk were preserved in the 4+ oxidation state during heating. In contrast, Ni ions at the surface were reduced to a lower oxidation state (from Ni^{4+} to Ni^{2+}) above 225°C, indicating that the surface of the cathode material had decomposed. The surface structure of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ is distinctly different from the bulk at high temperature. These results indicate that surface modification with inert or stable materials can be an effective way to improve the thermal stability of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathode material.

In this study, soft XAS spectra of the Ni $\text{L}_{\text{II,III}}$ -edge using the PEY mode were obtained to compare the thermal stability of the bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ materials, especially at the surface. The PEY measurements in the soft XAS technique give information about surface properties (to a depth of ~5 nm), whereas the FY measurements more or less identify bulk properties (up to 300 nm), similarly to XRD measurements. Because the surface sensitivity of PEY is higher than FY, we can determine the structural changes of the materials at elevated temperatures using the PEY mode. In Fig. 7, the spectra correspond to the Ni $2p \rightarrow 3d$ transition, split by the spin-orbit interaction of the Ni 2p core level. [20] The pristine Ni $\text{L}_{\text{II,III}}$ -edge PEY spectrum shows main peaks at ~851 and 868 eV due to the Ni 2p–3d electrostatic interaction and the crystal field effect of octahedral symmetry. [20] In the bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ material, we can observe the complete reduction of Ni^{4+} to Ni^{2+} at elevated temperature. When the sample was coated with ZrO_2 , the onset temperature for the reduction of Ni ions increased, as did the number of Ni ions remaining at the Ni^{4+} state at 350°C. These results indicate that the thermal stability of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ is improved by the ZrO_2 coating, which can also effectively prevent Ni ion reduction, especially at the surface of the material. Therefore, the enhanced electrochemical properties and thermal stability of the cathode material imparted by the ZrO_2 coating can be attributed to the suppression of undesirable Ni oxidation state changes at the surface.

4. Conclusions

We investigated the electronic structure differences between surface and bulk electrode materials through a soft XAS study in PEY modes. A deeper understanding of the electronic structure at both the surface and in the bulk was obtained for bare and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes at elevated temperature. The initial

capacity of the ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode was 153.6 mAhg^{-1} , which is similar to that of the bare electrode, and the powder XRD patterns for the both samples were identical. Nevertheless, improved electrochemical and thermal stability can be achieved for $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ by applying a stabilizing layered structure through the ZrO_2 coating of its surface. The enhanced electrochemical properties and thermal stability of the cathode materials imparted by the ZrO_2 coating can be attributed to the suppression of undesirable Ni oxidation state changes at the surface rather than in the bulk.

Acknowledgement

This work was supported by the R&D Convergence Program of NST (National Research Council of Science & Technology) of Republic of Korea and the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (Project no. 20142020103090) grant funded by the Korea government Ministry of Trade, Industry & Energy. This work was also supported by the Dongguk University Research Fund of 2014. The work done at Brookhaven National Lab. was supported by the U.S. Department of Energy, the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under Contract Number DE-SC0012704.

6. References

- [1] B.L. Ellis, K.T. Lee, L.F. Nazar, *Chem Mater*, 22 (2010) 691-714.
- [2] Y.K. Sun, J.M. Han, S.T. Myung, S.W. Lee, K. Amine, *Electrochem Commun*, 8 (2006) 821-826.
- [3] Y.K. Sun, S.T. Myung, M.H. Kim, J. Prakash, K. Amine, *J Am Chem Soc*, 127 (2005) 13411-13418.
- [4] W.S. Yoon, K.Y. Chung, J. McBreen, X.Q. Yang, *Electrochem Commun*, 8 (2006) 1257-1262.
- [5] K. Matsumoto, R. Kuzuo, K. Takeya, A. Yamanaka, *Journal of Power Sources*, 81 (1999) 558-561.
- [6] D.J. Lee, B. Scrosati, Y.K. Sun, *Journal of Power Sources*, 196 (2011) 7742-7746.
- [7] Y.C. Zhang, C.Y. Wang, *J Electrochem Soc*, 156 (2009) A527-A535.
- [8] W.S. Yoon, K.Y. Chung, M. Balasubramanian, J. Hanson, J. McBreen, X.Q. Yang, *Journal of Power Sources*, 163 (2006) 219-222.
- [9] J. Cho, Y.J. Kim, T.J. Kim, B. Park, *Angew Chem Int Edit*, 40 (2001) 3367-3369.
- [10] K.Y. Chung, W.S. Yoon, J. McBreen, X.Q. Yang, S.H. Oh, H.C. Shin, W. Il Cho, B.W. Cho, *J Electrochem Soc*, 153 (2006) A2152-A2157.
- [11] K.Y. Chung, W.S. Yoon, J. McBreen, X.Q. Yang, S.H. Oh, H.C. Shin, W.I. Cho, B.W. Cho, *Journal of Power Sources*, 174 (2007) 619-623.
- [12] S.H. Lee, C.S. Yoon, K. Amine, Y.K. Sun, *Journal of Power Sources*, 234 (2013) 201-207.
- [13] B.C. Park, H.B. Kim, H.J. Bang, J. Prakash, Y.K. Sun, *Ind Eng Chem Res*, 47 (2008) 3876-3882.
- [14] Y. Cho, J. Cho, *J Electrochem Soc*, 157 (2010) A625-A629.
- [15] Y. Cho, Y.S. Lee, S.A. Park, Y. Lee, J. Cho, *Electrochim Acta*, 56 (2010) 333-339.
- [16] K.Y. Chung, W.S. Yoon, H.S. Lee, J. McBreen, X.Q. Yang, S.H. Oh, W.H. Ryu, J.L. Lee, I.C. Won, B.W. Cho, *Journal of Power Sources*, 163 (2006) 185-190.
- [17] W.S. Yoon, M. Balasubramanian, X.Q. Yang, Z.G. Fu, D.A. Fischer, J. McBreen, *J Electrochem Soc*, 151 (2004) A246-A251.
- [18] W.S. Yoon, K.Y. Chung, J. McBreen, D.A. Fischer, X.Q. Yang, *Journal of Power Sources*, 174 (2007) 1015-1020.
- [19] K.W. Nam, S.M. Bak, E.Y. Hu, X.Q. Yu, Y.N. Zhou, X.J. Wang, L.J. Wu, Y.M. Zhu, K.Y.

- Chung, X.Q. Yang, *Adv Funct Mater*, 23 (2013) 1047-1063.
- [20] W.S. Yoon, K.Y. Chung, J. McBreen, D.A. Fischer, X.Q. Yang, *Journal of Power Sources*, 163 (2006) 234-237.
- [21] F.M.F. Degroot, *Journal of Electron Spectroscopy and Related Phenomena*, 67 (1994) 529-622.
- [22] S.M. Bak, K.W. Nam, W. Chang, X.Q. Yu, E.Y. Hu, S. Hwang, E.A. Stach, K.B. Kim, K.Y. Chung, X.Q. Yang, *Chem Mater*, 25 (2013) 337-351.
- [23] W.S. Yoon, O. Haas, S. Muhammad, H. Kim, W. Lee, D. Kim, D.A. Fischer, C. Jaye, X.Q. Yang, M. Balasubramanian, K.W. Nam, *Sci Rep-Uk*, 4 (2014).
- [24] K.Y. Chung, W.S. Yoon, K.B. Kim, B.W. Cho, X.Q. Yang, *J Appl Electrochem*, 41 (2011) 1295-1299.
- [25] W.S. Yoon, M. Balasubramanian, K.Y. Chung, X.Q. Yang, J. McBreen, C.P. Grey, D.A. Fischer, *J Am Chem Soc*, 127 (2005) 17479-17487.
- [26] B. Ravel, M. Newville, *J Synchrotron Radiat*, 12 (2005) 537-541.
- [27] H.W. Ha, N.J. Yun, K. Kim, *Electrochim Acta*, 52 (2007) 3236-3241.
- [28] X.Q. Yang, X. Sun, J. McBreen, *Electrochem Commun*, 1 (1999) 227-232.
- [29] A. M. Kannan, L. Rabenberg and A. Manthiram, *Electrochem Solid St*, 2003, 6, A16-A18
- [30] M. Guilmard, L. Croguennec, D. Denux, C. Delmas, *Chem Mater*, 15 (2003) 4476-4483.
- [31] M. Guilmard, L. Croguennec, C. Delmas, *Chem Mater*, 15 (2003) 4484-4493.
- [32] W.S. Yoon, M. Balasubramanian, X.Q. Yang, J. McBreen, J. Hanson, *Electrochem Solid St*, 8 (2005) A83-A86.

7. List of Captions for Figures

Figure 1. X-ray diffraction patterns of (a) bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and (b) ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$.

Figure 2. Low (A) and high magnification (a) HRTEM images for ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, and the corresponding EDS elemental mappings of O (b), Zr (c), Ni (d), Co (e), and Al (f).

Figure 3. (a) Initial charge-discharge curves of bare $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and ZrO_2 -coated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrodes at a current density of 0.2 C between 3.0 and 4.35 V and (b) rate performances of both electrodes

Figure 4. TR-XRD patterns of bare and ZrO₂-coated Li_{0.33}(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ electrodes.

Figure 5. The first charge curves of the bare Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ and ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ electrodes at current density of 0.1C.

Figure 6. *In situ* XRD patterns of (a) bare Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ and (b) ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ electrodes during first charge.

Figure 7. Normalized Ni L_{II,III}-edge XAS spectra of bare and ZrO₂-coated Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ cathode materials during heating using PEY mode.