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Charge compensation and capacity fading in $LiCoO_2$ at high voltage investigated by soft x-ray absorption spectroscopy*

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In order to obtain an in-depth insight into the mechanism of charge compensation and capacity fading in $LiCoO_2$, the evolution of electronic structure of $LiCoO_2$ at different cutoff voltages and after different cycles are studied by soft x-ray absorption spectroscopy in total electron (TEY) and fluorescence (TFY) detection modes, which provide surface and bulk information, respectively. The spectra of Co $L_{2,3}$-edge indicate that Co contributes to charge compensation below 4.4 V. Combining with the spectra of O K-edge, it manifests that only O contributes to electron compensation above 4.4 V with the formation of local O 2p holes both on the surface and in the bulk, where the surficial O evolves more remarkably. The evolution of the O 2p holes gives an explanation to the origin of O_2^- or even O_2. A comparison between the TEY and TFY of O K-edge spectra of $LiCoO_2$ cycled in a range from 3 V to 4.6 V indicates both the structural change in the bulk and aggregation of lithium salts on the electrode surface are responsible for the capacity fading. However, the latter is found to play a more important role after many cycles.

Keywords: soft x-ray absorption, $LiCoO_2$, charge compensation, capacity degradation

PACS: 78.70.Dm, 82.47.Aa, 82.30.–b **DOI:** 10.1088/1674-1056/27/10/107802

1. Introduction

Layered $LiCoO_2$ cathode, which is used in the first commercial lithium ion battery (LIB), still dominates the portable electronic device market nowadays.[1,2] Its theoretical capacity can reach up to 274 mAh·g^{-1}, with all the Li ions extracted. The practical capacity, however, is only about 140 mAh·g^{-1} with the cutoff voltage up to 4.2 V (versus Li/Li$^+$), corresponding to only 0.5 Li per CoO_2 extracted.[3] One way to enhance its capacity is to charge the battery cell to higher potential above 4.2 V. However, $LiCoO_2$ cycled with a cutoff voltage higher than 4.2 V suffers a severe capacity fading.[4,5] With the aim to improve both the energy density and cycling performance, the mechanism of capacity fading when $LiCoO_2$ serving at high cutoff voltage (> 4.2 V) has been studied intensively from the viewpoint of both structure and electrochemistry.[4,6–11] The irreversible phase transition in the bulk was first considered as the main reason of the capacity loss.[4] Later, the side reaction at the electrode/electrolyte interface was reported to play a more important role in the capacity loss,[6,7,10–12] which initiated the development of surface coating methods, to some extent, to improve the cycling stability.[13–15]

Because the lithiation/delithiation are always accompanied with insertion/extraction of electrons into/from the electrodes, investigation on the evolution of electronic structure of $LiCoO_2$ will provide new information for better understanding of the origin of extra capacity at high voltage and the mechanism of capacity fading.[16–20] Goodenough pointed out that the Co^{4+}/Co^{3+} redox couple at the top of the O band gave an intrinsic voltage limit and that the formation of peroxide with > 0.5 Li extracted led to a loss of O_2.[18] The charge transfer between electrode and electrolyte was thought to result in the formation of solid-electrolyte interface (SEI) film.[18,21] Experimental studies on the electronic structure were carried out by various spectroscopic characterization techniques.[22–33] Among them, soft x-ray absorption spectroscopy (sXAS) is one of the most powerful tools because of its elemental and chemical sensitivity, high energy resolution. More importantly, for 3d transition-metal oxides, the sXAS directly probes the metal-3d and oxygen-2p unoccupied electronic structure,

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which are the key states to regulate the fundamental properties and practical performances of most current metal-oxide cathodes. Therefore, it has been widely employed in the battery research.[34–40]

Several sXAS studies focusing on the electronic structure of $LiCoO_2$ have been reported.[24–26,28–30] Montoro *et al.*[24,25] showed that the Co ions remain mostly unaffected and always in trivalent low-spin states with Li deintercalated chemically. On the other hand, the O was partially oxidized during Li chemical extraction. Uchimoto *et al.*[26] studied the electronic structure of $LiCoO_2$ during the electrochemical reaction and concluded that the Co ions were still 3+ even with 0.8Li extracted from $LiCoO_2$ while the oxidation of O ions mainly took place. Conversely, Yoon *et al.*[28] demonstrated that charge compensation could be achieved in O and Co ions simultaneously with $LiCoO_2$ film electrode cycled in a range between 3 V and 4.2 V. They also suggested that the capacity fading of the $LiCoO_2$ could be related to the decrease of Co–O bond covalency. Chen *et al.*[30] studied the chemically delithiated $LiCoO_2$ and also demonstrated the contribution of Co ions should not be negligible in the charge compensation process. Meanwhile, they found that the oxidation of O^{2-} on the surface and in the bulk were different. Mizokawa *et al.*[41] emphasized the critical role of O 2p holes and thought that the O 2p holes were bonded to the Co^{4+} sites and Li^+ vacancy, which helped to improve the electronic and Li^+ conductivities. Obviously, the charge compensation from O has been confirmed through the sXAS studies, which strongly supports the model proposed by Goodenough. Meanwhile, the contribution of Co ions to the charge compensation process has also been verified gradually. Nevertheless, the detailed mechanism of the charge compensation from O is still under debate. According to Goodenough's model, $LiCoO_2$ will suffer structure collapse due to the O loss at the voltage higher than 4.2 V. However, all the studies above did not give any further description of the evolution of O related to the O loss on the surface or in the bulk. It should also be noted that the evolution of O 2p holes needs to be studied carefully because of the convolution of features at the pre-edge of O K-edge sXAS resulting from O 2p hole and the hybridization between Co and O. Furthermore, the correlation between capacity fading and evolution of electronic structure during cycling with the cutoff voltage higher than 4.2 V invokes more investigation.

In this work, we study the $LiCoO_2$ cathodes of commercial pouch cells from Contemporary Amperex Technology Ltd (CATL, Ningde, Fujian). Benefiting from the strict manufacturing processes, a solid evolution of surface and bulk electronic structure could be explored by measuring soft x-ray absorption spectra in TEY and TFY modes with surface (< 10 nm) and bulk (> 100 nm) sensitivity, respectively. In our case, the evolution of Co $L_{2,3}$ and O K-edge are examined carefully to investigate the charge compensation of O. The correlations between capacity fading and the evolution of electronic structure are studied by comparing the O K-edge spectra of $LiCoO_2$ cycled in the range of 3 V to 4.6 V and 3 V to 4.4 V both in TEY and TFY modes. This study can provide clues to the above debates and crucial information for seeking for a better treatment process to improve the cyclability.

2. Experimental methods

2.1. Battery test and sample preparation

Pouch full cells were prepared by the CATL Company. The cathode was composed of $LiCoO_2$, super P black (SP), and polyvinylidene difluoride (PVDF) in a weight ratio of 94:3:3. The anode was made of hard carbon and PVDF binder in a weight ratio of 92:8. The electrolyte of $LiPF_6$ (1 mol·dm^{-3}) was mixed in ethylene carbonate/diethyl carbonate (EC/DMC) with volume ratio 1:1. The assembly process was operated in a drying room.

All cells were tested by using the electrochemical workstation at 45 °C. For the 1st cycle, the cells produced in the same batch were firstly charged to 3.9 V at a rate of 0.1 C then to a certain cutoff voltage (i.e., 4.2 V, 4.4 V or 4.6 V) at a rate of 0.7 C and kept for 0.2 h, and then discharged to 3 V at a rate of 0.7 C and kept for 0.2 h. For the subsequent cycling test, the schedule was almost the same as that in the 1st cycle except that the charging rate to 3.9 V is 0.7 C.

All the tested cells were transported into Ar-filled glovebox and disassembled at an Ar atmosphere with O_2 and H_2O content lower than 0.1 ppm. The cathode samples were washed three times by using anhydrous DMC to remove the interference of electrolyte. To avoid any possible interference from the atmosphere, the samples were sealed with Al-plastic bags, taken to the Taiwan Light Source (TLS), and then transferred to the test chamber through an Ar-filled glovebox.

The samples with various cutoff voltage including 3.9 V, 4.2 V, 4.4 V, and 4.6 V at the 1st cycle were prepared for the charge compensation study. Samples at fully charged (4.4 V or 4.6 V) or discharged (3 V) states with the different capacity retention ratios (i.e., 100%, 99%, 51%, 42% at 4.6 V, and 100%, 72%, 50% at 3 V) and samples cycled 10 times between different voltage ranges (3 V–4.4 V versus 3 V–4.6 V) were prepared for studying the correlation between the evolution of the electronic structure and capacity fading.

2.2. Soft x-ray absorption spectroscopy

The sXAS measurements of the $LiCoO_2$ cathode were carried out at beamline 20A1 of the Taiwan Light Source (TLS) at HsinChu, Taiwan, beamline 08U of Shanghai Synchrotron Facility (SSRF) and beamline 12B-a of the National Synchrotron Radiation Laboratory (NSRL) at Hefei. In particular, the beamline 20A1 was equipped with a 6-m high-energy spherical grating monochromator (6-m HSGM) to supply a

photon beam with resolving power up to 8000. The spectra of Co $L_{2,3}$ and O K-edge were collected in TEY and TFY mode in an ultrahigh-vacuum chamber with a base pressure of about 5×10^{-10} Torr (1 Torr = 1.33322×10^{2} Pa). The TEY and TFY spectra were normalized to the photon flux of incident beam monitored by the Au mesh. The photon energy was calibrated with the spectra of reference samples (CoO for Co $L_{2,3}$-edge and $SrTiO_3$ for O K-edge).

3. Results and discussion

3.1. Competition between amount of Li^+ extraction and cycling performance

The amount of Li^+ extraction with various cutoff voltages is shown in Fig. 1(a). With the cutoff voltage increasing in steps of 0.1 V from 4.3 V to 4.6 V, the corresponding increments of the amount of Li^+ extraction are 0.0811, 0.0607, and 0.1083, which correspond to 8.1%, 6.1%, and 10.8% of the theoretical capacity of $LiCoO_2$, respectively. It indicates that each increment of voltage by 0.1 V from 4.3 V is crucial to improve the energy density of the $LiCoO_2$ cell, among which the increase from 4.5 V to 4.6 V is the most significant.

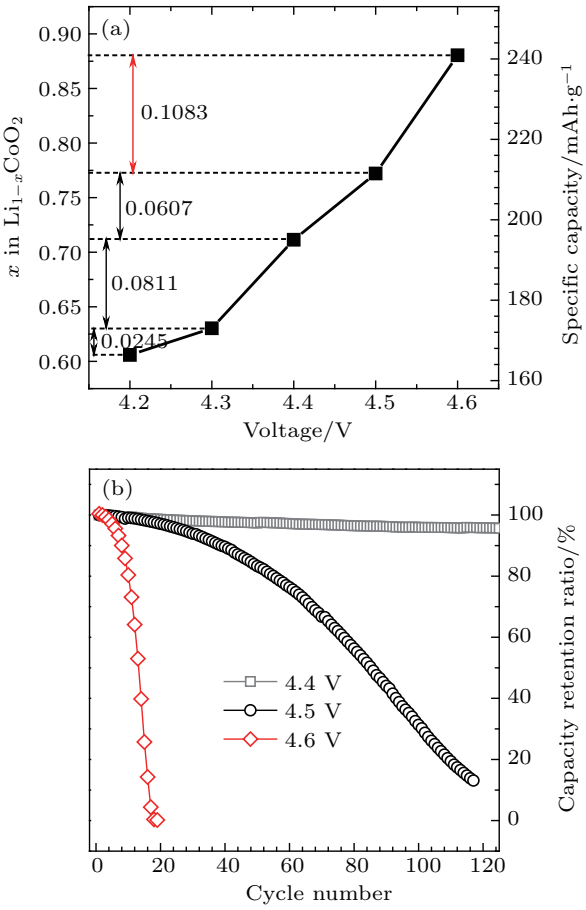


Fig. 1. (color online) Electrochemical tests of $LiCoO_2$, showing (a) amount of Li^+ increasing with upper cutoff voltage, and (b) cycling performances for the charge cutoff voltages of 4.4, 4.5, and 4.6 V.

The cycling performances with the upper cutoff voltage of 4.4, 4.5, and 4.6 V are shown in Fig. 1(b). The $LiCoO_2$/carbon battery cycled between 3 V and 4.4 V only has a capacity loss of 4.22% after 120 cycles. With the upper cutoff voltage increased to 4.5 V, the cells can only keep 19.40% of the initial capacity after 110 cycles. The capacity decreases sharply to 0 within 20 cycles with the upper cutoff voltage of 4.6 V. It demonstrates that the cycling performance is severely deteriorated by each increase of 0.1 V from 4.4 V even though the energy density can be improved notably.

3.2. Charge compensation during Li extraction

To avoid any possible interference from the side reaction at the electrode/electrolyte interface, the TFY spectra of Co $L_{2,3}$-edge and O K-edge, which reflect the bulk evolution, are firstly studied. As shown in Fig. 2(a), Co L-edge is divided into L_2 (792 eV to 802 eV) and L_3-edge (778 eV to 788 eV), which originate from the transition from the $2p_{1/2}$ and $2p_{3/2}$ states due to the core-hole spin-orbital coupling. Co L_3-edge of the initial $LiCoO_2$ has 3 peak features, marked as B, A, and C, respectively.

When charged to 3.9 V, the intensity of peak B increases notably while the peak A shifts to higher energy and becomes broader. During charging from 3.9 V to 4.4 V, the intensity of peak B continues to increase while peak A continues to shift to higher energy and become broader. However, there is almost no change when charging from 4.4 V to 4.6 V, as confirmed by the careful comparison in Fig. 2(c). In other words, all the features of the Co L_3-edge, including the increasing intensity of peak B and blue-shift of peak A, evolve below 4.4 V. In addition, it should be noticed that peak C disappears gradually when the battery is charged to 4.6 V. We cannot determine, however, whether it is an intrinsic evolution or just because of the broadening of peak A. Moreover, it has been suggested that peak C results from Co^{3+} in high spin state and is less sensitive to the distortion of Co–O octahedron.[42,43] Thus, only the evolution of features B and A are discussed. Peak B is attributed to the generation of Co^{2+} in some research.[44,45] If this assignment were true, we would conclude that a fair amount of Co^{2+} ions generate at least at 3.9 V during the 1st charging process. It contradicts with the experimental facts that major redox should be oxidized with Li^+ extracted. In addition, CoO is thought to be electrochemical inactive in the voltage range from 3 to 4.6 V.[46,47] Thus the assignment also contradicts with the good cyclability of $LiCoO_2$ with a cutoff voltage less than 4.2 V. A more reasonable assignment is the contribution from Co^{4+}.[41] The evolution of peak B indicates that the oxidation of Co^{3+} to Co^{4+} provides electrons with the battery being charged below 4.4 V. Peak A, which takes the major part in Co L-edge, is mainly related to Co^{3+}. It has been pointed out that the gravity of the L_3 shifts to higher energy mainly due to the oxidation of Co^{3+}.[45,48] Someone has suggested that the evolution of peak A is also closely associated with the re-hybridization between Co and O molecular

orbital.[28,49] Nevertheless, the evolution of peak A is consistent with peak B, indicating that the changes of Co occur below 4.4 V.

Next, the corresponding spectra of O K-edge are studied. As shown in Fig. 2(b), O K-edge spectra can be divided into two parts. The pre-edge peaks with the energy lower than 535 eV are assigned to the transitions from oxygen 1 s orbital to the states hybridized between O 2p orbital and Co 3d orbital. The hump above 535 eV is assigned to the transition to the states hybridized between O 2p and Co 4sp orbitals. The O K pre-edge of the pristine $LiCoO_2$ has only one notable feature, marked as peak a. Because most of Co^{3+} ions stay at the low-spin state,[24,45] where t_{2g} orbital is fully filled while e_g is completely unfilled (i.e. $t_{2g}^6 e_g^0$), peak a is thought to originate from the hybridization between Co^{3+} e_g states with O 2p states. When the battery is charged to 3.9 V, two new notable features b_1 and b_2 at lower energy appear. When they are charged from 3.9 V to 4.4 V, the intensity of peaks b_1 and b_2 increase a bit. Peaks b_1 and b_2 were reported to result from the hybridization of O 2p states with the t_{2g} and e_g states of Co^{4+}.[41] Thus the increasing intensity is consistent with the oxidation from Co^{3+} to Co^{4+}, where both the amount of holes in 3d states and the covalency of Co–O increase. So far, the spectral changes of the O K-edge XAS, though relatively more dramatic, are consistent with those of Co $L_{2,3}$-edge XAS with respect to the Li extraction. It should be noted that because of the convolution of features at O–K pre-edge resulting from both O 2p hole and the hybridization between Co and O, it is difficult to distinguish the contribution of O 2p holes to the electron compensation below 4.4 V.

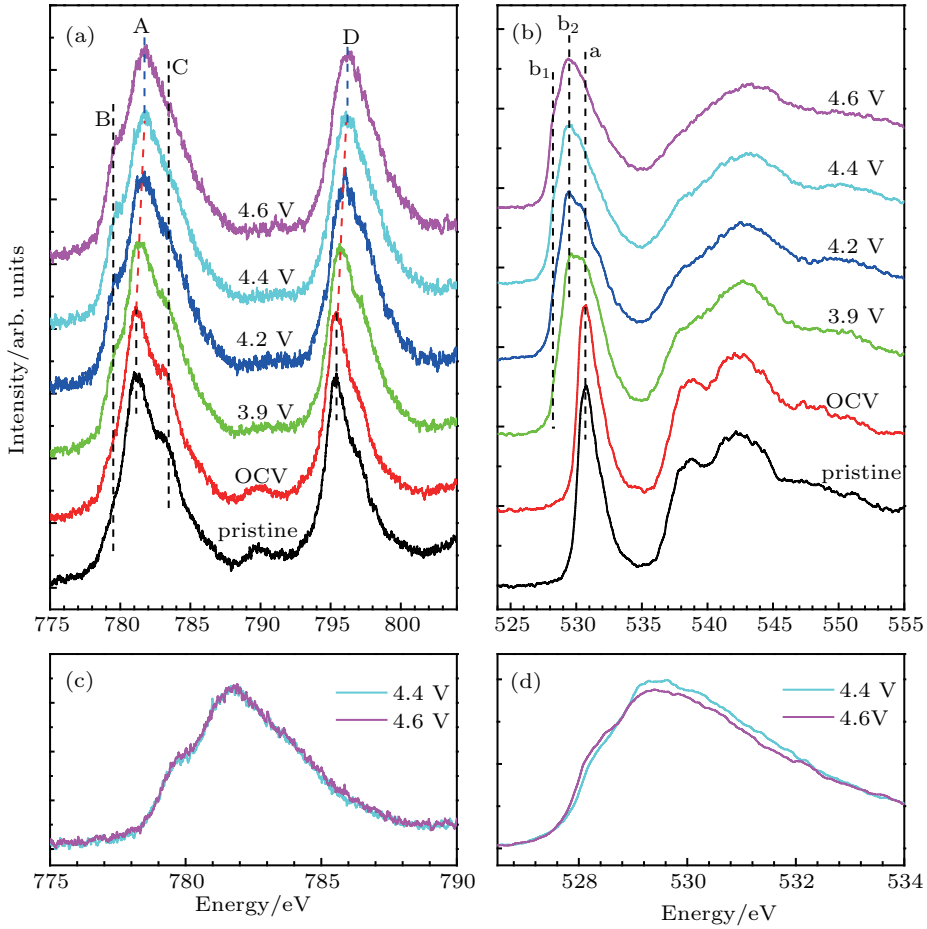


Fig. 2. (color online) (a) Normalized Co $L_{2,3}$-edge x-ray absorption spectra and (b) normalized oxygen K-edge x-ray absorption spectra of $Li_{1-x}CoO_2$ with respect to the cut-off voltage in the TFY mode, and ((c) and (d)) magnified parts of Co L_3 and O K pre-edge spectra above 4.4 V, respectively, which are convenient for comparison.

What is more attractive is the evolution of O K-edge above 4.4 V where there is no obvious variation at the Co $L_{2,3}$-edge. By careful comparison, as shown in Fig. 2(d), peak intensity in the range of about 528 eV–528.8 eV increases slightly while that in the range of about 529 eV–532 eV decreases from 4.4 V to 4.6 V. This evolution corresponds to the charge compensation from O, indicating the formation of O 2p hole with extra Li^+ extraction. Moreover, we can conclude that the O 2p holes are very local or even not related to the Co-O bond at all, otherwise the Co L-edge will change more or less. The feature in the range of about 529 eV–532 eV is different from that reported previously where O 2p holes were thought to lie between 530 eV–535 eV and led the intensity of peaks to increase with the Li^+ extracted.[50–52] The different position might result from a different coordination environment around O in the Li_xCoO_2 compared with those in

the Li-excess cathodes. The reducing intensity of this feature might be related to the increasing intensity of the feature in the range of about 528 eV–528.8 eV. This feature is consistent with the feature of O_2^- reported on KO_2 previously and has also been found in the study on Li_2MnO_3.[53,54] Thus the evolution of these two features might indicate that the formation of O_2^- may result from the combination of the O anions with a local hole, which gives an explanation to the origin of O_2^- or even the evolution of O_2 and needs more confirmation in future. Nevertheless, our results indicate that the evolution of O 2p holes can be found in $LiCoO_2$ conventional cathodes.

3.3. Surficial evolution with Li extraction

The TEY spectra of Co $L_{2,3}$ are shown in Fig. 3(a). The discussion on the Co TEY will be simplified as the evolution trend is very similar to that in the bulk in spite of a better signal-to-noise ratio leading to unambiguous evolution. We thus conclude that Co^{3+} turns into Co^{4+} below 4.4 V on the surface, which is confirmed by the careful comparison between the magnified parts, as shown in Fig. 3(c).

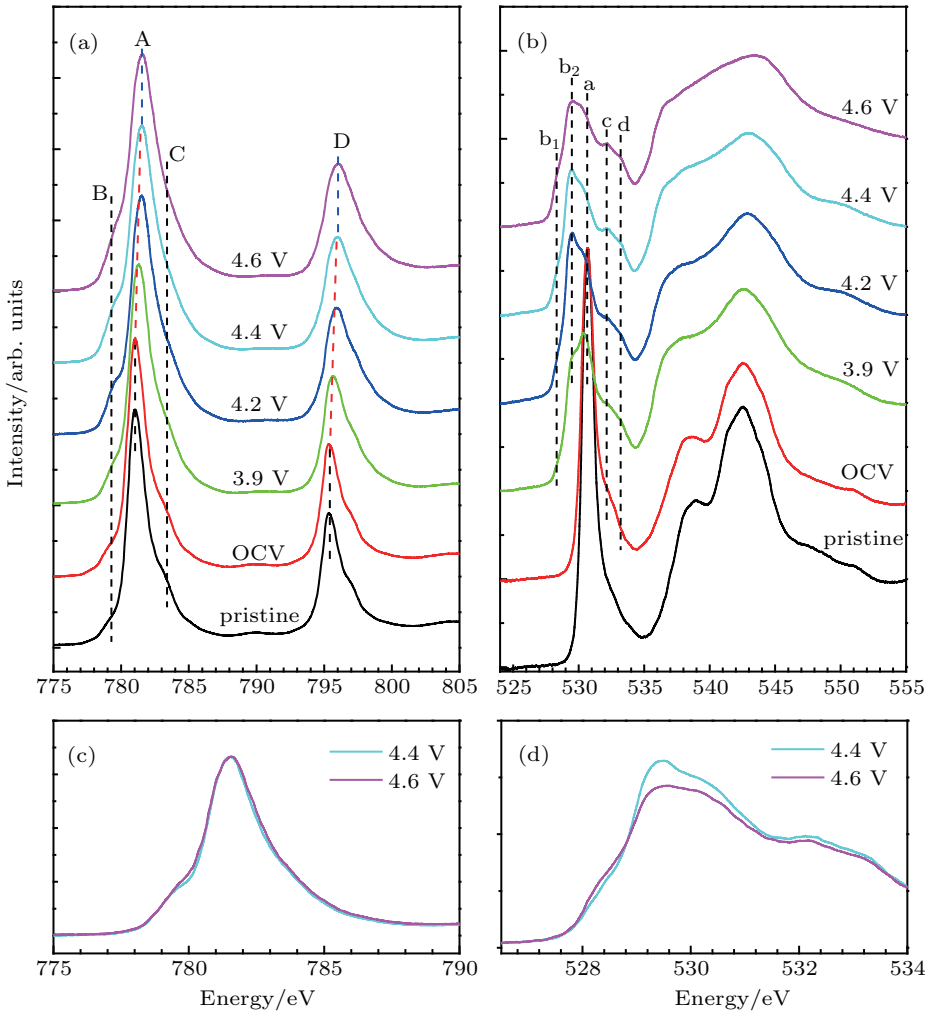


Fig. 3. (color online) (a) Normalized Co $L_{2,3}$-edge x-ray absorption spectra, (b) normalized oxygen K-edge x-ray absorption spectra of $Li_{1-x}CoO_2$ with respect to the cut-off voltage in the TEY mode, and ((c) and (d)) magnified parts of Co L_3 and O K pre-edge spectra above 4.4 V, respectively, which are convenient for comparison.

The evolution of surficial O is revealed by the TEY spectra of O K-edge in Fig. 3(b). While the battery is charged from 3.9 V to 4.4 V, relative intensities among b_1, b_2 and a evolve more notably than the changes of bulk O, indicating the interface undergoes more severe evolution than the bulk accompanied with side reactions. Besides, new peak features marked as c and d evolve. According to previous reports,[55,56] peaks c and d are assigned to the lithium salts from the reaction between $LiCoO_2$ and electrolyte. With the $LiCoO_2$ cathode immersed into the electrolyte in open-circuit voltage (OCV) state, the faint peaks c and d indicate that the interface changes a bit but is stable overall. When the battery is charged to 3.9 V, peaks c and d become more obvious, indicating that interfacial reactions already take place at 3.9 V. However, the invisible change of peaks c and d from 3.9 V to 4.6 V indicates that the side reactions turn very weak.

Like the case in the bulk, the O evolution above 4.4 V draws more attention. Through the careful comparison between 4.4 V and 4.6 V shown in Fig. 3(d), the evolution is the same as that in TFY spectra except that the amplitude in TEY spectra is larger, suggesting that more O 2p holes evolve on the surface.

3.4. Correlation between capacity fading and evolution of electronic structure

To shed light on the mechanism of capacity fading from the viewpoint of electronic structure, the sXAS spectra of $LiCoO_2$ cathodes with different capacity retention ratios are studied, where the samples cycled between 3 V and 4.6 V are taken for example because of the most severe capacity degradation. Since the O K-edge is more sensitive to the evolution than the Co L-edge, only the TEY and TFY spectra of the O K-edge are shown.

The TFY data of the $LiCoO_2$ cathodes in the 1st cycle are shown in Fig. 4(a). The fully discharged state (i.e., discharged to 3 V) looks like the pristine state except remaining weak features of b_1 and b_2. It indicates that most of the $LiCoO_2$ in the bulk evolves reversibly in spite of a bit residual of Co^{4+}. In comparison, the surficial evolution is much more severe as shown in Fig. 4(b). For the fully discharged state, the stronger features b_1 and b_2 while the weaker peak a indicate more residuals of Co^{4+} on the surface.

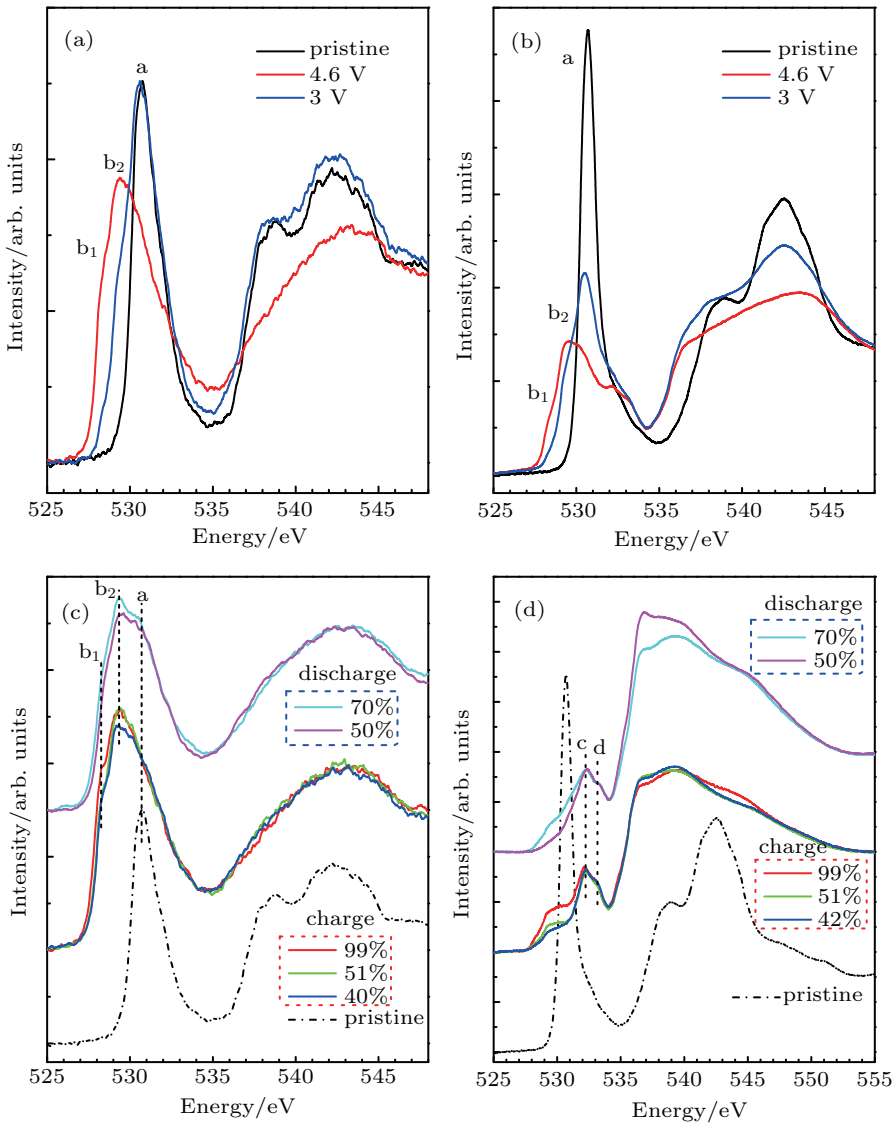


Fig. 4. (color online) (a) TFY and (b) TEY spectra of O K-edge of $LiCoO_2$ cathodes in the 1st cycle, (c) TFY and (d) TEY spectra of O K-edge of $LiCoO_2$ cathodes at fully charged state or fully discharged state with various capacity retention ratios.

The capacity degradation during cycling is further studied. As shown in Fig. 4(c), the TFY spectra of fully charged states regardless of capacity retention ratios have little changes compared with the fully charged state in the 1st cycle. It indicates the Co–O bonds at fully charged states are very similar regardless of capacity degradation. However, in the fully discharged states, the spectra with capacity retention of 72% and 50% look very similar to the fully charged states except a small hump corresponding to peak a, which is very different from the evolution in the 1st cycle. It indicates that more Co^{4+} ions cannot return back to Co^{3+} but stay at the fully charged state, leading to the capacity fading. The invisible evolution with the ratio from 72% to 50% might indicate that the structural change plays a less important role in the capacity fading after many cycles.

The TEY data are shown in Fig. 4(d) to study the surficial

evolution. The intrinsic signal from $LiCoO_2$ is submerged by peaks c and d with capacity fading regardless of charged states or discharged states. It indicates that a large quantity of lithium salts are generated on the surface of the $LiCoO_2$ cathode after many cycles. The intensity of peaks b_1, b_2, and a become weaker with the capacity retention ratio decreasing from 99% to 42% at the fully charged state and from 72% to 50% at the fully discharged state. It indicates more and more lithium salts aggregate on the surface and they might be the decisive factor to capacity degradation after many cycles. What is more, it should be noted that the difference in spectrum between the fully discharged state and fully charged state is much larger than the difference in spectrum between the different retention ratios at the same state. This indicates that the surface layer experiences reactions involving decomposition and formation with a certain reversibility during cycling.

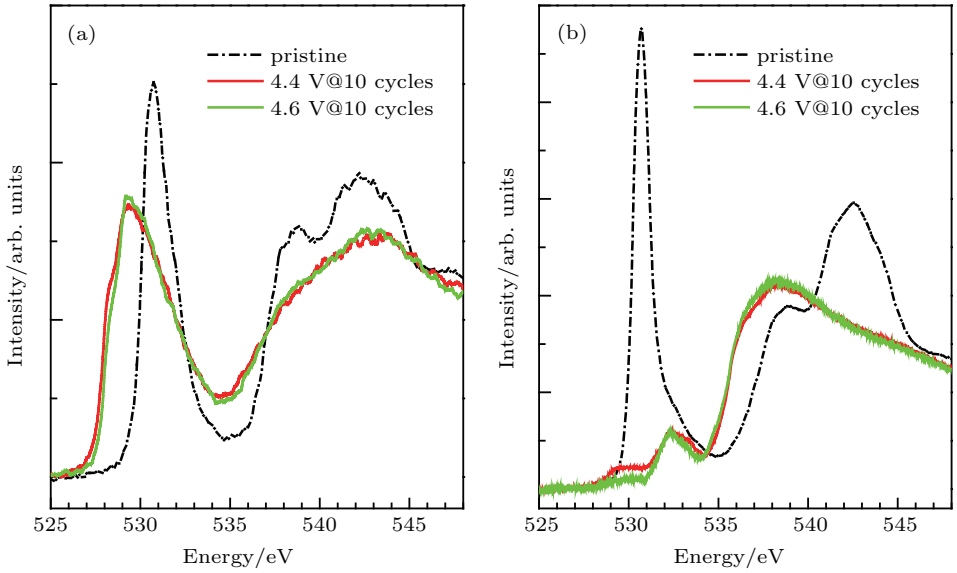


Fig. 5. (color online) (a) TFY and (b) TEY spectra of O K-edge of $LiCoO_2$ cathodes after 10 cycles with cutoff voltages of 4.4 V and 4.6 V.

The spectra of O K-edge of $LiCoO_2$ in fully charged state cycled 10 times with cutoff voltages of 4.4 V and 4.6 V are compared. As shown in Fig. 5(a), the TFY data are much similar, indicating that the Co–O bonds are almost the same at fully charged states. When we observe the TEY spectra shown in Fig. 5(b), peaks c and d become dominant in both cases, indicating that a large quantity of lithium salts cover the surface. The weaker intrinsic feature of the $LiCoO_2$ cycled at 4.6 V demonstrates the more aggregations of lithium salts, which contribute to a larger capacity fading.

4. Conclusions

In summary, the charge compensation and capacity degradation are studied by the soft x-ray absorption spectroscopy at Co $L_{2,3}$ and O K-edge in TFY and TEY modes.

The charge compensation from the oxidation of Co^{3+} is below 4.4 V while only O provide electrons above 4.4 V. The local O 2p holes are observed and its evolution gives an explanation to the origin of O_2^- or even O_2. Besides, the evolution of surficial O is more severe than that of the bulk.

The residual Co^{4+} in the bulk is detected with $LiCoO_2$ discharged to 3 V in the 1st cycle. More Co^{4+} ions appear on the surface as well as a bit of lithium salts are generated, which indicates that the interface undergoes more severe evolution including side reactions. By comparing the samples with various capacity retention ratios, Co–O bonds at the fully charged states are always found to be similar regardless of capacity degradation. In fully discharged states, a large number of Co–O bonds seem to be pinned at the fully charged states, where the mechanism needs further study. The similarity between the fully discharged states with ratios of 72% and 50% indicates that the structural change in the bulk is less related to the capacity degradation. The gradual aggregation of lithium salts on the surface, which is related to the decomposition and reformation of the surface layer, is found to be more important for the capacity degradation. The present study helps to understand the aggravating capacity degradation with cutoff voltage increasing from 4.4 V to 4.6 V.

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