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Unraveling the Cationic and Anionic Redox Reactions in Conventional Layered Oxide Cathode

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Abstract

The increasing interest in high energy and high capacity batteries triggers the demand of clarifying the reaction mechanism in battery cathodes during high potential operations. This is critical for further improving the performance of commercially viable Ni rich compounds, however, the mechanism often involves both transition metal and oxygen activities that remain elusive. Here we report a comprehensive study of the both the cationic and anionic redox mechanism of $LiNiO_2$ across a wide electrochemical potential window up to 5 V. Through the combined results of a wealth of characterization techniques, we are able to clarify the redox reactions of transition metals in the bulk and on the surface, as well as the clear evidences of oxygen activities including both the reversible lattice oxygen redox and irreversible oxygen release with the associated surface reactions. Selection of pure $LiNiO_2$ removes the complication of multiple transition metals. The many findings here bring the attention to the different types of oxygen activities and the effect of metal-oxygen interactions in conventional layered oxides, which is of crucial importance to the advancement of Ni-rich layered oxides for high capacity and long cycling performance.

Li-ion battery technology holds the promise to achieve the energy storage demand for portable electronics, electrical vehicles (EV), and other grid-scale applications. Extensive efforts have been devoted to further advancing the commercially viable transition-metal oxide layered oxide cathodes, such as $LiNi_xMn_yCo_zO_2$ (NMC) and $LiNi_xCo_yAl_zO_2$ (NCA) ($0 < x, y, z < 1$), for high-performance and low-cost Li-ion batteries.[1] One strategy that has attracted increasing interest is by increasing Ni content (0.9 – 0.95) to achieve a higher practical capacity at a given charge cutoff voltage and/or increasing charge cutoff voltage for materials of a given Ni content. However, many challenges exist, mostly related to the deterioration of the bulk and surface structure, especially at the highly delithiated states. These layered oxides with high Ni content exhibit many similarities to their parent compound, $LiNiO_2$. However, the detailed redox mechanism of $LiNiO_2$ involving both Ni and O has not been clarified, especially, the redox reactions at high voltage operation remain elusive, which hinders the mechanistic understanding of the fading mechanism in high Ni layered oxides and its optimization.

$LiNiO_2$ was initially proposed as a promising alternative to isostructural $LiCoO_2$ in early 1990s because of the slightly lower operating voltage of Ni redox compared to Co and its low cost.[2-4] Accordingly, challenges that hinder its practical fabrication include the control of stoichiometry and surface degradation upon exposure to air/moisture.[5-8] Nowadays, effective strategies have been developed to prevent Ni^{2+} occupying in the Li layers, thus forming off-stoichiometry $Li_{1-x}Ni_{1+x}O_2$.[9-12] Additionally, multiple phase transformation towards nearly full delithiation is intrinsic to $R\bar{3}m$ $LiNiO_2$, of which H2 – H3 phase transformation that occurs at ~0.75 Li^+ extraction (~200 mAh/g) is detrimental and largely accounts for the capacity fade upon high-capacity cycling.[9, 13-21] As a result, most works on $LiNiO_2$ focused on the low charge cutoff voltage (<4.3 V) to satisfy the capacity target,[5, 8, 15, 22-24] and the high voltage cycling has not been carefully examined.

The redox chemistry of $LiNiO_2$ is seemingly straightforward, sole Ni^{3+}/Ni^{4+} redox can perfectly accommodate 1 Li^+ extraction/insertion during the charge and discharge. However, the full oxidation of Ni^{3+} and full removal of 1 Li^+ from $LiNiO_2$ are difficult, therefore, the realization of pure Ni^{4+} in the system is always challenging. It is known that the surface Ni reduction and gas evolution often occur in layered oxide cathodes at high voltages, where the corresponding side reactions would further complicate the electrochemical process. Upon delithiation, oxidization of Ni^{3+} ($3d^7$ ($t_{2g}^6e_g^1$)) to tetravalent state in layered $LiNiO_2$ removes the electron from e_g orbital, therefore, electron transferring from O 2p band only occurs at highly charged state or low Li^+ content.[3-4, 22] In contrast, oxidization of Co ($3d^6$ ($t_{2g}^6e_g^0$)) in $LiCoO_2$ is accomplished by electron removal from t_{2g} orbital. Therefore, the charge compensation upon delithiation of $LiCoO_2$ is likely achieved in the O and Co simultaneously.[23] Indeed, the intriguing anionic oxygen contribution in $LiCoO_2$ was proposed in late 1990s, despite the lack of direct experimental evidence.[24-26]

There have been renewed interests in this topic since the reversible anionic oxygen contribution in Li-rich layered oxides has been verified in 2013.[27-36] Such interest has been naturally extended to conventional layered oxides, particularly, the trend of increasing charge cutoff voltage largely promotes the chance to oxidize lattice oxygen upon Ni^{3+} and Co^{3+} oxidation. Given the significant importance of high-voltage and high-capacity layered oxides, we believe it is imperative to investigate the anionic oxygen activity in these compounds. Indeed, very few studies have been focused on this aspect in Ni-rich layered oxides.[15, 37] Herein, we report the comprehensive charge compensation mechanism of both cationic Ni and anionic O in $LiNiO_2$, which not only is a parent system of Ni-rich compounds, but also naturally avoids the complication with multiple transition metals (TMs). Technically, the chemical state of Ni and O, from O^{2-} and O^{n-} (n<2) in the lattice to extreme case of O^0 in the evolved gas, is probed by X-ray absorption spectroscopy (XAS), high-effeciency mapping of resonant inelastic X-ray scattering (mRIXS) and operando differential electrochemical mass spectrometry (DEMS). The combination of these techniques independently reveals the reaction mechanism of both cationic Ni and anionic O redox in conventional layered $LiNiO_2$ across a wide voltage range.

Phase-pure $LiNiO_2$ was synthesized by a solid state reaction as reported elsewhere.[38] It exhibits a typical layered α–$NaFeO_2$ structure ($R\bar{3}m$) with negligible Li/Ni intermixing (1.4%) in the final product based on Reitveld refinement results (**Figure S1**, **Table S1**). The electrochemical characterization of $LiNiO_2$ with a particle size of <1 μm (**Figure S2**) is performed with a special focus on upper charge cutoff voltage, ranging from 4.3 to 5.0 V (**Figure 1**). At 4.3 V charge cutoff, ~0.79 and ~0.7 Li^+ is extracted from and inserted back into $LiNiO_2$, with several redox peaks associated with multiple phase transformations displayed in the dQ/dV plot.[9, 16] Increasing the charge cutoff voltage to 4.8 V leads to significantly increased Li^+ extraction (~0.95) during charge, with slightly higher Li^+ insertion (~0.74) during discharge. When $LiNiO_2$ is further charged to 5.0 V, the amount of reversible Li^+ insertion upon discharging remains unchanged, despite almost full Li^+ extraction upon charging. Varying charge cutoff voltage clearly shows a larger impact on the charge process, particularly, an anodic peak is revealed at 4.65 V during charge along with a subtle cathodic peak around 4.5 V (**Figure S3**). A subtle difference is revealed during discharge, where all cathodic peaks consistently show a minor shift to a slightly lower voltage at high charge cutoff voltages. This peak drift is attributed to the impedance growth relating to cathode-electrolyte interface and surface passivation/densification at higher cutoff voltage.[5, 13, 38-39] Indeed, this observation is in good consistency with the galvanostatic intermittent titration technique (GITT) (**Figure 1c**), showing slightly increased polarization upon discharging.

We first probe the chemical state of Ni at various states of charge by hard and soft XAS to gain the in-depth understanding of Ni redox behaviors in bulk and on surface. The threshold energy position of Ni *K*-edge is referred to the bulk $LiNiO_2$ (**Figure 2a, b**), where the change of the half-edge energy ($E_{0.5}$) is deduced by the half-height method.[40-42] At pristine state, the $E_{0.5}$ of the Ni *K*-edge in $LiNiO_2$ corresponds to Ni^{3+} and $E_{0.5}$ value increases to compensate for the Li^+ extraction from pristine material towards 4.8 V charge, with slight reduction at 5.0 V charge, which maybe related to the anionic oxygen redox according to the reductive coupling theory or Ni reduction on the surface upon oxygen release.[31, 43] Moreover, Ni chemical state is characterized by soft XAS total fluorescence yield (TFY) and total electron yield (TEY) mode to reveal information close to bulk (~200 nm) and at the surface (~10 nm), respectively. Soft XAS Ni L_3-edge is featured by two splitting peaks at 852.7eV (A1) and 855.0 eV (A2), the relative intensity of these two peaks provides a general guidance to the oxidation state of Ni, namely, the higher value of A2/A1 ratio indicates a higher Ni oxidation state.[44-45] TFY spectrum of Ni *L*-edge in pristine $LiNiO_2$ represents Ni^{3+} reference, showing a higher A2/A1 ratio compared to that of Ni^{2+} reference [46]. Ni L_3-edge TFY (**Figure 2c, d**) displays a lineshape evolution, indicating a similar trend of Ni states as from Ni *K*-edge: A2/A1 ratio increasing upon initial delithiation to 4.5 V, indicating the Ni oxidation, then followed by a slight reduction upon charging to 5.0 V. The reduction of Ni oxidation state on the surface is relatively stronger as observed in the surface sensitive Ni-L TEY signals (**Figure 2e, f**). The Ni oxidation state reaches a maximum at 4.3

V charge, with a clear drop at higher voltages. During discharge, all the three sets of XAS data show the Ni reduction upon Li^+ insertion, but majority of the Ni reduction takes place with voltage below 4.2V, leaving the high voltage discharge an open question that will be addressed below.

We would like to note again that all XAS results point to the same general trend of Ni reduction during charging at high voltages, however, the reduction of Ni on the surface takes place in different voltage range from that for the bulk, indicating a different origin. In the bulk, Such a counterintuitive reduction of Ni upon charging implies that lattice anionic oxygen exists and is associated with Ni states. On the surface, the reduction of Ni and other TMs could often be seen if electrodes are charged to relatively high voltages, [47-48] which mostly originates from energy loss and its associated phenomena such as surface reactions and densifications.

The O activates upon electrochemical cycling is directly probed using high-efficiency mapping of resonant inelastic X-ray scattering (mRIXS). mRIXS has recently been established as the tool-of-choice for detecting the lattice oxidized oxygen during charging in oxygen redox systems, because it disentangles the TM character and the intrinsic oxidized oxygen mixed in conventional O-*K* XAS signals. In particular, a feature around 523.7 and 531 eV of emission and excitation energies, respectively (indicated by the red arrows in **Figure 3a**), fingerprints the non-released lattice oxidized oxygen and evolves with electrochemical cycling. [35, 49-50] As shown in **Figure 3a**, while mRIXS signals are dominated by the typical broad and strong O^{2-}-*2p* features around 525 eV emission energy,[51] the oxidized lattice oxygen feature displays a systematic evolution on its intensity upon electrochemical cycling (red arrows in **Figure 3a**). The feature starts to emerge above 4.3 V during charging, grows in its intensity and becomes pronounced above 4.8 V charge. During discharge, the intensity of the feature displays a reversible behavior, which becomes less visible at 4.0 V discharge and completely disappears at 3.8 V discharge (**Figure 3a**). The emergence and disappearance of the oxidized oxygen mRIXS feature provides the direct experimental evidence of a reversible lattice oxygen redox that takes place at high potentials, i.e., above 4.3V during charge and above 4V during discharge. Such a high-voltage oxygen redox behavior is consistent with the observation of the reduction of bulk Ni at high charge voltages (**Figure 2**).

In addition to the mRIXS studies of the non-release lattice oxygen redox activities, we further performed *Operando* DEMS to investigate the gas evolution upon delithiation at high voltages (**Figure 3d :**NOTE: please see email on changes of Fig.3). Onset of oxygen gas release occurs at 4.3 V, which is in good agreement with that of Ni reduction at the surface. CO_2 evolution begins at a slightly lower voltage, 3.8 V, due to the presence of trace amount of carbonate residual, followed by a large burst of CO_2 release at 4.4 V resulting from further carbonate decomposition and possible electrolyte oxidation. These results are consistent with soft XAS O *K*-edge data, revealing the presence of carbonate at pristine state till 4.5 V charge (**Figure S4**). Overall, the total O_2 and CO_2 release detected from $LiNiO_2$ is 0.0316 and 0.968 μmol, corresponding to 2.0 and 60.8 μmol/g of $LiNiO_2$ active material. According to the titration result, 0.2 wt% lithium carbonate residual is present in pristine $LiNiO_2$ and CO_2 release upon its decomposition accounts for 40% total CO_2 release assuming all Li_2CO_3 is converted to CO_2. Assuming all O_2 release originates from the lattice oxygen, it corresponds to only 0.02% of oxygen in $LiNiO_2$, respectively, which represents a very small percentage of the total lattice oxygen.

Our results reveal a complete picture of the contribution of TM and O redox reactions, as well as surface activities, in $LiNiO_2$ upon (de)lithiation (**Figure 4a**). During charging, cationic Ni oxidation is dominating below 4.3 V, above which, lattice O oxidization starts to occur, accompanied by oxygen gas release and surface reactions upon further charging. Moreover, Ni redox shows charge heterogeneity across different depths of particles: Ni oxidization continues to occur until 4.5 V in the bulk, while Ni oxidation state reaches a maximum at 4.3 V at the surface (**Figure 4b**). The surface Ni reduction likely originates from the irreversible oxygen loss and side reactions involving electrolyte, while the bulk Ni reduction at ≥4.5 V relates to the lattice oxygen oxidation (**Figure 4c**). These results further strengthen the reductive coupling scenario about the important role of TM-O interaction in oxygen redox systems, which is critical for the ultimate understanding of the mechanism of lattice oxygen redox reactions, something remains a grand challenge in the field and require further intensive studies. Another finding from our mRIXS results is the reversible lattice oxygen redox in such a conventional layered $LiNiO_2$, which has very few direct experimental evidences,[32, 36, 52-54] although the overall contribution is relatively small in the $LiNiO_2$ system according to our combined electrochemistry, spectroscopy and gas analysis.

As pointed out earlier, this work is mainly motivated by the definitive goal of Ni-rich layered oxide cathode. We clearly reveal the occurrence of reversible lattice oxygen redox and irreversible oxygen release at high voltages towards nearly full delithiation of $LiNiO_2$. We believe this work highlights the importance of studying the oxygen activity in Ni-rich layered oxide materials (i.e., NMC, NCA) without excessive Li. The different electronic configuration of Ni^{3+}/ Ni^{2+} and Co^{3+} makes the charge compensation, especially oxygen activity, even more elusive. The oxygen oxidization in the materials based on Co^{3+} with empty e_g orbital maybe triggered at even lower voltages compared to those Ni^{3+}-based materials, thus the spectrum of redox chemistry (i.e., cationic TM, reversible O redox and irreversible oxygen release) would be completely different in layered oxides with varied Ni/Co content.[7, 55-56] Harvesting more reversible capacity from TM and O redox, especially over the long-term cycling, is a well-defined goal. Clearly, O oxidation spontaneously takes place at high voltages in $LiNiO_2$. Whether one redox is favored compared to the other is in question, they can certainly become active at some delithiation states, which maybe essential according to the reductive coupling theory. Meanwhile, irreversible oxygen loss that occurs at the particle surface leads to the deterioration of the surface microstructure, ultimately leading to performance decay upon cycling due to the slow Li^+ diffusion and reduced active redox. Therefore, suppression of irreversible oxygen loss at high voltages in these compounds is an important avenue to develop high-capacity Ni-rich layered cathodes. Proper surface passivation that can stabilize the surface oxygen through strong metal-oxygen bonding could be an effective strategy. Such material tailoring requires in-depth understanding of metal-oxygen interaction on oxygen activity in material chemistry.

Experimental Methods

$LiNiO_2$ was prepared by ball milling $Ni(OH)_2$ (Sigma Aldrich) and Li_2CO_3 (Sigma Aldrich) for 3 h, followed by annealing in oxygen atmosphere at 750 ^{0}C for 12 h. Scanning electron microscopy (SEM) was conducted on a JEOL JSM-7000F equipped with a Thermo Scientific EDS detector. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D2-Phaser with Cu Kα radiation (λ = 1.54178 Å). XRD pattern was further analyzed by the conventional Rietveld method using the general structure analysis system package with the graphical user interface (EXPGUI).

Electrode slurry was prepared by mixing 80 wt% of active material, 10 wt% of polyvinylidene fluoride (PVdF) binder and 10 wt% acetylene carbon black (Denka, 50% compressed) in N-methylpyrrolidone (NMP). The slurry was casted on carbon-coated aluminum current collectors (Exopack Advanced Coatings) using a doctor blade set to 150 μm height. The slurry was then dried under vacuum at 120 ^{0}C overnight and dried film was punched to get disk electrode with a diameter of ½ inch. Typical loading of the active material is 2.5-3.0 mg/cm^2. 2032-type coin cells, consisting of the as-produced $LiNiO_2$ positive electrode, Li metal anode, Celgard 2400 separator, were assembled in an Ar-filled glovebox (O_2, H_2O <0.1ppm). 1M $LiPF_6$ dissolved in 1:2 w/w ethylene carbonate - diethyl carbonate (Daikin) was used as the electrolyte. Galvanostatic charge and discharge and galvanostatic intermittent titration technique (GITT) measurements were performed at designated voltage ranges on a Maccor 4200 battery cycler. 1C was defined as 200 mA/g. All the cycled electrodes were immediately disassembled and collected from the cells and washed by DMC solvent multiple times to ensure the removal of soluble surface species. All the dried electrodes were transferred into the experimental vacuum chamber through a specially designed sample transfer kit in an Ar-filled glove box to avoid any air exposure.

Hard X-ray absorption spectroscopy was performed on beamline 2-2 in a transmission mode using a (220) monochromator at Stanford Synchrotron Radiation Lightsource (SSRL). Phi 0. energy was calibrated by the spectrum of Ni metal foil reference. The hard X-ray absorption near-edge spectroscopy (XANES) data were analyzed using SIXPACK software. The soft XAS measurements were carried out on beamline 10-1 at SSRL. The Ni *L*-edge and O *K*-edge spectra were acquired under ultrahigh vacuum (10^{-9} Torr) in a single load at room temperature using total electron yield (TEY) *via* the drain current and fluorescence yield (TFY) *via* Silicon Photodiodes.

mRIXS maps were collected in the ultra-high efficiency iRIXS endstation at Beamline 8.0.1 at the Advanced Light Sources (ALS).[57] Sample surface was mounted 45° to the incident beam, and the outgoing photon direction along the RIXS spectrograph is 90° with other technical details available in our previous report.[57] Experimental energy resolution is about 0.3 eV. All the electrode samples were handled in high purity Ar glove box, transferred in a home-made sample transfer kit that is sealed in Ar glove box and coupled to the iRIXS vacuum system without any air exposure. In particular, we note that we have carefully checked the radiation damage effect on the RIXS feature of the oxidized oxygen, and found the intensity of the oxidized oxygen feature is reduced with radiation damage and may disappear completely upon high dose of X-ray.[58] Therefore, other than the much lower x-ray flux that is allowed by our ultra-high efficiency spectrometer, we have kept the samples moving under X-ray exposure throughout the data collection to eliminate the radiation damage. Furthermore, the fact that radiation damage will decrease the oxidized oxygen feature intensity means the oxygen redox signature could only be under estimated here; therefore, the finding of the oxygen redox activities in $LiNiO_2$ is intrinsic and unambiguous.

Operando DEMS measurements were conducted on a customized Swagelok type cell connected to a high-pressure gas chromatography valve. The details were described in a previous publication.[33, 59] The DEMS cell initially rested at the open circuit voltage for 6 h and charge/discharge was done under potentiostatic control using a Bio-Logic SP-300 potentiostat.

Supporting Information

Full description of the experimental methods and additional data.

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Ning Li and Shawn Sallis made equal contribution.

Notes

The authors declare no competing financial interest.

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