The Role of Electron Localization in Covalency and Electrochemical Properties of Lithium-Ion Battery Cathode Materials

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Following the fundamental research conducted by J. B. Goodenough, the important role of electron localization induced by elemental substitution is studied. The size and electron negativity of host and substituting ions are two important factors in tuning material properties such as local structure and transition metal (TM) oxygen covalency. However, another factor, electron localization, which is widely studied in catalyst research but largely overlooked for battery materials, deserves systematic studies. A combined investigation using synchrotron-based X-ray spectroscopy and theoretical calculations is carried out on the Li-Co-Mn-O model system in which the substituting cation Mn$^{4+}$, with its 3d$^3$ electronic structure, is used as a promoter for electron localization. Results indicate that electron localization greatly influences the Co–O bond by making it less covalent, which increases the delithiation voltage. It is also found that during charge/discharge, electron localization tends to make TM K-edge X-ray absorption near edge spectroscopy (XANES) spectra show a more “rigid shift” behavior while electron delocalization makes the XANES exhibit a “shape change.” It clearly explains why the K-edge XANES data of some TM oxides show no “rigid shift” while the nominal valence states changed. This work highlights the importance of electron localization with guidance for XANES interpretation.

1. Introduction

Lithium-ion batteries (LIBs) are important energy storage devices that power systems from portable electronics to electric vehicles. In a battery system, the cathode part is particularly important due to its decisive effects on energy density. Currently, most of the widely used cathode materials are transition metal (TM) oxides and polyanion compounds, which are based on the pioneering findings of J. B. Goodenough about materials such as LiCoO$_2$ and LiFePO$_4$. In the past decade, the cathode material research for LIB went through rapid development. In the coming decade, new cathode materials with high energy and power density, long cycling life and low cost are critically needed. In addressing these challenges, an important strategy is to introduce substituting element(s) for the improvement of electrochemical properties, as can be seen by the fact that more and more commercial cathode materials contain multiple metal elements.

Understanding the effect of the substituting element on the properties of cathode materials is very important for material design. For example, the crystal structure of cathode materials can be significantly changed by elemental substitution. It has been reported that substituting cations of desirable size can be incorporated into the lattice of layer structured cathodes to modify the interlamellar distances and...
thereby improve the lithium diffusion kinetics.\textsuperscript{[12]} In addition, the electronic structure of cathode materials can also be influenced by the substituting elements. In the early works of J. B. Goodenough, it was clearly stated that many important properties of cathode materials, such as output voltage and conductivity, are closely related to the electronic structure of cathode materials, which determines the active redox reactions and the covalency between TM and anion.\textsuperscript{[13–15]} J. B. Goodenough innovatively introduced the chemical concept of “inductive effect” to explain the mechanism about how substituting elements can change the output voltage of host cathode materials.\textsuperscript{[16–19]} Through substituting neighboring cations or anions by ions with different electronegativity, the covalency between the center TM/oxygen and surrounding oxygen/TM can be manipulated. This strategy has been widely used in both polyanion and oxide systems for lithium-ion battery cathodes.\textsuperscript{[20–22]}

In this study, inspired by the works of J. B. Goodenough, we explore other effects that substituting elements can impose on the electronic structure of cathode materials. The substituting element we are focusing on is Mn, especially its tetravalent cation. Mn is chosen because it is widely used in practical LIB cathodes. For example, Li-rich layered materials, which deliver the highest capacity among intercalation cathodes, usually contain a lot of Mn\textsuperscript{IV} cations.\textsuperscript{[23–25]} In spinel systems, Mn\textsuperscript{IV} is also the main content in materials like LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} and LiCoMnO\textsubscript{4}.\textsuperscript{[26–30]} While tetravalent Mn is used so commonly, the effect of its substitution has not been systematically studied and reported. This is partially due to the fact that tetravalent Mn is “inactive” in the sense that it is not involved in the redox reaction and therefore has no contribution to the overall capacity. However, Mn\textsuperscript{IV} does have some unique properties that can be used for material design. For example, Mn\textsuperscript{IV} is a high valence cation, with large capability to attract electrons and therefore high electronegativity. As a result, it has the potential to change the covalency of TM–O bond through the inductive effect as discussed above. In addition, Mn\textsuperscript{IV} has the 3d\textsuperscript{4} electronic structure with all three electrons occupying the spin up 1\text{g} orbital, suggesting the large energy penalty in pairing electrons.\textsuperscript{[31,32]} Such large on-site repulsion energy leads to considerable electron localization,\textsuperscript{[33,34]} which may also have consequences on the nature of TM–O bond. In this work, the Li–Co–Mn–O system is used as a model compound to understand the impact of electron localization on covalency and spectroscopic properties of the cathode materials. The layer-structured LiCoO\textsubscript{2} (L-LCO) and cubic structured spinel LiCoMnO\textsubscript{4} (S-LCMO) are practical cathode materials and one contains Co only and the other has Mn substitution. However, a direct comparison between these two materials would not provide much valuable information since they are different both in chemical composition and crystal structure. To bridge the gap, a cubic structured spinel LiCoO\textsubscript{2} (S-LCO) was synthesized and studied since it has the same chemical composition as L-LCO but the same crystal structure as S-LCMO. Comparison is first made among these three materials and then made between different states of charge (SOC). Both spectroscopic measurements and density functional theory (DFT) calculations are employed to understand how electron localization influences the Co–O covalency and spectroscopic properties. We found that electron localization induced by Mn substitution in S-LCMO decreases the covalency and increases the ionicity of the Co–O bond, leading to an increased working voltage. It also makes the TM K-edge X-ray absorption near edge spectroscopy (XANES) show a rigid edge shift during charging/discharging. In contrast, electron delocalization tends to make the TM K-edge XANES show “shape change only” behavior in LiCoO\textsubscript{2}. Such correlation can be used to explain the different behaviors between LiNiO\textsubscript{2} and LiCoO\textsubscript{2} where electrons tend to localize in the former but delocalize in the latter.

2. Results

2.1. Material Electrochemical Charging Behavior and TM K-Edge X-Ray Absorption Spectroscopy (XAS) Results

The XANES is an effective probe for understanding the nature of the TM–O bond. XANES is based on X-ray photon-induced electronic excitations from the core level to unoccupied electron states for the element being probed with appropriate symmetry determined by the selection rule. XANES at the K-edges of both TM and O were measured ex situ at different SOC as marked by color-coded dots on the charging voltage profile of three materials shown in Figure 1a,c,e. The charging voltage curves are almost the same as those previously reported by other groups.\textsuperscript{[27,35,36]} The overall charging profiles for L-LCO and S-LCO are similar in shape consisting of two plateaus separated at \( x = 0.5 \) except that the second plateau of S-LCO is higher in voltage than that of L-LCO, which has been credited to Li ions sitting at tetrahedral sites in S-LCO instead of octahedral sites in L-LCO.\textsuperscript{[35–37]} In comparison, charging voltages of S-LCMO is much higher than that of S-LCO and S-LCO throughout the whole delithiation process. The corresponding XANES results at different delithiation states are shown in Figure S1 in the Supporting Information for Mn K-edge in S-LCMO and Figures 1 and 2 for Co and O K-edge, respectively, for all three materials. Mn and Co spectra of the pristine materials indicate that Mn is tetravalent in S-LCMO while Co is trivalent in all three cases. During delithiation, Mn spectra of S-LCMO show almost no change (Figure S1, Supporting Information), indicating that tetravalent Mn is electrochemically inactive in this material. On the other hand, Co spectra for both L-LCO and S-LCO show typical edge-shape change behavior as reported in the literature for the oxidation process from Co\textsuperscript{3+} to Co\textsuperscript{4+}.\textsuperscript{[38,39]} indicating that Co is the redox-active element. Since the crystal structure of L-LCO and S-LCO are completely different, the similar edge-shape-change behavior of these two materials seems to hint such behavior is an intrinsic property of Co containing metal oxides. Actually, in most of the published spectra, the edge-shape-change only behavior is reported for Co during delithiation. Very interestingly, the Co spectra of S-LCMO during delithiation show clear rigid-edge-shift behavior (especially in the deep delithiation region). As far as we know, this is the first time such rigid-edge-shift behavior is reported for Co K-edge during delithiation and certainly deserves further investigation. Since the only difference between S-LCO and S-LCMO is the Mn substitution, this edge change behavior must be originated from changes in electronic structure caused by the Mn\textsuperscript{4+} substitution. It is expected that the bonding nature between Co and O also be changed as a result. This is evidenced
by the pre-edge peak intensity change shown in the inset graphs of Figure 1b,d,f. The pre-edge corresponds to the excitation from core level 1s electron to unoccupied states close to the Fermi level. If these states are purely 3d in nature as in an ideally ionic bonding case, the dipole (quadrupole transitions are much weaker) selection rule would result in no pre-edge intensity since p symmetry is required for transition. On the other hand, the pre-edge can gain intensity if there is some covalency between TM and O where O 2p states hybridize with TM d states so that p symmetry is mixed into the unoccupied TM d states. Therefore, the intensity of the pre-edge peak has been widely used to indicate the strength of the covalent bond between TM and O.[40]

For L-LCO and S-LCO, there is a continuous growth of pre-edge intensity during delithiation, suggesting that Co–O covalency is likely to increase during this process. In contrast, for S-LCMO, the pre-edge intensity shows much less increase during the early stage of delithiation and the intensity even decreases from Li0.5 state to Li0.15 state suggesting the decreased covalency of Co–O bond during deep delithiation in S-LCMO. This decreased covalency of Co–O bond is very likely caused by the Mn4+ substitution. Since the O K-edge XANES spectrum is very sensitive to the changes in hybridization between TM and O electronic states, O K-edge XANES experiments were carried out and the results are discussed below.

2.2. O K Edge XAS Results and DFT Partial Density of States (pDOS) Calculation Results

Figure 2a–c shows the O K-edge XANES spectra in partial fluorescence yield (PFY) mode for L-LCO, S-LCO, and S-LCMO at pristine and deep-delithiated states. The first group of peaks in the energy range between 526 and 535 eV is the pre-edge peaks, which correspond to electron transitions from O 1s to the empty
hybridized states between TM 3d and O 2p. The second group of peaks in the energy range between 535 and 555 eV are main-edge peaks corresponding to the transitions from O 1s to the empty hybridized states between Co 4sp and O 2p. It has been reported that the intensities of the pre-edge peaks are closely related to the TM–O hybridization, or covalency.\cite{41,42} A stronger covalency would introduce more p-featured orbitals into the unoccupied states, leading to more intense pre-edge peaks. The integrated pre-edge intensities are shown in Figure 2d and they indicate how the pre-edges change upon deep delithiation vary from case to case. In both L-LCO and S-LCO, the pre-edge peaks get significantly enlarged upon deep delithiation, suggesting that Co–O covalency is strengthened. However, for S-LCMO, the pre-edge intensity decreases after deep delithiation, suggesting that TM–O covalency is weakened. These results agreed very well with those from Co K-edge XANES discussed above.

To understand the detailed origins of pre-edge peaks, the density of states (DOS) from DFT calculation for unoccupied electronic states above Fermi level is compared with the measured spectrum. Figure 3 shows O XANES pre-edge parts aligned with both O 2p- and TM 3d-projected spin-polarized pDOS. For accurate results of lowest unoccupied molecular orbital levels, hybrid functional was adopted in DFT calculation with mixing parameter of 0.2 based on previous theoretical studies on LiCoO\textsubscript{2} (details of calculation setup are discussed in the Experimental Section). According to the dipole selection rule, the O 2p-projected pDOS indicate the available channels for the core level 1s electron excitation. The TM 3d-projected pDOS is also shown as it identifies the specific orbital (t\textsubscript{2g} or e\textsubscript{g}) that O 2p is hybridized with in forming those unoccupied states. XANES background subtraction and alignment methods follow those used by de Groot et al.\cite{43} and Suntivich et al.\cite{44} A qualitatively good agreement between measured O XANES and calculated pDOS is reached. Pre-edge features A, B, and C generally correspond to subgroups of empty O 2p states marked in gray, yellow, and green, respectively. The slight mismatch in peak positions may result from the influence of O 1s core-hole, which is present in the XANES but not treated in the calculation.\cite{45} The measured pre-edge peaks are more broadened than the calculated pDOS as the core-hole lifetime broadening and instrument broadening in a XANES experiment are not considered in the pDOS calculation. Figure 3 indicates that for the pristine states, while pre-edge peaks are relatively narrow for L-LCO and S-LCO, they are fairly broadened for S-LCMO. The pDOS results reveal that such broadening arises from a significant energy difference between unoccupied Mn and Co electronic states. When L-LCO and S-LCO are deeply delithiated, the originally narrow peaks for the pristine states are significantly broadened, which originates from two causes: i) the originally degenerate Co e\textsubscript{g} spin-up and spin-down states in the pristine material split during delithiation; ii) some t\textsubscript{2g} states originally occupied in the pristine material becomes unoccupied and dispersive with delithiation. The O 2p states hybridized with them contribute to the pre-edge broadening. For S-LCMO, even though delithiating S-LCMO also leads to the splitting of Co e\textsubscript{g} states and availability of unoccupied Co t\textsubscript{2g} states as what happens in L-LCO and S-LCO, the pre-edge peaks of the delithiated state are not obviously more broadened than those of the pristine state. This is due to the fact that Co t\textsubscript{2g} states in L-LCO and S-LCO are more dispersive than Co t\textsubscript{2g} states in S-LCMO. Less dispersive electronic states in fact indicate a localized feature.
The comparison between XANES and pDOS results indicate that electrons are more localized in S-LCMO than in L-LCO and S-LCO. Combining the results of Co K-edge XANES, O K-edge XANES, and pDOS calculation, the key factor of Mn$^{4+}$ substitution is the contribution to the electron localization. To directly evaluate the localization status of electrons, we further calculate the electron localization function (ELF) for these three materials.

### 2.3. ELF Calculation Results and Partial Charge Density Distribution

The ELF is a scalar function between 0 and 1, which directly evaluates the localization status of electrons. It measures the excess kinetic energy density of electrons caused by the Pauli repulsion. Regions with similar ELF values suggest that the electrons have similar local kinetic energy, which favors electron delocalization.\(^{46-49}\) As shown in Figure 4, the ELF domains are displayed by isosurfaces with isovalue of 0.08. The comparison between materials with two different Li contents demonstrates the change of electron localization status when three materials get charged. For both L-LCO and S-LCO, the change is dramatic. At pristine state, well-separated localized domains coexist, which correspond to cores of Li, Co, O, and valence of Co–O bond in $t_{2g}$ symmetry. When charged to high SOC, the valence domains and O core domains get strongly deformed toward each other and become interconnected, forming continuous pathways for electrons to travel through. This change means that more delocalized electrons exist between Co and O in charged L-LCO and S-LCO compared with the pristine one. In contrast, in S-LCMO the ELF domains barely change after delithiation. At pristine state, the core and valence domains are separated from each other, suggesting a localized feature of electrons. When charged, the domains remain separated and no interconnected pathways are formed for electrons. The O domains around Co also get slightly deformed toward Co though at a much weaker degree compared with that in L-LCO and S-LCO. The O domains around Mn get no observable deformation, implying fixed localization. It can be presumed that though electrons between Co and O tend to delocalize, strong localization between Mn and O blocks the overall circulation of electrons and altered the electronic structure globally. More localized feature of electrons usually relates to weak covalent interaction because of less overlap between electron clouds. To study the change of electron overlapping, the partial density of electrons was calculated in the energy region where TM 3d hybridizes with O 2p.

As shown in Figure 5, the slices of partial charge density along the TM–O plane are visualized. To identify the energy range where TM 3d and O 2p hybridize, crystal orbital overlap populations (COOPs) were calculated for three materials as plotted in Figure S3 in the Supporting Information. It can be clearly seen in Figure 6 that below the Fermi level, the TM–O
the overlap gets much stronger between Co and O atoms. In contrast, when S-LCMO gets delithiated, the electron cloud barely changes around Mn–O and the overlap for Co–O only becomes slightly stronger. If we compare the electron distribution between S-LCMO and L-LCO/S-LCO, it would be clear that in delithiated S-LCMO, Co–O electron cloud overlap is much weaker than that in L-LCO and S-LCO. The presence of Mn⁺⁺ weakens the covalent bond between Co and O at high state of charge. Though Mn⁺⁺ is electrochemically inactive, Mn⁺⁺ imposes influences on the active redox Co and O through changing the electronic structure (increasing the electronic localization). Furthermore, the change of electron density is in high accordance with the change of ELF implying that the distribution of electron is tuned by the localization of electrons.

3. General Discussion on the Effects of Electron Localization

Elemental substitution is a commonly used strategy to tune redox behavior in cathode material for LIBs. Many mechanisms have been proposed to understand the effect of substitution on the oxidation/reduction process. One important example is the inductive effect, which was introduced by Goodenough and co-workers[17–19] to explain the influence of elemental substitution on the delithiation voltage of lithium polyanionic compounds such as LiMPO₄ and Li₃M₂(XO₄)₃. When phosphorous is substituted by the more electronegative element X, the stronger X–O covalent bond would weaken the neighboring covalent M–O bond through inductive effect, which will lower the energy level of highest occupied antibonding states and result in increased lithium deintercalation voltage. S-LCMO could be considered as S-LCO with Mn substitution and has Co–O–Mn configuration. Mn⁺⁺ is more electronegative than Co⁺⁺[50] and such substitution would lower the energy of highest occupied Co 3d(t₂g)–O 2p hybridized antibonding state and increase the oxidation potential of Co⁺⁺, as we can see for the initial charging voltage increase for S-LCMO compared with S-LCO as shown in Figure 1. After delithiation, Co³⁺ is oxidized to Co⁴⁺, accompanied by lowering of 3d level of Co which should lead to stronger hybridization between Co and O. This is true for both L-LCO and S-LCO where the Co–O hybridization does become stronger after delithiation as indicated by the increased pre-edge peak of O 1s absorption spectrum shown in Figure 2. However, for S-LCMO oxygen XANES, the integrated intensity of pre-edge peak slightly decreased indicating that Co–O hybridization stays almost the same and may even get weakened. This phenomenon is contradictory to what would be anticipated if we only consider the “inductive effect” of Mn⁴⁺ substitution. The inductive effect is proportional to the electronegativity difference between the substituting cation and the host cation. Since the electronegativity difference between Co⁺⁺ and Mn⁺⁺ is smaller than that between Co⁺⁺ and Mn⁺⁺, the inductive effect by Mn⁺⁺ on Co⁴⁺–O should be weaker than that on Co³⁺–O. Therefore, if only “inductive effects” are considered, the covalency between Co⁴⁺–O in S-LCMO (reflected by the integrated intensity for oxygen pre-edge peaks in Figure 2) at charged state should be stronger than that at pristine state. However, XANES results are against this expectation. This can
be explained by the other effect of Mn$^{4+}$ substitution, which is the localization of electrons as shown in Figures 4 and 5. For Mn$^{4+}$ (3d$^3$) at the octahedral site the onsite d–d Coulomb repulsion and exchange interactions (U) is much larger than that for Co$^{4+}$ and Co$^{3+}$, inducing strong electron localization even after delithiation.$^{[34,51]}$ An obvious resulting from localization is decreased electron cloud overlapping between Co and O and the weakened Co–O hybridization in spinel LiCoMnO$_4$ as shown in Figures 4–6. In fact, this weakened TM–O covalency induced electron localization effect of Mn$^{4+}$ substitution can also be used to explain some results reported in the literature for other materials. For example, if we compare the charging profile of layer structured LiNiO$_2$ and LiNi$_{0.5}$Mn$_{0.5}$O$_2$, it is obvious that the redox voltage of Ni$^{3+}$/Ni$^{4+}$ is higher in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (caused by the localization effect, not the electronegativity effect of Mn$^{4+}$ substitution) than that in LiNiO$_2$.$^{[29,52,53]}$

Alongside the effect of decreasing covalency between neighbor TM and O, another consequence of electron localization is the charge separation among TM ions during the charging process. In an electron-delocalized material, such as L-LCO and S-LCO at charged state,$^{[54,55]}$ charge transfer happens easily between adjacent TM ions. When electrons around a certain TM ion get depleted during delithiation, electrons from neighboring TM ions could easily move into the center ion and compensate for the loss of charge. Consequently, TM cations get oxidized corporately, contributing to the charge compensation. In contrast, for a material in which electrons tend to localize, it is difficult for electrons to transfer between adjacent TM cations. During delithiation, TM cation gets oxidized more individually, resulting in charge separation. This phenomenon is significant in electron localized cathode materials such as LiNiO$_2$, which contains Jahn–Teller active Ni$^{3+}$ ions. In LiNiO$_2$, NiO$_6$ octahedron is distorted due to Jahn–Teller effects, breaking the O$_6$ symmetry and inducing strong electron localization.$^{[56–58]}$ Through DFT calculation, we analyzed the oxidation state distribution of Ni ions in LiNiO$_2$ at different delithiation states by calculating the atomic magnetic moment of each Ni ion since Ni$^{3+}$ ion has a magnetic moment of 1 $\mu$B while Ni$^{4+}$ has zero. The result is shown in Figure 6a. It clearly shows that after delithiation, some Ni$^{3+}$ cations are oxidized to Ni$^{4+}$ while others stay unchanged, resulting in charge separation among Ni cations. A similar analysis is conducted for Co ions in S-LCO and S-LCMO and results are shown in Figure 6b,c. As expected, with electron localization induced by the introduction of Mn$^{4+}$ substitution, charge separation appears in S-LCMO after delithiation while all Co$^{3+}$ cations get oxidized corporately in S-LCO. The Co K-edge XANES evolution in electron localized materials shows completely different behaviors from that in the electron delocalized materials. In electron localized material, due to the charge separation after delithiation the XANES spectrum measured is, in fact, a concentration weighted average spectrum of two end-member cations (Co$^{3+}$/Co$^{4+}$ or Ni$^{3+}$/Ni$^{4+}$). Therefore, the Co K-edge XANES spectra shift rigidly from one end to the other in LiCoMnO$_4$ with increasing SOC (Figure 1c) just like the situation of Ni, the K-edge XANES of which has been well established before and shown in Figure S5 in the Supporting Information for reference.$^{[59,60]}$ In comparison, for electron delocalized material, after delithiation, fractional oxidation state of TM cations could appear caused by strong charge transfer between TM and coordinated O. The chemical potential felt by the electrons in TM orbitals changes dynamically with increasing SOC of cathode material. Therefore, the spectra’s evolution is complicated and involves obvious shape changing as in the case shown in Figure 1b. In fact, confirmed by the O K-edge XANES results that probe TM–O hybridization directly, this “shape-changing-only” type of TM K-edge XANES evolution during delithiation process can be used as an indicator for strong TM–O hybridization in TM oxide cathode material, especially if we limit the case to octahedral 3d TM cations. A natural question may be that

Figure 6. The atomic valence states distribution of a) Ni in layer structured LiNiO$_2$, b) Co in spinel LiCoO$_2$, and c) Co in spinel LiCoMnO$_4$ at different delithiation states. The viewing is along the direction perpendicular to the TM plane. The different valence states of Co/Ni cations are marked by the color referenced by the color bar on the right. The gray dot stands for Mn cation.
can such “rigid shift” type of behavior for Co K-edge XANES also be realized in layer structured materials with Mn substitution (such as in LiNi$_x$Mn$_{1-x}$Co$_2$O$_4$ materials). The answer is it might be difficult. Since high Mn content is required to reduce the covalence of Co–O to a detectable level and high Mn would cause the material to change the structure from layer to spinel, we have not been successfully making such model material for similar experiment reported in this work.

4. Conclusion

In conclusion, after the introduction of Mn substitution, the average charging voltage of S-LCMO cathode material is increased and the Co–O hybridization is weakened comparing with the unsubstituted L-LCO and S-LCO. Careful X-ray absorption measurement and DFT calculation reveal that electrons are more localized with Mn substitution causing the electron cloud overlapping between Co and O that gets weakened. Although the voltage increase can be partly explained by the conventional inductive effects caused by Mn, since Mn is more electronegative than Co, the weakening of Co–O valency at high SOC in spinel LiCoMnO$_4$ cannot be attributed to the inductive effect. The more localized electrons caused by Mn substitution are proposed to be responsible for the weakened Co–O covalency. Electron localization/delocalization also has a great impact on the TM K-edge XANES spectral properties. XANES of cathode materials with localized electrons tend to show rigid-edge-shift during charging/discharging. In contrast, XANES of cathode materials with electron delocalization tend to show shape-change-only behavior. Such correlation is also verified by the comparison between LiNiO$_2$ and LiCoO$_2$ where electrons tend to be more localized in LiNiO$_2$ and the XANES show clear rigid-edge-shift behavior. Recently, RIXS results have directly demonstrated that in LCO, oxygen oxidation does happen when highly charged. Hence, possibly the “shape-changing-only” type TM K-edge XANES evolution during delithiation of cathode material could also be used as an indicator for potential anion oxidation reaction, therefore provide some hints on the possibility of anion redox in cathode material design. In summary, the results reported in this work highlight the importance of electron localization in battery material design and spectroscopic data interpretation.

5. Experimental Section

**Material Synthesis:** The layered LiCoO$_2$ powder material was prepared by a solid-state reaction using precursors of Li$_2$CO$_3$ (99%) and Co$_3$O$_4$ (99.7%). An excess of 5% Li$_2$CO$_3$ was used to compensate for the Li loss during high temperature synthesis. The starting materials were ground in an agate mortar and the mixed powder was heated at 1000 °C for 10 h in an alumina crucible to form the intermediate products. Then, the intermediate products were ground again in an agate mortar and heated for a second time at 900 °C for 10 h to get the final products. The spinel LiCoO$_2$ was synthesized using a method described previously by Manthiram’s group.[33] LiCoMnO$_2$ was synthesized by an original two-step method. The first step was the synthesis of MnCoO$_2$, 2.10 mmol CoCl$_2$·6H$_2$O plus 1.75 mmol MnCl$_2$·4H$_2$O was dissolved in 66 mL of distilled water. Then, 2.460 g of urea, 2.500 g of ascorbic acid, and 2.000 g of polyvinylpyrrolidone (PVP, MW ~40 K) were then dissolved in the CoCl$_2$/MnCl$_2$ solution under stirring. After 1 h, the solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 6 h. The CoMnCo$_2$ microspheres were obtained after being centrifuged, washed with water and ethanol several times, and dried at 60 °C overnight. The obtained CoMnCo$_2$ microspheres were calcinated in air at 400 °C for 5 h to obtain the CoMnO$_2$ microspheres. Then, 0.700 g of CoMnO$_2$ and 0.165 g of Li$_2$CO$_3$ were mixed and calcinated at 800 °C for 24 h in an O$_2$ atmosphere to obtain the LiCoMnO$_2$ product.

**X-Ray Absorption Spectroscopy:** Co, Mn K-edge XAS measurements were performed at QAS (7-BM) beamline of the National Synchrotron Light Source II (NSLS II) at Brookhaven National Laboratory (BNL) in the transmission mode. The XANES and extended X-ray absorption fine structure (EXAFS) spectra were processed using the Athena software package.[62] O K-edge XAS was collected by using PFY modes at the I05 (23-ID-2) beamline of NSLS II, BNL. PFY spectra were collected using a Vortex silicon drift detector. All of the XAS measurements were performed at room temperature in an ultrahigh-vacuum chamber (base pressure, ~10$^{-10}$ Torr).

**Computational Details:** All DFT calculations were performed with the Vienna ab initio simulation package (VASP) with projected augmented wave (PAW) approach.[33,64] For the crystal structure relaxation of layer LiCoO$_2$, exchange–correlation functional in the form of the local density approximation (LDA) was adopted since it has been proved to give a better description of lattice parameters over the whole phase diagram of Li$_2$CoO$_2$.[65–67] As suggested by the previous researches, the O3 and H1-3 structures were used to simulate the atomic configuration of pristine and charged LiCoO$_2$.[65,67] The H1-3 stands for the hybrid of O1–O3 stacking in Li$_{1.6}$CoO$_2$ with v3 x v3 in-plane Li ordering. For the structural relaxation of spinel LiCoO$_2$ and spinel LiCoMnO$_2$, the generalized gradient approximation (GGA) type exchange–correlation functional in the parameterization of Perdew, Burke, and Ernzerhof (PBE) was adopted.[68] To simulate the ground state configuration of Li vacancy and Co–Mn distribution, all the inequivalent configurations were generated in a unit cell in cubic symmetry with 64 atoms by using an enumeration method and a full structural relaxation of the 30 configurations was done with the lowest Ewald energy.[69–71] The structure with the lowest DFT total energy was used as an approximation of the ground state structure. The unit cells used are shown in Figure S2 in the Supporting Information. For the calculation of electronic structure for the relaxed structure, the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional was adopted, which is reported to give more accurate results than the common DFT+$U$ functional, especially in describing empty states above Fermi level.[72,73] For HSE type functional, the choice of mixing parameter is important since it directly determines how much electron exchange is taken into account and relates to the accuracy of results closely. Rigorous approach to obtain mixing parameter is nonempirical tuning the fraction of mixing as suggested by Kronik and co-workers.[74,75] For LiCoO$_2$, previous theoretical studies had concluded that the mixing parameter of 0.2 can give adequate estimation LiCoO$_2$ bandgap.[76,77] Therefore, in the calculation of this work, the mixing parameter of 0.2 was taken for consistency. For all calculations, the cutoffs of the wave function and charge density were 500 and 756 eV, respectively. A k-mesh with the density of one point per √3 Å$^{-3}$ was generated using the Monkhorst–Pack method to ensure the precision of the calculated total energy. For the relaxations of model structures, the forces felt by each of the atoms were well converged below 0.005 eV Å$^{-1}$. The chemical bonding status was evaluated with the calculation of COOP. By generating an overlap population-weighted density of states, COOP analysis can differentiate the bonding and antibonding states. The COOPs were computed based on DFT calculations by Lobster program.[77–79] In COOPs, positive/ negative values indicate bonding/antibonding, respectively.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

X.W. and X.F. contributed equally to this work. The work done at Brookhaven National Laboratory was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technology Office of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program under contract DE-SC0012704. The work done at Institute of Physics, Chinese Academy of Sciences was supported by the National Natural Science Foundation of China (Grant No. 11772321) and the Youth Innovation Promotion Association (Grant No. 2016005). S.D.S. was supported in part by a DOE Early Career Award. This research used beamlines 7-8M, 23-ID-2 of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704. This research also used the Scientific Data and Computing Center, a component of the Computational Science Initiative operated by Brookhaven National Laboratory under Contract No. DE-SC0012704.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

covalency, DFT calculation, electron localization, Li-ion battery cathodes, spectroscopy

Received: February 20, 2020
Revised: April 23, 2020
Published online: