Short communication

In situ X-ray diffraction studies on the mechanism of capacity retention improvement by coating at the surface of LiCoO$_2$

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Abstract

Synchrotron based *in situ* X-ray diffraction technique has been used to study the mechanism of capacity fading of LiCoO$_2$ cycled to a higher voltage above the normal 4.2 V limit and to investigate the mechanism of capacity retention improvement by ZrO$_2$ surface coating on LiCoO$_2$. It was found that the capacity fading of LiCoO$_2$ cycled at higher voltage limit is closely related to the increased polarization rather than the bulk crystal structure damage. The capacity of uncoated LiCoO$_2$ sample dropped to less than 70 mAh g^{-1} when charged to 4.8 V after high voltage cycling. However, when the voltage limit was further increased to 8.35 V, the capacity was partially restored and the corresponding structural changes were recovered to the similar level as seen in fresh sample. This indicates that the integrity of the bulk crystal structure of LiCoO$_2$ was not seriously damaged during cycling to 4.8 V. The increased polarization seems to be responsible for the fading capacity and the uncompleted phase transformation of LiCoO$_2$. The polarization-induced capacity fading can be significantly improved by ZrO$_2$ surface coating. It was proposed that the effect of ZrO$_2$-coating layer on the capacity retention during high voltage cycling is through the formation of protection layer on the surface of LiCoO$_2$ particles, which can reduce the decomposition of the electrolyte at higher voltages.
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1. Introduction

During discharge–charge cycling, the LiCoO$_2$ cathode undergoes a series of structural changes with a wide range interlayer distance (the lattice parameter "*c*") variation as lithium ions intercalate or de-intercalate into or from the layered structure. When it is cycled within limited composition range (charging voltage limited below 4.2 V), the capacity retention is very good. Unfortunately, at this voltage limit, only 50% of the lithium ions can be extracted from the LiCoO$_2$ cathode and the specific capacity is also limited to 150 mAh g^{-1}. More capacity will be utilized if the charge limit can be raised above 4.2 V. The problem is, the cell capacity fades very rapidly during high voltage cycling. If this capacity fading problem (together with the thermal stability problem) at higher voltage can be solved, it will significantly increase the capacity and cycling life of the lithium battery using

LiCoO$_2$ cathode material. Among the efforts to improve the electrochemical performance of LiCoO$_2$ at high voltage, one is to modify the cathode surface by coating LiCoO$_2$ with various metal oxides (such as Al$_2$O$_3$, and ZrO$_2$ [1–3], 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 is far from clear. It was reported by Cho et al. [1] that the capacity retention of LiCoO$_2$ type cathode material at high voltage can be significantly improved through coating its surface by ZrO$_2$. These results were confirmed by Chen and Dahn [2]. However, these two authors 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 et al. In Cho et al.'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. Using *in situ* XRD Chen and Dahn [2] provided creditable evidence to show that the ZrO$_2$ coating does not affect 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 cycling with a voltage limit as high as 4.3 V, they challenged the "zero-strain" mechanism proposed by Cho et al. [1]. 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.

In our previous works [3], we showed that the ZrO_2-coated $LiCoO_2$ has a similar structural change behavior as the Al_2O_3-coated $LiCoO_2$ [4]. It was found that the variation range of the "c" axis is concurrently related to the capacity retention, that is, the larger the range of the lattice parameter variation during cycling, the better the capacity retention. We had suggested that the increase of polarization is very closely related to the capacity fading of $LiCoO_2$ cycled with high voltage limit. Chen and Dahn also reported that the capacity fading of $LiCoO_2$ cycled to 4.5 V might be due to the impedance growth, but not the structural changes of the bulk [6]. However, only first charge results on the lattice constant changes of ZrO_2-coated and uncoated $LiCoO_2$ were presented in this reference, which was not sufficient to support their conclusion on the multiple cycling. Therefore, it is very important to investigate the structural changes of $LiCoO_2$ after multiple cycling when the samples have significantly faded capacity. In our another work, we have provided the evidence that the effect of ZrO_2 coating is very closely related to the protection of the $LiCoO_2$ cathode surface and the reduction of electrolyte decomposition at higher voltages [5]. In that paper, one of the evidences for the effect of the ZrO_2-coating layer on the capacity retention improvement was the observation of the complete phase transformation series from H1 to O1 phases via H2 and O1a phases during a 5.5 V high limit charging for the ZrO_2-coated $LiCoO_2$, which had been cycled at 4.8 V limit and experienced significant capacity fading. If the capacity fading were originated from the bulk structural damages caused by the stress during cycling, quite different structural changes would have been observed.

However, it will be more convincing if the complete phase transformation series from H1 to O1 phases via H2 and O1a phases can be observed for the uncoated $LiCoO_2$ sample, which had gone through multiple cycles with high voltage limit and suffered serious capacity fading. If this structural change behavior can be observed under certain charging conditions, it will tell us that the integrity of the bulk structure is not seriously damaged by the high voltage cycling, even for the uncoated $LiCoO_2$ sample with significant capacity fading and so called ZrO_2 coating induced bulk structure stabilization effects proposed by Cho et al. [1] is not valid. Therefore, we designed experiments to cycle the cell using uncoated $LiCoO_2$ cathode, which had significant capacity fading due to 4.8 V cycling, to a voltage as high as 8.35 V and studied the structural changes during this charge. Structural changes studies were also carried out during the subsequent charge to show that the integrity of the bulk structure of degraded $LiCoO_2$ was not damaged seriously. The results reported in this paper will provide further evidence to support the mechanism we proposed for the capacity fading during 4.8 V limit cycling, as well as for the effectiveness of surface coating.

2. Experimental

The $LiCoO_2$ material with average particle size of 5 μm was obtained from JESECHEM Corporation and the uncoated samples were used as received. The ZrO_2-coated $LiCoO_2$ are prepared by mechanochemical method, which is explained in detain elsewhere [3,5]. The observation of the coated particles using scanning electron microscopy shows that the coating layer looks like loose flakes or clusters of flakes attached to the surface of $LiCoO_2$ particles similar to those reported previously by Kannan et al. [7]. The cathodes used in this study were prepared by slurrying the active material with 3% poly-vinylidene fluoride (PVDF), and 10% acetylene black (w/w) in an *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. For *in situ* XRD cell, Mylar windows were used as has been described in detail elsewhere [8]. In order to assure that the data collected on the in situ cell is reliable, a parallel study using the standard 2032 coin cell was conducted. The in situ XRD cell showed slight but negligible IR increases comparing with the reference coin cell. *In situ* XRD patterns 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 wavelengths 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 patterns 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

In our previous report, we have shown that the ZrO_2 coating is effective in improving capacity retention of $LiCoO_2$ when cycled to high voltage limit of 4.8 V. This was attributed to the ZrO_2-coating layer's ability to protect the surface of $LiCoO_2$ particles from the precipitation of electrolyte decomposition [3,5]. In order to see if the uncoated $LiCoO_2$ sample with significant capacity fading due to the 4.8 V cycling will be able to complete the phase transitions as the fresh sample under different charge condition, we also designed experiments to raise the charge limit to a voltage as high as 8.35 V and investigated the difference between the structural changes of this uncoated $LiCoO_2$ and the ZrO_2-coated $LiCoO_2$.

Fig. 1 shows the 12th charge curves of the ZrO_2-coated and the uncoated $LiCoO_2$ after cycling 11 times between 2.5 and 4.8 V at C/4.5 rate. The charging current was calculated based on theoretical capacity. The 4.8 V high voltage limit was chosen

to accelerate the capacity fading of the samples in order to complete the experiment in the given beamtime. The samples had been cycled at $C/4.5$ rate from the 1st to 10th cycle and at $C/15$ rate in the 11th cycle. Since the samples had been cycled at a wider voltage limit, their capacity had faded more significantly compared to other samples in the literature. In the 12th cycle, the capacities achieved at 4.8 V was 100.14 mAh g^{-1} for the ZrO$_2$-coated LiCoO$_2$ and 69.46 mAh g^{-1} for the uncoated. For the ZrO$_2$-coated LiCoO$_2$, 54 scans of XRD spectra were collected during charging to 5.5 V and two more were collected during subsequent resting period. The selected XRD scan numbers are marked on the charge curves. For the uncoated LiCoO$_2$, 87 scans of XRD spectra were collected during charging to 8.35 V and 22 more were collected during subsequent resting period.

The *in situ* XRD patterns collected during the 12th charge of the cell using ZrO$_2$-coated LiCoO$_2$ cathode are plotted in Fig. 2 for the regions with Bragg reflections (indexed based on a hexagonal cell) from $(0\,0\,3)$ to $(1\,0\,2)$. The scan numbers marked beside the patterns correspond to the numbers marked on the charge curve for the ZrO$_2$-coated LiCoO$_2$ in Fig. 1. The first thick line at the 21st scan indicates where the sample reached 4.8 V and the second thick line at the 54th scan indicates where the charge current was cut-off. After this scan, the resting period started. All *in situ* spectra in this paper are treated in the same way. The structural changes of the LiCoO$_2$ during first charging have been studied in literature [9–11]. It was reported previously that the structure of LiCoO$_2$ starts as an H1 phase before charge,

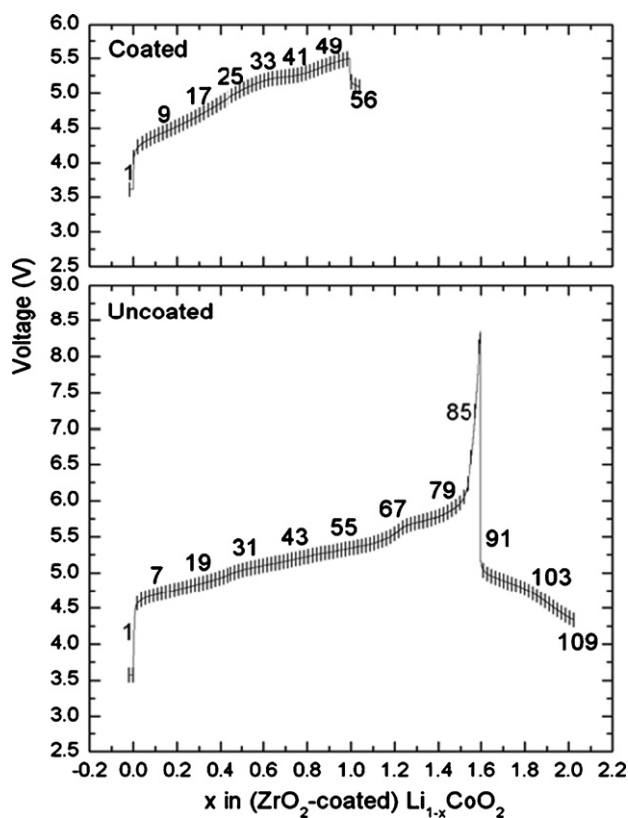undergoes a series of phase transformation through H2, O1a, and finally to a hexagonal phase O1 at voltage around 4.8 V [9]. However, in Fig. 2, the peaks representing the O1a phase are barely observed at 4.8 V. $(0\,0\,1)_{O1a}$ peak is very broad and weak. $(1\,0\,0)_{O1a}$ peak is hardly recognizable and $(1\,0\,2)_{H1}$ peak is still present. This incomplete phase transformation at 4.8 V is the apparent evidences that the sample had been deteriorated significantly. After passing the 4.8 V, the sample underwent a series of phase transitions through the O1a phase ended at the final O1 phase at around scan 45 ($\sim$5.3 V), which was delayed to a much higher voltage region than those of the fresh LiCoO$_2$. Even though the phase transitions took place at higher voltages, the same series of phase transitions as seen in the fresh samples, from H1 to H2, then O1a, and finally to O1 were observed. This indicates that the integrity of the bulk structure of the ZrO$_2$-coated LiCoO$_2$ cathode was not seriously damaged during the cycling. What has been changed most is at the surface, where the decomposition products of the electrolyte significantly increased the impedance [5]. This result confirms that the ZrO$_2$-coating layer has the surface protection effect on LiCoO$_2$. It will be more convincing if we can monitor the true bulk structural damage and study the structural changes during the subsequent cycling. Therefore, we raised the charge limit to 8.35 V and collected the *in situ* XRD patterns during charge for an uncoated LiCoO$_2$ sample, which had gone through the same cycling history as the ZrO$_2$-coated LiCoO$_2$.

Fig. 3 shows the *in situ* XRD patterns of uncoated LiCoO$_2$ collected during 12th charging to a high voltage of 8.35 V at $C/4.5$ rate. At 4.8 V (scan 15), the major phases observed were H1 and H2 phase. The first signature of the O1a phase was
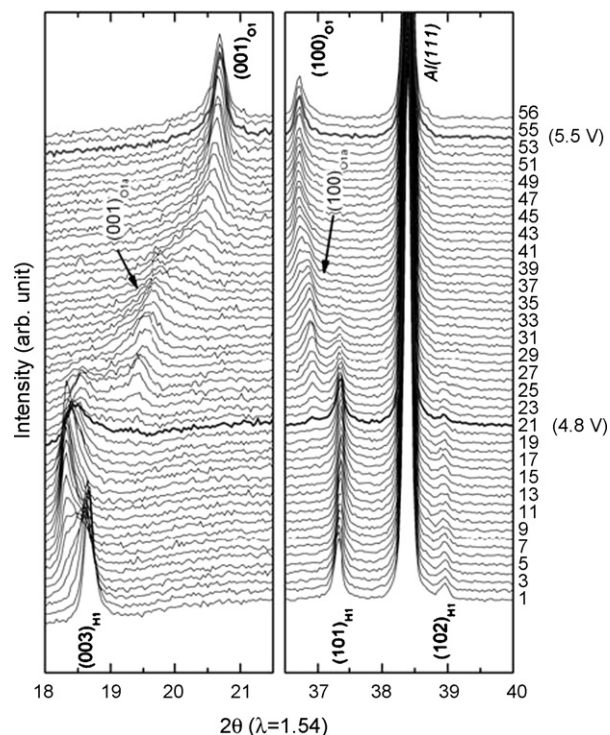

Fig. 1. The 12th charge curve of uncoated and ZrO$_2$-coated Li$_{1-x}$CoO$_2$. The sample was charged at $C/4.5$ rate to 5.5 V for the coated one and to 8.35 V for the uncoated.

Fig. 2. The *in situ* XRD patterns of ZrO$_2$-coated Li$_{1-x}$CoO$_2$ collected during the 12th charge to 5.5 V at $C/4.5$ rate in the $(0\,0\,3)$ to $(1\,0\,2)$ range.

observed at 5.04 V which is much higher voltage than that in ZrO_2-coated $LiCoO_2$. A small signature of O1a phase still remains even after the cell voltage passed 5.69 V (scan 71). The phase transformation to O1 phase seems to be completed at 6.05 V (scan 83). The cell voltage shoots up to 8.35 V rapidly after scan 83. Although, each phase transition takes place at a much higher voltage value than those in Fig. 2 for ZrO_2-coated $LiCoO_2$, it can be clearly seen that the complete phase transformation from H1 to O1 phase was observed in uncoated $LiCoO_2$ with significant capacity fading. It demonstrates that the capacity fading of the uncoated $LiCoO_2$ is also related more closely to the polarization increase rather than to the integrity damage of the bulk structure. Thus the effect of ZrO_2-coating layer is confirmed to be more closely related to the protection of $LiCoO_2$ surface rather than structure stabilization. A very interesting structural change behavior should be noted in Fig. 3 is the structural reversal during resting period after cutting off the charging current: the O1 phase reversed to the O1a phase during the resting period. This is due to the non-uniformly distributed precipitation of the electrolyte decomposition products. This structural reversal during resting had been observed for very high rate charging. Under the condition of very high rate charging, the bulk structure is at non-equilibrium state, after the charge current is cut-off, the system will be relaxed to its equilibrium state, reflecting a structural reversal in its XRD patterns. For this uncoated sample after 4.8 V cycling, large parts of the $LiCoO_2$ particle surface were blocked by the electrolyte decomposition products. This resulted in the non-uniformity of lithium concentration at the surface and in the bulk, as well as the non-equilibrium state of the phase transition, which is quite similar as the high rate charging, even when the
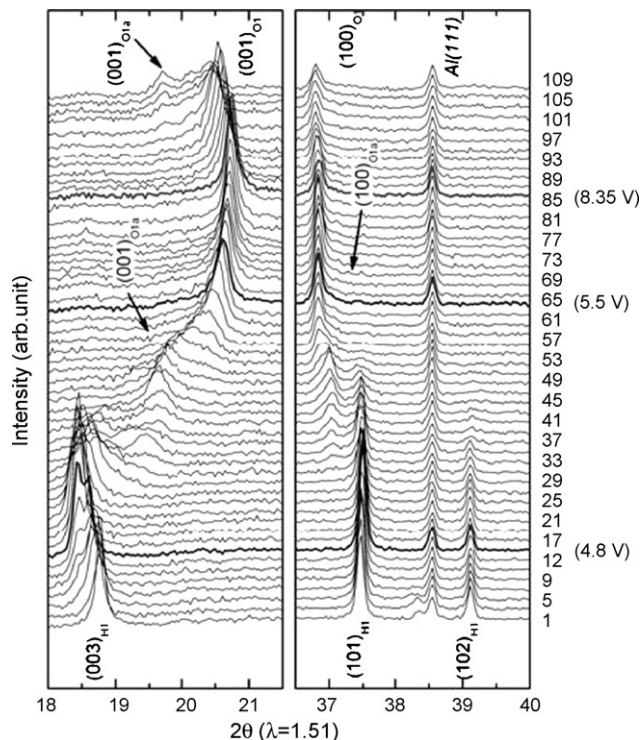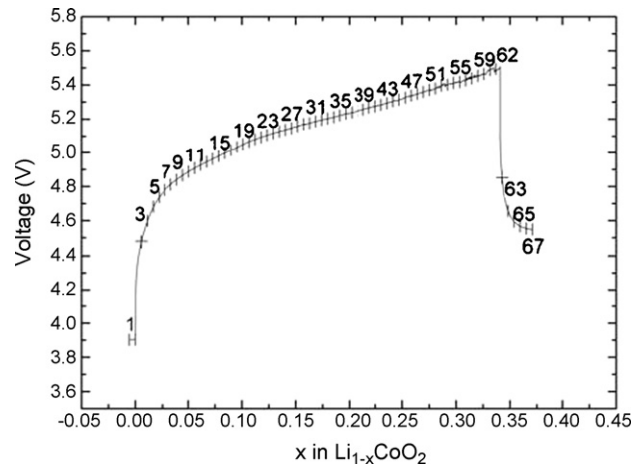

Fig. 4. The 13th charge curves of uncoated $Li_{1-x}CoO_2$ to 5.5 V at $C/15$ rate. The sample was charged to 8.35 V at $C/4.5$ rate in the 12th charging.

real charging rate was quite low. This is an additional supporting evidence for the capacity fading mechanism we have proposed.

After this very high voltage charge at 8.35 V, we cycled the sample used in Fig. 3 and collected the *in situ* XRD patterns during the 13th charging to 5.5 V. Figs. 4 and 5 shows the charging curve and the *in situ* XRD patterns collected. Since the sample had been charged to a very high voltage of 8.35 V and approximately 1.5 times the theoretical capacities of charges had been derived from the sample, the problem caused by the electrolyte decomposition is much more severe. In the subsequent charging, i.e. in the 13th charging (Fig. 4), only 34% of the theoretical capacities were achieved when charged to 5.5 V. In the practi-
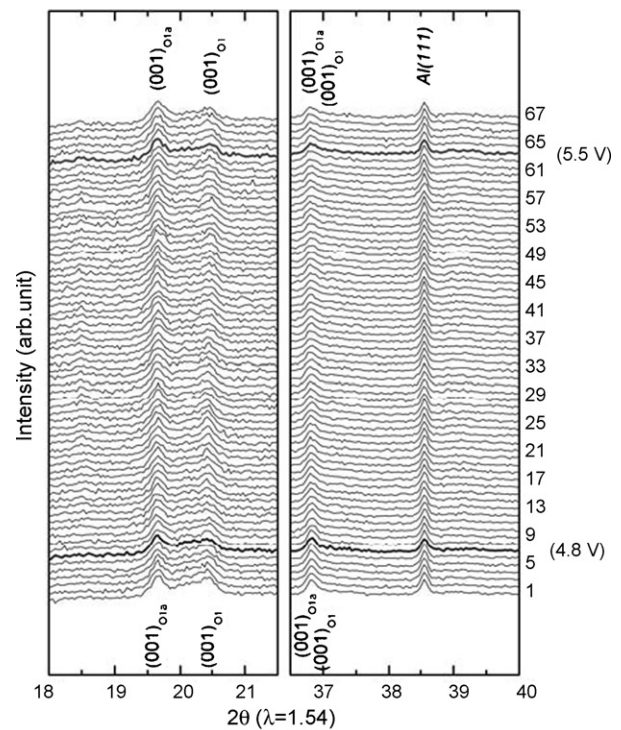

Fig. 3. The *in situ* XRD patterns of uncoated $Li_{1-x}CoO_2$ collected during the 12th charging to 8.35 V at $C/4.5$ rate in the (0 0 3) to (1 0 2) range.

Fig. 5. The *in situ* XRD patterns of uncoated $Li_{1-x}CoO_2$ collected during the 13th charging to 5.5 V at $C/15$ rate in the (0 0 3) to (1 0 2) range.

cal upper cut-off voltage of 4.2 V, negligible capacities were achieved. The *in situ* XRD patterns in Fig. 5 clearly show that the cathode material is far from the equilibrium state indicated by the charge curve. At the beginning of 13th charge, the starting structure is not the H1 structure it should be, but is a mixture of O1a and O1 phase with the O1a phase being the dominant phase. During charge, no changes were observed. The positions of the peaks indexed to O1a phase and O1 phase did not move at all and the intensities of those peaks did not change either. It clearly shows that the surface of the cathode particle had been severely blocked. Further studies will be needed to see if the bulk structure had been damaged too. The *in situ* XRD patterns in Fig. 5 clearly show that the reduction in the variation range of lattice constants is a good gauge to monitor the capacity fading of the cathode materials. This also further confirms that when $LiCoO_2$ is cycled under 4.8 V, the major factor contributing to the capacity fading is the polarization increase at the surface of $LiCoO_2$.

4. Conclusion

In this study, synchrotron based *in situ* X-ray diffraction has been used to confirm the effect of ZrO_2 coating on $LiCoO_2$. Both ZrO_2-coated and uncoated $LiCoO_2$ showed the completion of the phase transformation from H1 to O1 via H2 and O1a at 5.3 and 6.05 V. However, all the phase transitions started and finished at much higher voltages than those for uncycled fresh $LiCoO_2$. This demonstrates that the integrity of the bulk structure of the ZrO_2-coated $LiCoO_2$ cathode was not seriously damaged during the cycling, what has been changed most is at the surface, where the decomposition products of the electrolyte significantly increased the impedance. In the subsequent cycling of uncoated $LiCoO_2$ after charging to 8.35 V, the *in situ* XRD patterns show no phase transformation, peak shift, or intensity variation of the peaks. Thus, it could be concluded that the effect of ZrO_2-coating layer on the capacity retention improvement is on the protection of the surface of $LiCoO_2$ particles and reducing the electrolyte decomposition at higher voltages, not the stabilization of the structure. When cycled with a voltage limit at 4.8 V, the bulk structural damage is minimal.

Acknowledgements

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