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Journal of Power Sources 163 (2006) 185–190

JOURNAL OF POWER SOURCES

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Short communication

In situ XRD studies of the structural changes of ZrO_2-coated $LiCoO_2$ during cycling and their effects on capacity retention in lithium batteries

Kyung Yoon Chung[a], Won-Sub Yoon[a,*], Hung Sui Lee[a], James McBreen[a], Xiao-Qing Yang[a], Si Hyoung Oh[b], Woon Hyoung Ryu[b], Jae Lyong Lee[b], Won Il Cho[b], Byung Won Cho[b]

[a] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, United States*

[b] *Eco- & Nano Research Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea*

Received 8 August 2005; received in revised form 14 December 2005; accepted 20 December 2005
Available online 13 February 2006

Abstract

Synchrotron based in situ X-ray diffraction was used to study the structural changes of a ZrO_2-coated $LiCoO_2$ cathode in comparison with the uncoated sample during multi-cycling in a wider voltage window from 2.5 to 4.8 V. It was found that the improved cycling performance of ZrO_2-coated $LiCoO_2$ is closely related to the larger lattice parameter “*c*” variation range, which is an indicator of how far the structural change has proceeded towards the two end members of the phase transition stream during charge–discharge cycling. At fifth charge, the lattice parameter variation ranges for both uncoated and ZrO_2-coated $LiCoO_2$ were reduced compared with those for the first charge, reflecting the capacity fading caused by the high voltage cycling. However, this variation range reduction is smaller in ZrO_2-coated $LiCoO_2$ than that in the uncoated sample, and so is the capacity fading. These results point out an important direction for studying the fading mechanism and coating effects: the key issues are the surface protection, the interaction between the cathode surface and the electrolyte and the electrolyte decomposition. In order to improve the capacity retention during cycling, the variation range of lattice parameter “*c*” of $LiCoO_2$ should be preserved, not reduced.

Keywords: ZrO_2-coated $LiCoO_2$; In situ X-ray diffraction; Phase transitions; Lithium batteries

1. Introduction

$LiCoO_2$ is the most widely used cathode material for commercial lithium secondary batteries. It has been used as a cathode since the first commercialization of lithium secondary batteries. When a lithium ion cell or a $Li/Li_{1-x}CoO_2$ half cell is cycled within limited composition range (charging voltage limited below 4.2–4.3 V), it shows good capacity retention. However, at this voltage limit, only 50% of the lithium ions can be extracted from the $LiCoO_2$ cathode. When the charge limit is raised above 4.2–4.3 V, its capacity fades rapidly. If this capacity fading (together with the thermal stability problem) at higher voltage can be solved, more potential capacity will be utilized. There have been many efforts to improve the electrochemical performance of $LiCoO_2$ at high voltage. One technique is the modification of the cathode surface by coating with various metal oxides, e.g. Al_2O_3 [1], ZrO_2 [2,3], etc.

Although various types of coatings have been studied and significant improvements in capacity retention have been demonstrated, the mechanism of capacity fading during cycling with high voltage charge limit and the effects of surface coating are far from clear. It was reported by Cho et al. [2] that the capacity retention of $LiCoO_2$ type cathode material at high voltage can be significantly improved through coating its surface by metal oxides. They claimed that the coating $LiCoO_2$ with high fracture toughness oxides makes a zero-strain cathode material and among various metal oxides they tested, ZrO_2 is the most effective one. In Cho’s work, the effectiveness of ZrO_2 surface coating was attributed to the suppression of the variation of “*c*” axis of the $LiCoO_2$ unit cell which results in the improvement of the structural stability. The effectiveness of ZrO_2 coating for improving the capacity retention during high voltage cycling was also verified by Chen and Dahn [3]. However, they did not agree with the mechanism of capacity fading of $LiCoO_2$ at high voltage and the origin of the effectiveness of the surface coating proposed by Cho. Using in situ XRD Chen and Dahn [3] provided creditable evidence to show that the ZrO_2 coating does not affect

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[*] Corresponding author. Tel.: +1 631 344 6145; fax: +1 631 344 5815.
E-mail address: wonsuby@bnl.gov (W.-S. Yoon).

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doi:10.1016/j.jpowsour.2005.12.063

the variation of lattice parameters during cycling at all. By arguing the similarity of structural changes for both ZrO_2-coated and uncoated $LiCoO_2$ during charge to a voltage as high as 4.3 V, they challenged the "zero-strain" mechanism proposed by Cho et al. [2]. However, Chen and Dahn did not provide experimental data to show the main differences in structural changes during cycling between the coated and uncoated materials, and only suspected that the improvement of the cycling behavior may be caused by a reduction in the contact area between $LiCoO_2$ and electrolyte. Therefore, how does the ZrO_2 coating improve the capacity retention has still not been answered yet. Using synchrotron based in situ XRD, Liu et al. [4] studied the effects of Al_2O_3 coating on capacity retention during high voltage cycling and proposed the structural origin of these effects. Therefore, it will be very interesting to see if the structural changes of ZrO_2-coated $LiCoO_2$ and Al_2O_3-coated $LiCoO_2$ follow the same pattern.

In this paper, the results of high voltage cycling and in situ XRD of uncoated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$ by wet coating process samples will be presented. The in situ XRD data were collected on both coated and uncoated $LiCoO_2$ multiple cycled in the voltage range between 2.5 and 4.8 V (some cells were charged as high as 5.2 V). The 4.8 V high voltage limit was chosen for accelerating the structural damage of the uncoated sample. Clear differences in structural changes between the coated and uncoated $LiCoO_2$ cathode materials were observed. It was found that the larger the range in the lattice parameter "c" variation, the better the capacity retention. The variation range of the lattice parameter "c" is a good indicator of how far the structural change has proceeded towards the two end members of the phase transition stream during charge–discharge cycling. It looks like that the major role of the ZrO_2 coating is in protecting the surface of the cathode, but not in altering the bulk structure of cathode. This is in good agreement with the results reported by Liu et al. [4].

2. Experimental

The ZrO_2-coated $LiCoO_2$ by wet coating method are prepared using the following procedures. Commercially available $LiCoO_2$ with average particle size of 5 μm was used as a starting material. Coating solution was prepared by dissolving 3 wt.% $Zr(OH)_x(CH_3COO)_y$ $(x+y-4)$ in distilled water and stirring for more than 24 h at room temperature. Proper amount of $LiCoO_2$ powders were added into the coating solution and ultrasonically agitated for 30 min. The amount of $LiCoO_2$ powders to be added into the coating solution was determined based on the calculation that makes the final product with 2 wt.% coating layer. Then the solution was allowed to dry at room temperature followed by vacuum drying at 120 °C for 2 h to completely remove the residual moisture at the surface of precursor powders. The final product ZrO_2-coated $LiCoO_2$ powders were obtained by heat treatment of the precursor powders at 500 °C for 6 h in a furnace. The cathodes used in this study were prepared by slurring the active material powder with 3% poly-vinylidene fluoride (PVDF) and 10% (w/w) acetylene black in a n-methyl pyrrolidone (NMP) solvent, then coating the mixture onto Al foil. After vacuum drying at 100 °C for 12 h, the electrode disks (2.8 cm^2) were punched and weighed. The cathodes were incorporated into cells with a Li foil negative electrode and a Celgard separator. The electrolytes used were 1.2 M $LiPF_6$ electrolyte in a 3:7 ethyl carbonate (EC)/dimethyl carbonate (DMC) solvent. The cells were assembled in an argon-filled glove box. Electrochemical characterization was performed in a standard coin cell configuration. For in situ XRD cell, Mylar windows were used as has been described in detail elsewhere [5]. All of these in situ XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using a wide angle position sensitive detector (PSD). The wavelength used were 0.9999 Å. The PSD can collect one XRD scan in a period as short as a few minutes and cover 90° of 2θ angles simultaneously with good signal to noise ratio. It significantly reduced the data collection time for each scan, giving us a great advantage in studying the phase transition in real time. The 2θ angles of all the XRD spectra presented in this paper have been recalculated and converted to corresponding angles for $\lambda = 1.54$ Å, which is the wavelength of conventional X-ray tube source with Cu Kα radiation, for easy comparison with other published results in literature.

3. Results and discussion

Fig. 1 shows cycle performances of ZrO_2-coated $LiCoO_2$ and uncoated $LiCoO_2$ at various conditions. When $LiCoO_2$ is cycled between 3.0 and 4.2 V, it shows reasonably good capacity retention. The initial and 50th cycle capacities are 142.4 and 125.6 mAh g^{-1}, respectively. It retains 88% of its initial capacity at 50th cycle. By increasing the charge cutoff voltage to 4.5 V, the initial capacity increased to 188.0 mAh g^{-1}, which is 32% greater value than when the charge cutoff voltage was 4.2 V. It would be great if this additional capacity can be utilized in real battery cells. Unfortunately, the capacity retention becomes rather poor when charge cutoff voltage is raised to 4.5 V. The capacity at 50th cycle is 134.4 mAh g^{-1}, which is only 71% of

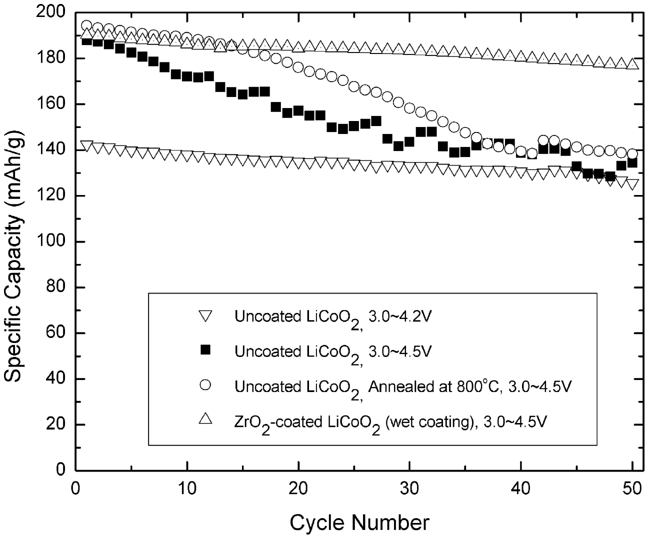

Fig. 1. Comparison of cycle performances of ZrO_2-coated $LiCoO_2$ and uncoated $LiCoO_2$ at various conditions.

its initial capacity. Its decreasing tendency tells that it will be even worse in further cycling. In order to compare the effects of high temperature annealing with surface coating on capacity retention, the cycling performance data for a $LiCoO_2$ cathode which had been annealed at 800 °C right before cell assembling is also plotted in Fig. 1. It shows improved capacity retention at the early stage of cycling and a slight increase in the initial capacity, comparing to the untreated sample. However, its capacity fading becomes comparable to the untreated one as it reaches around 40th cycle. One possible solution to improve the capacity retention of $LiCoO_2$ cycled at a wider voltage window is coating its surface with metal oxides [1–3]. The cycle performance of ZrO_2-coated $LiCoO_2$ shown in Fig. 1 demonstrates that surface coating is a much more effective way to reduce the capacity fading than the high temperature annealing. Since the amount of the coating material is very small (2 wt.% of $LiCoO_2$), the negative effects on the initial capacity is negligible. Actually, the initial capacity for coated $LiCoO_2$ when charged to 4.5 V is 190.2 mAh g^{-1}, which is slightly lower than the 194.3 mAh g^{-1} for annealed sample but higher than the 188.0 mAh g^{-1} for the uncoated one. This suggests that the surface of uncoated $LiCoO_2$ may have lost part of its capacity due to the surface reaction with air during storage period, while the surface coating protected the surface from this reaction and the annealing may have restored the lost capacity. At 50th cycle, 176.9 mAh g^{-1} capacity was obtained for this ZrO_2-coated $LiCoO_2$, which is 93% of its initial value. In the term of percentage capacity retention, the ZrO_2-coated $LiCoO_2$ cycled between 3.0 and 4.5 V is even better than that of uncoated $LiCoO_2$ cycled between 3.0 and 4.2 V.

In order to study the effects of ZrO_2 coating on the structural changes of $LiCoO_2$ during cycling, and their relationship to the capacity retention, synchrotron based in situ XRD technique was used. In situ XRD patterns were collected during cycling uncoated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$ between 2.5 and 4.8 V. The wider cutoff voltage limits were used to accelerate the deterioration of the sample, for the purpose of completing the experiment in limited time. Fig. 2 shows the first and fifth charge curves of uncoated $LiCoO_2$ up to 4.8 V at *C*/4.5 rate. The specific charge capacity obtained during the first charge is 294.6 mAh g^{-1}, which is greater than the theoretical capacity of $LiCoO_2$ (273.9 mAh g^{-1}). It is clear that part of this capacity is not real but reflecting the electric current consumed to decompose the electrolyte at high voltage. Fifty-seven scans of XRD spectra are collected during charge and five more are collected during subsequent resting period. The scan numbers are marked on the charge curve. At fifth charge, the specific capacity was 143.4 mAh g^{-1}, which is less than half of its initial capacity. Because the sample was cycled at a wider voltage window of 2.5–4.8 V, capacity fading is even faster than that shown in Fig. 1. Note that that the first plateau at the fifth charge is moved up to around 4.1 V from the 4.0 V region in the first charge. This indicates that the cell polarization had been increased during cycling, resulted from the impedance increase due to the electrolyte decomposition at high voltage.

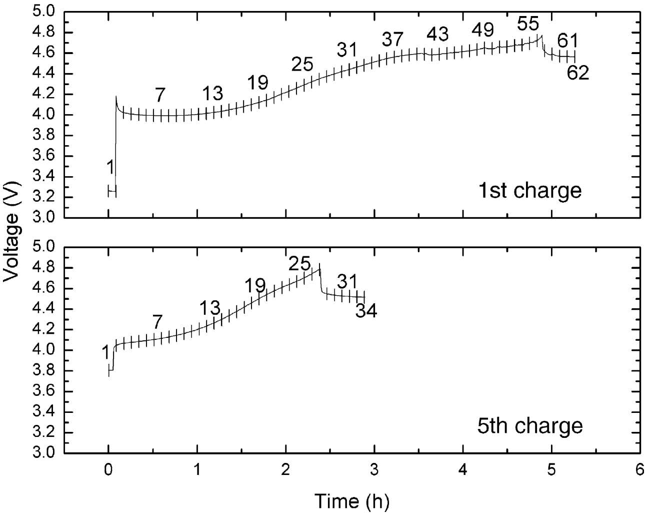

Fig. 2. The first and fifth charge curves of uncoated $LiCoO_2$ cycled between 2.5 and 4.8 V at *C*/4.5 rate.

The in situ XRD patterns collected during the first charge of the cell using uncoated $LiCoO_2$ cathode are plotted in Fig. 3 for the regions with Bragg reflections (indexed based on a hexagonal cell) from (0 0 3) to (1 0 4). The scan numbers marked beside the patterns correspond to the numbers marked on the first charge curve in Fig. 2. According to the previous reports, the $LiCoO_2$ undergoes phase transition of H1, H2a, H2, O1a, O1 during charge to 5.2 V [4–7]. The final phase O1 is formed around 4.8 V [6]. The XRD spectra during first charge show this complete phase transition. (0 0 3) peak of H1 phase at the beginning of charge transformed to (0 0 1) peak of the final O1 phase at the end of charge through multiple phase transformations. The H2a phase which is present for a short range of *x* value in $Li_{1-x}CoO_2$ between H1 and H2 phase are not as clearly observed in Fig. 3 as in the previous report [6], the reason for which is a greater charging rate. When in situ XRD patterns are collected from the sample cycling at high *C* rate, the peaks smear into one another and small peaks from the phases which are present for a short period of time may bury under the feet of larger peaks. The structural changes of $LiCoO_2$ shown in Fig. 3 are pretty much

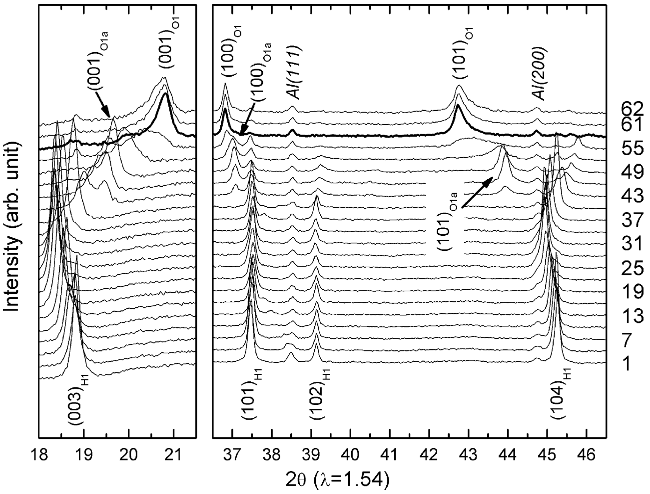

Fig. 3. The in situ XRD patterns of uncoated $LiCoO_2$ collected during the first charge to 4.8 V in the (0 0 3)–(1 0 4) region.

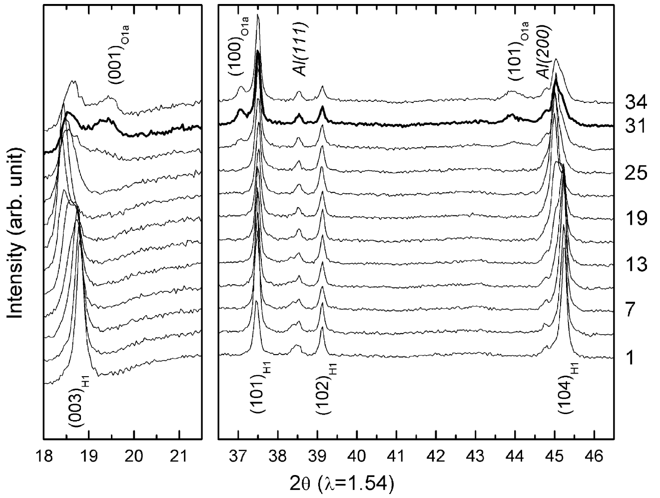

Fig. 4. The in situ XRD patterns of uncoated $LiCoO_2$ collected during the fifth charge to 4.8 V in the (0 0 3)–(1 0 4) region. The sample was cycled four times previously between 2.5 and 4.8 V.

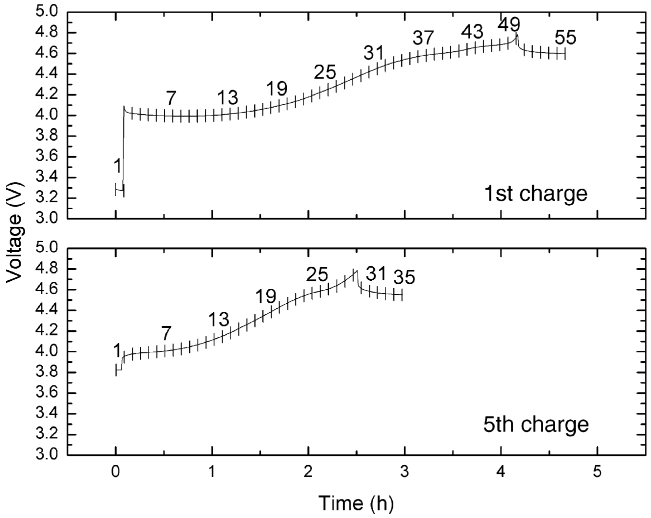

Fig. 5. The first and fifth charge curves of ZrO_2-coated $LiCoO_2$ cycled between 2.5 and 4.8 V at *C*/4.5 rate.

the same as reported in Ref. [5]. During the phase transition from H1 to H2a and H2, the lattice parameters "*a*" and "*b*" are almost unchanged, therefore, the (1 0 1), (1 0 2) and (1 0 4) peaks for H2a and H2 phase are indistinguishable from those for H1. At scan 43, new (1 0 0) and (1 0 1) peaks of O1a phase emerged and their intensity increased in expense of intensities of (1 0 1), (1 0 2) and (1 0 4) peaks of H2 phase during the subsequent scan. Finally, the peaks from H2 phase totally disappeared and O1a phase started to transform once again to the O1 phase. The XRD spectra collected during the first charge show that the phase transitions proceeded completely to the final phase O1 at the end of charge.

However, in the fifth charge for the uncoated sample, the XRD spectra clearly show that this series of phase transitions did not reach the final structure O1 at the end of charge. Fig. 4 shows the in situ XRD spectra collected during the fifth charge of uncoated $LiCoO_2$. The phase transformation of $(0\,0\,3)_{H1}$ proceeded only to $(0\,0\,1)_{O1a}$ and $(0\,0\,3)_{H2}$ is still present at the end of charge. (1 0 1) and (1 0 2) peaks from hexagonal phases are also present at the end of charge. The (1 0 0) peak representing the O1a phase is weak and broad, and no signature of the formation of final O1 phase can be observed. It reveals that at the end of fifth charge, the structure of the uncoated $LiCoO_2$ is in a state of the two-phase coexistence of H2 and O1a. This incomplete phase transition compared to those in the first charge clearly reflects the capacity loss during multi-cycling. When lithium ions are deintercalated from $LiCoO_2$, the average oxidation state of Co is increased to compensate the charge and the lattice parameter (mostly in "*c*") is contracted due to the smaller Co ion size at higher oxidation states. Therefore, the larger the variation ranges of the lattice parameter, the larger the specific capacity. The reduced variation range means reduced amount of lithium can been deintercalated from the cathode during charge.

Now we can examine the structural changes of the ZrO_2-coated sample. Following the same trend to the cycle performances shown in Fig. 1, ZrO_2-coated $LiCoO_2$ shows better capacity retention comparing to the uncoated $LiCoO_2$ during cycling at a wider voltage window of 2.5–4.8 V. The first and fifth charge curves of ZrO_2-coated $LiCoO_2$ are shown in Fig. 5. It was cycled at the same condition as for the uncoated $LiCoO_2$ shown in Fig. 2, i.e. cycled between 2.5 and 4.8 V at *C*/4.5 rate. Specific charge capacity obtained during the first charge was 250.6 mAh g^{-1}. The reasons why the ZrO_2-coated $LiCoO_2$ shows smaller specific capacity during the first charge compared to the uncoated $LiCoO_2$ can be ascribed mainly to the reduction of the decomposition of electrolyte. The charge curve of the first cycle in Fig. 5 shows smooth increase to 4.8 V unlike the one in Fig. 2. The first charge curve in Fig. 2 shows some fluctuation after it passed 4.6 V, which is a strong evidence of electrolyte decomposition. It is very likely that ZrO_2 coating layer isolates the $LiCoO_2$ surface from the electrolyte and suppresses the decomposition of electrolyte by means of covering the active centers which served as catalyst sites. Therefore, the false capacity from the electrolyte decomposition observed in Fig. 2 is not observed in Fig. 5, thus the calculated capacity of ZrO_2-coated $LiCoO_2$ in the first charge is less than that of uncoated $LiCoO_2$. A total of 49 scans of XRD spectra are collected during the first charging and 6 more are collected during subsequent resting period. At fifth charge, the specific capacity obtained is 151.2 mAh g^{-1}, which is greater than that of uncoated $LiCoO_2$ (143.4 mAh g^{-1}) and about 60.3% of its initial capacity. Therefore, it is certain that capacity retention of ZrO_2-coated $LiCoO_2$ is better than that of $LiCoO_2$ at a wider potential range of 2.5–4.8 V, following the same trend as in Fig. 1. Another interesting thing to note is that the coated one has less polarization than uncoated $LiCoO_2$ during the fifth charging. The coated one forms the first plateau near 4.0 V while the uncoated one forms near 4.1 V. This is consistent with our assumption that the ZrO_2 coating layer could protect the surface of $LiCoO_2$ from the precipitation of electrolyte decomposition products.

The in situ XRD patterns of ZrO_2-coated $LiCoO_2$ collected during the first and fifth charging are shown in Figs. 6 and 7, respectively. Similar to the case of uncoated $LiCoO_2$, the spectra during the first charge (Fig. 6) show complete phase transition to

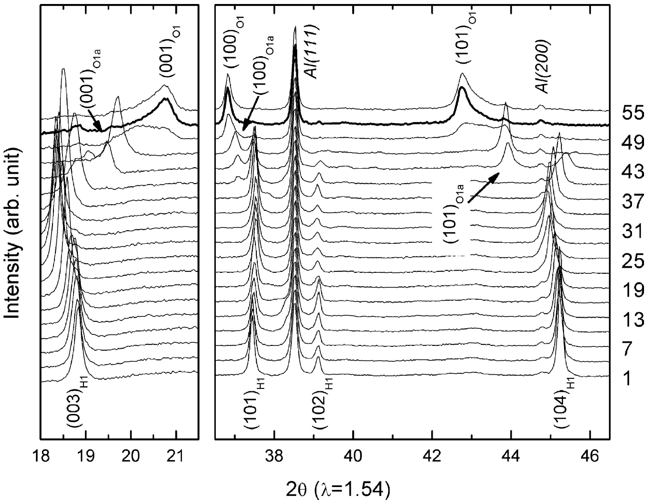

Fig. 6. The in situ XRD patterns of ZrO_2-coated $LiCoO_2$ collected during the first charge to 4.8 V in the (0 0 3)–(1 0 4) region.

O1. The phase transformations of ZrO_2-coated $LiCoO_2$ during the first charging are very similar to those of uncoated $LiCoO_2$. However, the phase transformations in the fifth charge of these two samples show significant differences. The XRD spectra during fifth charge (Fig. 7) show phase transition to O1a, but the peak of $(0\,0\,1)_{O1a}$ is much sharper and more intense compared to that in fifth charge of uncoated $LiCoO_2$ (Fig. 4). Although the $(1\,0\,1)_{H2}$ and $(1\,0\,4)_{H2}$ peaks of hexagonal phase do not disappear completely, the intensity of $(1\,0\,2)_{H2}$ peak does reduce to almost zero. The growing intensity of $(1\,0\,0)_{O1a}$ and $(1\,0\,1)_{O1a}$ peaks and the peak sharpening at the end of charge give indication that the H2 phase completely transformed to the O1a phase at the end of fifth charge. This clearly demonstrated that ZrO_2-coated $LiCoO_2$ had reached a stage more close to the final structure at the end of fifth charge, comparing with the uncoated $LiCoO_2$.

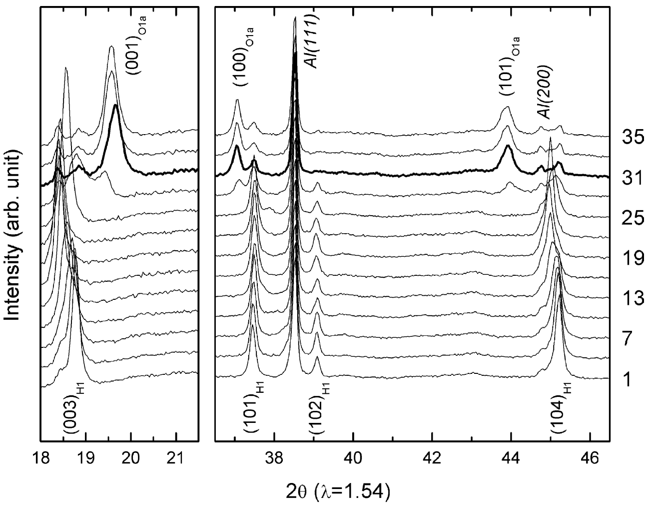

Fig. 7. The in situ XRD patterns of ZrO_2-coated $LiCoO_2$ collected during the fifth charge to 4.8 V in the (0 0 3)–(1 0 4) region. The sample was cycled four times previously between 2.5 and 4.8 V.

From the comparison of the in situ XRD spectra and capacity retention of ZrO_2-coated $LiCoO_2$ and uncoated $LiCoO_2$, it is quite clear that the capacity loss is directly related to the reduced range of lattice parameter variation, reflecting the decreased amount of lithium content change during lithium deintercalation. The ZrO_2 coating is playing a critical role in improving the capacity retention of $LiCoO_2$ at a wider cutoff voltage over 4.5 V by forming a protecting layer at the surface of the $LiCoO_2$ cathode.

4. Conclusion

Based on in situ XRD diffraction studies using synchrotron X-ray source, the effects of ZrO_2 coating on improving the capacity retention of $LiCoO_2$ cathode cycled in wider voltage window and related structural changes have been studied. It was found that ZrO_2-coated $LiCoO_2$ shows better capacity retention during multiple cycling compared to uncoated $LiCoO_2$ when cycled at wider voltage window, i.e. 2.5–4.8 V. The structural changes show that larger lattice parameter variation range was preserved. At the end of first charge, both uncoated and ZrO_2-coated $LiCoO_2$ samples showed complete phase transformations from initial H1 phase to final O1 phase through multiple phase transformations. At fifth charge, the lattice parameter variation ranges for both uncoated and ZrO_2-coated $LiCoO_2$ were reduced, i.e. none of them could reach the final O1 structure. However, ZrO_2-coated $LiCoO_2$ showed less deterioration compared to uncoated $LiCoO_2$. Uncoated $LiCoO_2$ did not complete the phase transition into O1a phase and ended with a two-phase coexistence region of H2 and O1a at the end of charge. In comparison, the ZrO_2-coated $LiCoO_2$ almost completed phase transformation into O1a phase at the end of charge. It confirmed that the structural changes are closely tracking the performance difference between ZrO_2-coated $LiCoO_2$ and uncoated $LiCoO_2$. The incomplete phase transition after multiple cycling compared to those in the first charge shows the capacity loss is directly related to the reduced range of lattice parameter variation, reflecting the decreased amount of lithium content change during lithium deintercalation. Therefore, the improvement of capacity retention by coating is not related to the suppression of structural changes during cycling as described in Ref. [2], but related to preserving the lattice parameter variation range, in other words, the larger the lattice parameter variation range, the larger the capacity. From the comparison of the polarization increases after multi-cycling between uncoated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$, it can be clearly seen that the polarization increase for ZrO_2-coated sample is much less than the uncoated one, indicating that ZrO_2 coating layer may play an important role in protecting the surface of $LiCoO_2$ from the precipitation of electrolyte decomposition products. However, more work is needed to study the interactions between the $LiCoO_2$ cathode and the electrolyte during high voltage charging, the effects of coating on reducing the electrolyte decomposition and the precipitation of decomposed products on the cathode surface, as well as on the structural changes related to the capacity fading.

Acknowledgements

The work done at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract Number DE-AC02-98CH10886. The work done at KIST was supported by a grant (code #: 04K1501-01910) from ‘Center for Nanostructured Materials Technology’ under ‘21st Century Frontier R&D Programs’ of Ministry of Science and Technology, Korea and by ‘Development of Basic Technology for Next Generation Li-composite Secondary Battery’ of KIST. We also appreciate the technical support from beam-line personnel of X18A of National Synchrotron Light Source (NSLS), which is supported by U.S. DOE.

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