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The impact of nickel substitution into model Li-rich oxide cathode materials for Li-ion batteries

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Abstract: Developments in lithium-ion batteries for energy storage are currently focused on improving energy density, cycle life, and reducing cost to match targets set by the automotive industry. An important class of cathodes, known as Li-rich layered oxides, Li-Ni-Mn-Co-O, is considered promising for next-generation electrode materials, yet a poor understanding of a number of detrimental processes, for which the underlying mechanisms are not clear, has hindered their commercialization. Numerous model systems have been studied trying to fully understand the discreet mechanisms taking place during battery operation. Given that Ni is relied upon more and more in commercial materials, we build here upon the previous work on model systems by studying Li-Ni-Sb-O and Li-Ni-Te-O materials to better understand the impact of Ni substitution into this complex class of materials. Using a combination of detailed electrochemical tests, X-ray diffraction, online electrochemical mass spectrometry, X-ray absorption near edge spectroscopy and X-ray photoemission spectroscopy, we find a stark contrast between the electrochemistry taking place in the bulk of particles as compared to that taking place at the surface. We find that oxidation of oxygen results in reduction of nickel, as was seen previously in the Li-Fe-Sb-O, and this has detrimental impact on the discharge capacity. However, the reductive couple occurs solely at the surface of particles in Ni-containing materials due to mitigated oxygen gas production in these materials. The consequences of this contrast between the surface and the bulk are discussed in order to guide further development of next-generation electrodes.

Introduction

Currently there is a massive effort underway to develop advanced battery technologies for critical applications in electric vehicles and grid energy storage, supporting intermittent renewal energy production. Though lithium-ion batteries (LIBs) are heavily favoured for application in personal electric vehicles, their energy density and lifetime so far perform well below long-term targets set by automotive companies¹. To meet these targets, an important class of nextgeneration cathodes has been extensively studied: Li-rich layered oxides. This class of materials seem to improve upon LiCoO₂ by increasing the lithium content and substituting cobalt with other more inexpensive, environmentally benign transition metals. While the use of excess lithium has a dramatic impact on the electrochemical performance of the materials, allowing capacities approaching 300 mAh/g (compared to about 150 mAh/g for LiCoO₂), this increase in capacity is accompanied by a number of changes in the voltage profiles, some of which are detrimental to the materials' performance.²⁻⁴ It has also become clear that during cycling, the transition metals cannot fully account for the redox reactions taking place. This has led to numerous studies showing the change in the oxygen oxidation states during cycling, in either a reversible manner to form oxidized oxygen either as localized holes or as peroxo-like species^{3, 5-} ⁶, or to irreversibly produce oxygen gas at potentials above 4.2 V vs. Li⁷⁻⁹. The oxygen gas produced by the cathode has also been found to be active in the battery, as it reacts with carbon sources within the cell (such as carbon black or the electrolyte), and results in performance degradation of the battery 10 .

The extreme level of complexity of the electrochemistry and structural changes in the Li-rich oxides has led scientists to search for model systems with only one redox active transition metal in order to decouple individual features seen in the Li-rich NMC electrochemistry, where three

redox active transition metals complicate matters dramatically. In all model systems, no oxygen gas evolution is seen below 4.2 V vs Li, as is the case in the Li-rich NMC. Previously studied model systems such as Ru- and Ir-based materials showed reversible oxygen redox but no oxygen gas evolution as all their capacity occurs below 4.2 V^{3-4, 11-12}. Since Li-rich NMC materials operate both below and above 4.2 V, other materials such as Li-Fe-Te-O were studied to account for reactions in the upper voltage window. This material showed no capacity below 4.2 V and in fact all of the charge capacity was found to be due to the production of oxygen gas.⁹ Upon next discharge, the oxygen gas was found to react with the electrolyte and ultimately precipitate on the electrode in such a way that capacity faded rapidly.⁹

This mechanism proved to be important in other Li-rich oxides as well. Li-Fe-Sb-O¹⁰ was studied in detail as it showed activity both above and below 4.2 V (i.e. this model system approaches the next-generation cathode candidates in complexity of electrochemistry). This material showed iron oxidation from Fe^{+3} to Fe^{+4} , accompanied by some oxidation of oxygen at about 4 V. As charging continued to higher potentials, a large amount of oxygen gas was evolved and iron was *reduced* back to Fe^{+3} . This reduction of the transition metal during charge resulted in a dramatically reduced discharge capacity. The negative impact on further cycling of oxygen gas evolution was also observed, as seen in Li-Fe-Te-O. It is therefore critically important to determine whether these detrimental mechanisms are present in next-generation NMC materials.

Since the Li-Fe-Te-O and Li-Fe-Sb-O studies, there has been no reports studying model systems in this context. It is thus important to look for other model materials to progress towards Li-rich NMC materials, considered as next-generation cathode material contenders. In particular, the next logical step is to replace iron with nickel, as the latter is being relied upon more and more in commercialized NMC materials with efforts to stabilize Ni-rich layered oxides and in the Li-rich NMC next-generation cathodes, in an attempt to eliminate cobalt. In addition, certain commercialized layered materials such as Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O₂ already use nickel as the main redox centre of the material¹³. Herein, we therefore study Li-Ni-Te-O and Li-Ni-Sb-O materials with an emphasis on clarifying the impact of nickel substitution on reversible and irreversible oxygen redox and its effects on nickel oxidation during cycling.

Experimental methods

Three materials were synthesized with the following target compositions: $Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$ ($L_{1.15}NSO$), $Li_{1.10}Ni_{0.53}Sb_{0.37}O_2$ ($L_{1.10}NSO$) and Li_4NiTeO_6 (LNTO). All pristine materials were synthesized by solid-state reactions in which stoichiometric amounts of Li_2CO_3 , $Ni(OH)_2$, and Sb_2O_3 or TeO_2 were ball milled with 5% excess Li_2CO_3 and pressed into pellets before heat-treatment for 12 h in air at either 800 °C or 900 °C, consistent with the respective literature reports¹⁴⁻¹⁵. Powder X-ray diffraction (PXRD) was performed using a Bruker D8 Discover Diffractometer with a Cu-K α source. Inductively coupled plasma (ICP) elemental analysis was used to determine the compositions of all three pristine materials after the synthesis.

All three materials were tested extensively electrochemically. Swagelok cells were assembled under argon using lithium metal as the counter electrode, GF/D Microfiber filters (Whatman) as the separator, and 1M LiPF₆ in 1:1 EC:DMC (SoulBrain MI) as the electrolyte. The electrodes were prepared by ballmill (Form-Tech Scientific) active material with 20 wt.% carbon black for 10 minutes, while keeping good crystallinity of the synthesized materials (no peak broadening was observed in XRD patterns). Galvanostatic cycling was performed at various rates and cut-off potentials. The extent of oxygen gas release during cell operation was determined by online electrochemical mass spectrometry (OEMS). An in-house developed cell was used for experiments as described elsewhere¹⁶, with more details provided in the S.I. A slurry, consisting

of 80% of cathode active material, 10% of conductive carbon SC65, and 10% of polyvinylidene fluoride (PVDF) binder, was coated on Al mesh (22 mm in diameter) with a wet thickness of 100 μ m. OEMS cells were assembled using lithium metal as the counter electrode, one piece of Celgard 2400 separator, and 120 μ L of 1M LiPF₆ in EC:DEC (3:7 w/w) as the electrolyte.

Only two materials were studied extensively *ex situ*: LNSO and LNTO. For this purpose, approximately 50-85 mg of active materials were cycled to various cut-off potentials using Swagelok cells. In an argon-filled glovebox, the samples were then recovered, rinsed multiple times with dimethyl carbonate, and dried. These samples were then first studied using PXRD in an airtight holder to protect samples from exposure to ambient atmosphere. All XRD patterns were refined using the Rietveld method as implemented in Rietica with the compositions as determined by ICP. *Ex situ* X-ray absorption near-edge structure (XANES) spectra were collected in transmission mode. All samples were sealed in between layers of Kapton tape in a glovebox, and then transferred to a helium enclosure for XANES measurements. The measurements were performed at the 20-BM-B beamline at the Advanced Photon Source, Argonne National Laboratory¹⁷. X-ray photoelectron spectroscopy (XPS) was used to observe the near-surface chemistry, including the Ni 2p_{3/2} peak (845-880 eV range). Analysis was performed using both the XPSPEAK4.1 and Avantage software.

Results and discussion

X-ray diffraction and electrochemical characterization

All samples were synthesized as single-phase materials as determined from PXRD (Figure 1). The two LNSO and LNTO samples were refined in the $R\bar{3}m$ and C2/m space groups, respectively. Although pristine (L_{1.10}NSO) shows superstructure peaks that are not present in the

refinements, both the space group and the lattice parameters (Table S1) of all three pristine materials are consistent with literature^{14, 18}. Furthermore, as can be seen in Table 1, the ICP results for the pristine materials coincide with available literature results. The $L_{1.15}$ NSO sample was found to be slightly richer in Li than the target composition, indicating that not all excess Li was lost during synthesis — again, in good agreement with literature^{14, 18-19}. Similarly, LNTO is also slightly high in Li content, by approx. 2.5% above the target.

The voltage profiles and dQ/dV plots for both $L_{1,15}$ NSO and LNTO (Figure 2 and S1) show remarkable similarities with that seen for Li₄FeSbO₆¹⁰. Not only are the results in good agreement with both material references^{14, 18}, but in our work the data have been extended to broader potential windows. There is an important feature that points to the possible formation of oxygen gas evolution during cycling, based on previous work in Li₄FeSbO₆. This feature is the decreasing reversibility of the redox plateau in the vicinity of 4.0 V vs. Li (3.9 V for LNSO and 4.1 V for LNTO – Figure 2) as the charge cutoff increases (this feature can most clearly be seen as a shrinking of the dQ/dV peak during discharge). It is also of note that a reduction feature below 2.0 V seen for LNTO only may also indicate oxygen gas involvement as discussed briefly in the S.I. (Figure S1). In addition, $L_{1,10}$ NSO also showed the decline in discharge capacity (Figure 3) when cycled to high voltage, and this effect is diminished at higher cycling rates. It should be noted that both $L_{1,10}$ NSO and $L_{1,15}$ NSO were studied here because refs. ¹⁸⁻¹⁹ showed a contrast in their electrochemistry. Here, however, we find no such contrast and only $L_{1.15}NSO$ was selected for further study below. Thus, all three materials studied here show electrochemistry consistent with oxygen gas release reducing the nickel redox: the release of oxygen gas is limited by diffusion such that rapid cycling minimizes the time spent at high potential and thus less oxygen gas is released. It should also be noted that the strange rate

performance seen previously in $L_{1.15}NSO^{19}$ is not observed here (Figures 4 and S2). This is attributed to the fact that the materials here were neither nanosized nor carbon coated (this is discussed in detail in the S.I.).

Given the similarity of electrochemical features seen for all three materials here as compared to Li-Fe-Sb-O, both L_{1.15}NSO and LNTO were selected for ex situ in depth study to better understand the role of Ni-substitution in the materials. Three ex situ samples were obtained for each material as follows: charging to 4.3 V (half-charge), charging to 5.0 V (full-charge) and charging to 5.0 V followed by discharging to 3.6 V (full-discharge). The voltage curves obtained for the large ex situ samples (50-85 mg) are shown in Figure S3. First, ex situ XRD patterns of L_{1.15}NSO and LNTO (two different rates) were collected to determine to what extent structural changes are taking place during electrochemical cycling. Two different rates were used for LNTO in an attempt to increase the amount of oxygen gas released by giving the material more time at high potentials. Figure 5 shows the XRD patters for pristine, fully charged, and fully discharged samples. All patterns can be indexed in the space group of the pristine material, except for one small peak, visible in the fully discharged LNTO sample at 2 mA/g. The refined lattice parameters obtained from Rietveld fits are shown in Table S1, while Figure S4 gives calculated unit cell volumes. In all cases, the unit cell decreases in size during charge and increases again (almost reversibly) during discharge. Thus, while Li₄FeSbO₆ showed a dramatic transformation from an O3 to an O1 structure during charge, its nickel counterpart shows a robust O3 structure that is maintained during the entire first cycle. No other trend was found in the XRD refinements (for example, the nickel content on the Li layer was poorly constrained by the data and was found to insufficiently impact the quality of the fits for it to be considered reliable). Nonetheless, the differences seen here in the structural evolution during cycling, when

compared to iron containing materials, show the importance of nickel in preventing the shearing of atomic planes resulting in transformations from O3 to O1 structures.

Online electrochemical mass spectroscopy

OEMS data (Figures 6 and S5) for both LNTO and LNSO were collected to determine the extent of gas evolution during battery operation. At the cycling rate of 10 mA/g (Figure 6), a gas evolution rate of 1554 nmol min⁻¹ g⁻¹ would be required if oxygen evolution would be the only one contributing to the current. For both samples (Figure 6), O2 generation rate is below 7 nmol $\min^{-1} g^{-1}$, while CO₂ is nearly identical in both data sets and is not higher than 80 nmol $\min^{-1} g^{-1}$. The CO_2 can either be due to electrolyte decomposition and/or O_2 gas released from the active material reacting with a carbon source (either carbon black or the electrolyte solvents). Thus, even if all CO₂ detected is due to released oxygen gas reacting with conductive carbon, the upper bound on the amount of oxygen produced accounts for only 5% of the current. By contrast, previous work in Li-Fe-Sb-O found that the O₂ produced accounted for about 50% of the current over much of the first charge, and in Li-Fe-Te-O it accounted for about 90% of the current for the most of the first charge¹⁰. We therefore conclude that O₂ gas evolution is greatly mitigated by structural stabilization due to the presence of nickel. Figure S5 shows the result for LNTO at a current of 2 mA/g and Table S2 shows the cumulative oxygen and CO₂ evolution during first charge. All results lead to the conclusion that only a small amount of oxygen gas is evolved in the nickel containing materials, such that we can speculate that it occurs at the surface of the particles only. Comparing the gassing with the two different cycling rates used for LNTO, it is clear that oxygen evolution at faster cycling rates is diminished, consistent insufficient time for the slow oxygen diffusion to take place within the bulk of the particles, again suggesting that primarily only surface oxygen is being evolved.

Comparison of XANES to XPS

To identify the impact of oxygen evolution on the material, the oxidation state of nickel on the surface of the particle was compared to the nickel oxidation state in the bulk. XANES was used to determine the average nickel oxidation state throughout the entire material, while XPS, owing to its surface sensitivity, was used to probe particle surface. XANES spectra with the Ni K-edge evolution for each of the LNSO and LNTO samples, depending on the potential cut-off and cycling rate conditions, are shown in Figures 7 and S6. In all cases, the charging process results in a shift of the edge consistent with change in nickel oxidation state of >1. However, the extent of reversibility varies dramatically: the LNTO materials showed very little reversibility in nickel oxidation state, particularly when cycled slowly (at 2 mA/g). This is consistent with the results from the electrochemistry, wherein the discharge plateau at around 4 V was greatly diminished by extending the cut-off potential to 5.0 V. The nickel oxidation state was quantified as described in the S.I. using Figures S7 and Table S3. The pristine materials show Ni oxidation states to be +2.44 and +2.55 for L_{1.15}NSO and LNTO, respectively, in adequate agreement with those of +2.40 and +2.33 inferred from the ICP results in Table 1. Interestingly, all three materials show nickel oxidation states well above +3 in the half and fully charged states. It is of note that the Ni in the LNTO, charged at 2 mA/g, shows a lower oxidation state than that seen with 10 mA/g rate, despite the higher total capacity, as this is consistent with the reductive couple acting during oxygen gas production. In all cases, the change in nickel oxidation does not account for all of the capacity seen in the electrochemical testing. Therefore, the extra capacity is attributed to oxygen redox (either reversible or irreversible), permitting us to calculate the average oxidation state of oxygen which is included in the mechanism scheme in Figure 8. In the two materials cycled at 10 mA/g, the changes in the oxygen oxidation state are reversible, while

in the LNTO cycled at 2 mA/g (which shows the greatest oxygen loss based on the OEMS data, Table S1), the average oxygen oxidation state does not return to -2.0 during discharge. It is also of note that for both L_{1.15}NSO and LNTO the nickel oxidation state changes by about 1.0 during discharge, while in the slowly cycled LNTO the Ni oxidation state change only accounts for 0.37. Thus, in this study, the reversibility of the nickel redox is directly impacted by the oxygen gas released, even though the amount of oxygen gas is relatively small.

To contrast the behavior of nickel in the bulk and the surface of particles, XPS was also performed on these same samples as shown in Figures 9 and S8. Though more comprehensive than the XPS study shown in literature¹⁴, our results are consistent with previously published work as discussed thoroughly in the S.I. We identify three peaks attributed to nickel oxidation states: 855.1 eV to Ni⁺², 856.5 eV to Ni⁺³, and a third peak at 858.5 eV to Ni⁺⁴ (this peak appears as a shoulder in the Ni⁺³ peak), and such peak attribution is consistent with recent literature.²⁰⁻²² All XPS patterns were therefore fit with these three peaks as well as an additional satellite peak centered near 861 eV. At half charge, the appearance of Ni⁺³ and Ni⁺⁴ peaks at 856 and 858 eV, respectively, can be resolved from the data, and at full charge the Ni⁺⁴ peak visibly decreases. Interestingly, Ni⁺² is present in significant amounts in all samples and the reversibility of the nickel redox is extremely limited here, in sharp contrast to the XANES results, probing the bulk. To quantify the trends seen in the XPS data, Table S4 shows weighted averages of the nickel oxidation states for each sample, these values are also shown as the surface nickel oxidation state in Figure 8. It is of note here that large 5-10 µm secondary particles make up these samples, as indicated in Figure S9, implying that the depth probed by the XPS does in fact only represent a very small fraction of the total volume.

The mechanism, based on our results and presented in Figure 8, reveals a number of important points to consider and allows understanding the consequences of the use of nickel in the Li-rich oxides. Firstly, the surface nickel has systematically a lower oxidation state than that seen in the bulk of the particle, and this effect is especially strong after oxygen gas has been evolved (e.g. the LNTO sample fully charged at 2 mA/g has surface nickel with an average oxidation state 1.04 lower than that of the bulk). The fact that a large amount of Ni⁺² is still detected at the surface, even in the fully charged materials, suggests that the reductive couple is quite strong here; it is simply mitigated by how little oxygen gas is released. This is most clearly seen in the fully discharged LNTO, cycled at 2 mA/g, where Ni has an average oxidation state of Ni^{+2.5}, even though the bulk shows +3.39, while that of the fully discharged L_{1.15}NSO shows near perfect agreement between the surface and bulk states with values of +2.48 and +2.50, respectively. This reductive coupling mechanism has also been identified in Li-Fe-Sb-O, where Fe was reduced all the way back to its pristine state of Fe^{+3} , when sufficient oxygen gas release occurred. Here, the reduction is more mitigated, primarily affecting the nickel at the surface. Nonetheless, in LNTO, this process also results in the nickel to remain trapped in a high oxidation state within the bulk, even after discharge. This demonstrates that a relatively small amount of oxygen release can have a dramatically detrimental impact on the overall electrochemistry in nickel-containing cathodes, as the changes occurring at the surface prevent reversibility within the bulk.

Conclusions

Herein, the electrochemical performance of two Ni-containing model Li-rich layered oxides is studied to gain insights into the performance of next-generation layered oxides that rely heavily on a high nickel content. A number of conclusions are of importance in this context: 1. Nickel can be oxidized from Ni⁺² to Ni⁺⁴, but part of this occurs at very high potentials (4.5 V and above), at which point oxygen redox (both reversible and irreversible) becomes significant. 2. The oxygen redox (both reversible as seen in $L_{1.15}$ NSO and irreversible seen in LNTO at 2 mA/g) results in nickel not being oxidized all the way to Ni⁺⁴. This strongly suggests that the reductive couple acting in materials such as Li_4 FeSbO₆¹⁰ does in fact also operate in nickel-containing materials, however it is primarily acting at the surface as demonstrated by consolidation of XPS and XANES data.

3. Oxygen gas evolution is dramatically reduced when Ni is used (as compared to Fe) in the model materials. Furthermore, whether Te or Sb is the spectator cation has an important impact on the Fe containing model systems (the electrochemistry of Li-Fe-Sb-O is very different from Li-Fe-Te-O), whereas there is very little difference seen here in the electrochemistry of the LNSO and LNTO materials. This suggests that further substitution of the spectators with Mn and Co to give Li-rich NMC materials may not eliminate the negative mechanisms elucidated here.
4. The sharp contrast seen here between XPS and XANES data is of high significance: XPS cannot be relied on to resolve oxidation states in the particle's bulk for Ni-containing cathodes, unlike materials that do not undergo oxygen gas release during cycling (such as Li-Ru-Sn-O).
5. Protecting the surface of particles in nickel-containing oxides is crucial. This is clear given that oxygen oxidation at the surface reduces nickel and bulk-nickel loses reversibility by remaining trapped in an oxidized state.

Such a dramatic contrast between the electrochemistry at the surface and in the bulk has not been seen previously. The current study brings an extra dimension to the model systems that have been studied to date in order to more fully understand the behaviour of Li-rich Ni-Mn-Co oxides relying heavily on Ni and O redox. As these materials are of extreme interest as next-generation battery cathodes, the deepened understanding of the role of nickel provided here will guide further efforts to bring this class of materials to commercialization.

Associated Content

Supporting Information

Supporting information associated with this paper is available free of charge on the ACS Publications website (www.pubs.acs.org).

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Tables:

Table I: Composition of the pristine materials as determined by ICP-OES. The oxygen content is determined by assuming Te⁺⁶, Sb⁺⁵, Ni^{+2,3}. The average nickel oxidation is calculated based on the ICP from this study.

Target material	ICP (this study)	Average Ni oxidation	Literature ICP ¹⁹
Li ₄ NiTeO ₆ (LNTO)	Li _{4.11} Ni _{0.94} Te _{0.95} O ₆	+2.33	
Li1.10Ni0.53Sb0.37O2	Li1.10Ni0.58Sb0.32O2	+2.24	Li1.02Ni0.54Sb0.38O2
Li _{1.15} Ni _{0.47} Sb _{0.38} O ₂ (LNSO)	Li1.24Ni0.40Sb0.36O2	+2.40	Li1.22Ni0.46Sb0.37O2

Figure Captions:

Figure 1: Cu K α PXRD pattern of pristine Li_{1.10}Ni_{0.53}Sb_{0.37}O₂ with R $\overline{3}$ m Rietveld refinement (a), LNSO with space group R $\overline{3}$ m used in the Rietveld refinement (b) and LNTO with the C2/m space group (c).

Figure 2: Electrochemical cycling of LNSO at 11 mA/g (a and c) and LNTO at 5.5 mA/g (b and d). The different colors refer to different cells cycled to different upper cutoff voltages.

Figure 3: The electrochemistry of $Li_{1.10}Ni_{0.53}Sb_{0.37}O_2$. The first electrochemical cycle at 7 mA/g (a) and 140 mA/g (b) with different cutoff voltages. The extraction of 1 lithium per formula unit corresponds to 231.5 mAh/g. The corresponding dQ/dV plots are shown for 7 mA/g (c) and 140 mA/g (d).

Figure 4: First 10 discharge capacities from this study compared to those in the literature¹⁸⁻¹⁹ for LNSO cycled over a large range of rates.

Figure 5: XRD of *ex situ* samples for pristine (blue), charged to 5V (red), and discharged to 3.6V (yellow) of a) LNSO cycled at 10 mA/g b) LNTO cycled at 10 mA/g and c) LNTO cycled at 2 mA/g

Figure 6: OEMS of LNSO cycled at 10 mA/g (a) and LNTO cycled at 10 mA/g (b). The voltage curves are shown in the top panel while the corresponding O_2 and CO_2 production rates are in the middle and bottom panels, respectively. For the oxygen gas to account for the entire current, a rate of 1554 nmol/min/g would be required.

Figure 7: XANES Ni K-edge of *ex situ* samples for pristine (blue), charged to 5V (red), and discharged to 3.6V (yellow) of LNSO cycled at 10 mA/g (a), LNTO at 10 mA/g (b) and LNTO

at 2mA/g (c). The black arrow corresponds to a transition of 1.0 in nickel oxidation state based on the reference materials shown in Figure S5.

Figure 8: Overall changes in Ni and O oxidation states at different points of the electrochemical cycling for LNSO cycled at 10 mA/g (top), LNTO cycled at 10 mA/g (middle) and LNTO cycled at 2 mA/g (bottom). The numbers within the blue circles correspond to the *overall* oxidation states within the whole particles (*ie.* not solely the core) whereas the numbers within the yellow circles correspond to the surface nickel oxidation based on the XPS data. Cell-to-cell variation in specific capacity results in an uncertainty on the calculated oxygen oxidation states of no more than 0.03.

Figure 9: *Ex situ* Ni XPS spectra of LNSO and LNTO charged at 10 mA/g and 2 mA/g respectively. Dashed lines represent the peak positions attributed to Ni^{2+} , Ni^{3+} , and Ni^{4+} as labelled.



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8



Figure 9

TOC figure:

