

**Stabilization of O-O bonds by d⁰ cations in Li_{4+x}Ni_{1-x}WO₆ (0 ≤ x ≤ 0.25) rock salt oxides
as the origin of large voltage hysteresis**

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Abstract

Multinary lithium oxides with the rock salt structure are of technological importance as cathode materials in rechargeable lithium ion batteries. Current state of the art cathodes such as $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ rely on redox cycling of earth-abundant transition metal cations to provide charge capacity. Recently, the possibility of using the oxide anion as a redox center in Li-rich rock salt oxides has been established as a new paradigm in the design of cathode materials with enhanced capacities (> 200 mAh/g). To increase the lithium content and access electrons from oxygen-derived states, these materials typically require transition metals in high oxidation states, which can be easily achieved using d^0 cations. However, Li-rich rock salt oxides with high valent d^0 cations such as Nb^{5+} and Mo^{6+} show strikingly high voltage hysteresis between charge and discharge, the origin of which is uninvestigated. In this work, we study a series of Li-rich compounds, $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($0 \leq x \leq 0.25$), adopting two new and distinct cation-ordered variants of the rock salt structure. The phase $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ ($x = 0.15$) has a large reversible capacity of 200 mAh/g, without accessing the $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couple, implying that over two-thirds of the capacity is due to anionic redox, with good cyclability. The presence of the $5d^0$ W^{6+} cation affords extensive (> 2 V) voltage hysteresis associated with the anionic redox. We present experimental evidence for the formation of strongly stabilized localized O-O single bonds that explain the energy penalty required to reduce the material upon discharge. The high valent d^0 cation associates localized anion-anion bonding with the anion redox capacity.

Introduction

Li-containing rock salt oxides form one of the most studied families of positive electrodes for rechargeable lithium ion batteries. Following the success of the first commercial Li-ion systems using LiCoO_2 as a cathode material, extensive exploration of other LiMO_2 analogues has led to the discovery of higher performing materials among which are the current state of the art NMC phases ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$). The maximum capacity of these materials is however still limited due to the 1:1 Li:M ratio, and great hope is being placed in the “Li-rich” rock salt oxides ($\text{Li}_x\text{M}_y\text{O}_{x+y}$ with $x > y$) which can be accessed by partial substitution of the transition metal with excess Li associated with increase of the mean metal oxidation state above +III, *e.g.*, $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ or Li_2MnO_3 . Such compounds can deliver capacities exceeding 200 mAh/g, making them promising cathode materials for future Li-ion rechargeable batteries. These capacities exceed expectations based on purely metal-based redox within the expected manifold of oxidation states in cathode materials with $\text{Li}/\text{M} > 1$. This is now well understood as the contribution of oxygen to the redox activity, made possible by the presence of non-bonding oxygen states close to the Fermi level in Li-rich rock salt oxides, as some O 2p orbitals do not take part in the formation of M-O bonding and antibonding orbitals.¹⁻³ Oxygen-based redox reversibility can be enhanced by moving from 3d to 4d and 5d cations which avoids the formation of gaseous O_2 upon anion oxidation.⁴ Chemistries that enable reversible oxygen oxidation with earth-abundant components would bring these capacities within practical reach.

Despite their large diversity of structures and compositions, few Li-rich rock salt oxides have been studied as cathode materials. By carefully selecting the transition metals used, these compounds can exhibit complex cation-ordered superstructures⁵⁻⁸ and their Li content can be varied extensively ($\text{LiMO}_2 \rightarrow \text{Li}_2\text{MO}_3 \rightarrow \text{Li}_3\text{MO}_4 \rightarrow \text{Li}_4\text{MO}_5\dots$),^{9,10} resulting in considerable diversity of candidates for new cathode materials and a great opportunity to explore the role played by different cations in triggering oxygen redox. Following this idea, Yabuuchi and coworkers have shown the possibility of using high-valent d^0 cations such as Nb^{5+} or Mo^{6+} to increase the Li content in rock salt oxides, create non-bonding oxygen states close to the Fermi level and activate the redox activity of oxygen.^{11,12} Interestingly, several of these materials show extremely large voltage hysteresis with most of the discharge capacity recovered below 2 V, but its origin has not been investigated so far. Although such low energy efficiency is detrimental to their use in practical Li-ion batteries, understanding the origin of this feature will help in the design of future cathode materials as the voltage hysteresis issue is pervasive in materials showing anionic redox activity, including the long-sought-after Li-rich NMC phases.¹³⁻¹⁵

In this work, we investigate a family of Li-rich rock salt oxides $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($0 \leq x \leq 0.25$), derived from the Li_4NiWO_6 phase reported by Mandal et al.,¹⁶ and vary the Li/Ni ratio to tune the structural and electrochemical properties of the material. Using a combination of spectroscopic techniques (XPS, XAS, Raman), the role of Ni and O in the charge compensation during electrochemical (de)lithiation

was investigated, revealing the influence of redox-inactive W^{6+} ($5d^0$) cations on the formation of stable discrete O-O bonds upon oxidation of oxide and the associated voltage hysteresis.

Results

Synthesis and structure of $Li_{4+x}Ni_{1-x}WO_6$ materials

The initial synthesis experiments to prepare the stoichiometric Li_4NiWO_6 phase were carried out by a classical solid-state method using NiO, WO_3 and a 10 % molar excess of Li_2CO_3 (1:1:4.4) to compensate for Li_2O volatility during high temperature synthesis (Methods). This resulted in a dark brown powder which initially appeared pure from lab PXRD. However, upon further analysis by synchrotron PXRD, neutron powder diffraction and TEM-EDX, the sample turned out to be non-stoichiometric and contain a small amount of cubic $Li_{1-x}Ni_xO$ impurity, thus providing evidence for the existence of a solid solution of the form $Li_{4+x}Ni_{1-x}WO_6$. By revising the initial synthetic conditions, using different Ni/W ratios and sacrificial powder to better control the Li stoichiometry (see Methods), we were able to obtain the stoichiometric pale green Li_4NiWO_6 phase without impurity, as well as the $Li_{4+x}Ni_{1-x}WO_6$ solid solution with $0.05 \leq x \leq 0.25$. The compositions of the different phases were confirmed by ICP-OES and TEM-EDX analysis (see Note 1 in Supporting Information (SI)). Although all members of the non-stoichiometric $Li_{4+x}Ni_{1-x}WO_6$ solid solution could be approximately indexed with the structural model reported by Mandal et al.,¹⁶ the diffraction pattern of the stoichiometric Li_4NiWO_6 ($x = 0$) could not be matched with the reported structure, and turned out to be a new structure type. A thorough structural investigation was therefore undertaken on the Li_4NiWO_6 and $Li_{4.1}Ni_{0.9}WO_6$ samples using synchrotron X-ray and neutron powder diffraction data (detailed structural analysis in Notes 2 and 3 in SI).

The structure of the stoichiometric Li_4NiWO_6 phase was solved in the $C2/c$ space group ($a = 5.84579(10)$ Å, $b = 17.58769(35)$ Å, $c = 5.109138(9)$ Å, $\beta = 124.768(1)^\circ$, $V = 431.506(2)$ Å³, see Table S1 in SI for full structural parameters) and can be thought of as a monoclinic distortion of the archetype $Li_3Ni_2TaO_6$ ($Fddd$) based on the same ordering pattern of the almost fully occupied W sites, which follows that of Ta in the archetype (Figure 1b), but a different Ni/Li ordering.¹⁷ The relationship between the two cells is shown in Figure S1 in SI. Pauling's rule of electroneutrality prevents two highly charged W^{6+} cations from being coordinated to the same oxygen, in other words W^{6+} cannot be situated in the first two cation neighbouring shells of any W^{6+} cation, at translations $T_1 = (a/2, a/2, 0)$ and $T_2 = (a, 0, 0)$, where a is the rock salt cubic cell dimension. As a result, they form isolated WO_6 octahedra arranged to minimize electrostatic repulsions between W^{6+} cations, separated by $T_3 = (a, a/2, a/2)$ (see Figure 3a), adopting one of the ten such arrangements noted by Hauk *et al.*¹⁸. As a consequence, all oxygen atoms in the structure are coordinated to only one W atom. $Li_3Ni_2TaO_6$ and the new Li_4NiWO_6 structure can be described as a staggered six-layer repeat sequence of a single mixed cation layer with six distinct octahedral sites (Figure 1, bottom). The reduction in symmetry from $Li_3Ni_2TaO_6$ to Li_4NiWO_6 , with a lower Ni content and the higher charge of the d^0 W^{6+} cations, arises from an enhanced Li/Ni ordering,

which changes the number of distinct cation sites from four to six in Li_4NiWO_6 , by splitting site 2 (site 3) of the $Fddd$ structure (Figure 1b) into sites 2 and 6 (sites 3 and 5) of the $C2/c$ structure (Figure 1a). The W^{6+} cations in Li_4NiWO_6 are almost fully ordered onto site 1, with 4.7% Li^+ on this site and the remaining 4.7% W^{6+} distributed between two of the remaining five cation sites (sites 4 and 6). The Ni^{2+} occupancy of all other sites is driven by their interaction with highly charged W^{6+} cations in this particular arrangement. Sites 2 and 6 have only five W^{6+} cations in the three neighbouring cation shells at \mathbf{T}_1 , \mathbf{T}_2 and \mathbf{T}_3 (see Table S2 in SI), compared to eight for the other sites, making them more likely to contain Ni^{2+} due to lower electrostatic repulsion. The d^0 configuration of W^{6+} leads to asymmetric displacement from the center of its octahedron, moving away from site 6 and towards the edge shared with site 2 (see Table S3 and S4 in SI), attributed to second-order Jahn-Teller effects.^{19,20} This destabilizes one site at the expense of the other, leading to a high occupation of site 6 by Ni^{2+} (57%) and a low occupation of site 2 (8.9%). For the same reason, site 3 is further away from the W^{6+} cations and has a higher Ni^{2+} content (27.6%) compared to site 5 (4.2%). This contrasts with the near-statistical distribution of cations in sites 2 and 3 in $\text{Li}_3\text{Ni}_2\text{TaO}_6$, where the d^0 cation has a lower charge and is not displaced from the octahedron centroid. Finally, site 4 is almost fully occupied by Li^+ (94%), due to electrostatic repulsion from its W^{6+} neighbours, and the large distortion enforced by the two edge-shared and two corner-shared neighbouring WO_6 octahedra (Figure S2 and Table S4 in SI), which would be less favorable for high-spin Ni^{2+} than the other less distorted sites. To obtain the final Rietveld fit (Figure 4a), it was necessary to include an $Fddd$ minority Li_4NiWO_6 phase isostructural with $\text{Li}_3\text{Ni}_2\text{TaO}_6$, of refined weight fraction 11.8(6) %, which can be interpreted as either regions of lithium and nickel site disorder within the material, or the consequence of small Li/Ni ordered domain sizes resulting in a significant antiphase boundary content. The asymmetric displacements of W atoms occur in opposing directions along $[010]$ and $[0\bar{1}0]$ axes, resulting in no overall dipole in the material (Figure 5a). Such displacements are absent (or disordered) in the less ordered $Fddd$ analogue, where the average positions of the tungsten sites are located at the centroids of the octahedra at Wyckoff site $8a$ (which has point symmetry 222 and thus no dipole).

Turning to $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$, initial peak fitting was performed on laboratory PXRD data based on the reported Li_4NiWO_6 cell ($a = 5.090(3)$ Å, $b = 8.810(4)$ Å, $c = 5.079(1)$ Å, $\beta = 109.60(5)^\circ$)¹⁶ in the $C2/m$ space group, which accounted for all of the Bragg reflections and gave a satisfactory Le Bail fit. With an increased Li content, $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ moves further away from the $\text{Li}_3\text{Ni}_2\text{TaO}_6$ stoichiometry and adopts a monoclinic structure with four distinct cation sites, similar to the archetypal layered Li_5ReO_6 rock-salt superstructure.²¹ The WO_6 octahedra in $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ are again isolated from each other, with similar W-W distances to Li_4NiWO_6 (Figure 3) that also corresponds to the third cation shell at $\mathbf{T}_3 = (a, a/2, a/2)$ in order to minimize electrostatic repulsions, but in a motif distinct from that found in Li_4NiWO_6 . Cations order through the adoption of a two layer structure where $(\text{Li}/\text{Ni})\text{O}_6$ octahedra surround WO_6 units in a ‘honeycomb’ arrangement in one layer (layer 1 in Figure 2), which alternates

with a mixed Li/Ni layer (layer 2 in Figure 2). Ni is distributed over three of the four cation sites (sites 2, 3 and 4), with a preference for site 2 in the W layers. Site 2 has the lowest electrostatic repulsion from W^{6+} cations, with only five W^{6+} in the first three cation shells compared to eight for sites 3 and 4 (see Table S6 in SI). This Li/Ni ordering is similar to that in related Li_4NiMoO_6 but differs from Li_4NiTeO_6 , in which Ni is only localized in site 2.^{12,22} The similar W-W network and influences on Li/Ni order suggests the two structures are close in energy, with the increased Li content in $Li_{4.1}Ni_{0.9}WO_6$ favoring the layered structure of Li-rich Li_5ReO_6 . Furthermore, oxygen atoms in both structures have similar coordination environments, each belonging to one WO_6 octahedron, although the partial Ni/Li ordering in the two materials could lead to several local coordination configurations around oxygen ($OWNiLi_4$, $OWNi_2Li_3$ or $OWLi_5$), which will necessarily have an effect on the electrochemical properties. These two variants of W ordering deriving from the $C2/m$ and $Fddd$ space groups have also been reported for Os in Li_4MgOsO_6 and Re in Li_4MgReO_6 ,^{23,24} depending on synthesis conditions. As for the $Li_{4+x}Ni_{1-x}WO_6$ system studied here, the difference between the two variants in these systems could be related to a tight balance in the Li/Mg ratio. The Rietveld model in $C2/m$ gave a poor fit to the SXRD and NPD in comparison to the Le Bail fit (see Note 3 in SI). The symmetry was reduced to the non-centrosymmetric Cm by displacement of the tungsten site off-center towards one apex of the WO_6 octahedron (Figure 5b and Table S7 in SI), thereby removing the two-fold rotation axis, maintaining the total number of cation sites at four but doubling the number of anion sites from two (Wyckoff sites $8j$ and $4i$, point symmetry 1 and m respectively) to four (sites $4b$ and $2a$, point symmetry 1 and m , respectively). Here, the off-centering of W differs from that in the $C2/c$ Li_4NiWO_6 phase and the displacement propagates ferrodistorively throughout the lattice, resulting in an overall permanent dipole. The final structural parameters of the combined SXRD and ND Rietveld refinement (Figure 4b), including 2.7(2) wt% $Li_{0.3}Ni_{0.7}O$ impurity, can be found in Table S5 in SI, with the final cell parameters ($a = 5.113747(23)$ Å, $b = 8.791326(40)$ Å, $c = 5.093213(23)$ Å, $\beta = 110.1564(12)^\circ$). Exploring the $Li_{4+x}Ni_{1-x}WO_6$ solid solution, we found that the same Cm structure is preserved up to $x = 0.25$, and observed a linear decrease of lattice parameters with increasing value of x (Figure S3 in SI). This is consistent with the increasing content of smaller and more highly charged Ni^{3+} when Ni is substituted by Li. For $x \geq 0.2$, impurity reflections corresponding to Li_4WO_5 were observed, suggesting that the limit of solid solution lies between nominal values of $0.15 \leq x \leq 0.20$.

Electrochemical properties

Li_4NiWO_6 and $Li_{4.15}Ni_{0.85}WO_6$ ($x = 0.15$) samples were chosen for initial electrochemical studies in order to maximize the differences between the two structures and compositions while avoiding the presence of Li_4WO_5 impurity for samples with $x \geq 0.2$. Ball-milling of the active materials to reduce the particle size from 5-20 μm to 0.5-3 μm (Figure S4 in SI) was found to help both in the preparation of the casting and in achieving better electrochemical performance. The first charge/discharge cycles for the two materials are compared in Figure 6a. Both materials show very high capacities of 270 mAh/g

when charged to 5 V, with some irreversible capacity on discharge. This is more pronounced for Li_4NiWO_6 , whose reversible capacity is less than 140 mAh/g on the first cycle (52% reversibility) and decreases to 110 mAh/g on the 10th cycle, whereas a higher reversible capacity was observed for $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ with 200 mAh/g on the first discharge (74% reversibility), decreasing to 150 mAh/g after 10 cycles (Figure 6b). Except for the lower reversible capacity of the stoichiometric phase, which could simply be related to the higher amount of Ni it contains, both materials show very similar features on charge/discharge suggesting similar redox processes. This is particularly clear when comparing the differential capacity curves of the two materials for the first two cycles (Figure S5 in SI). Because $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ displays a higher capacity and its structure is comparable to previously investigated materials,^{12,22} further characterizations were performed on this sample only.

Figure 6c shows the differential capacity curve of the first and second cycles of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$, with three redox processes occurring at 3.7, 4.2 and 4.7 V vs Li^+/Li on the first charge, and most of the redox activity on discharge happening at 1.7 V. Such a large voltage hysteresis (2-3 V) is uncommon for rock salt oxide cathode materials, and was therefore investigated further. On the next cycles, different processes are observed, with $\sim 0.35 \text{ Li}^+$ deintercalated at 2 V and the remaining 2.25 Li^+ at 3.7 and 4.4 V. The irreversible capacity on the first cycle and subsequent modification of the voltage-capacity curve indicate a change in the material upon initial charging, similar to the first activation cycle of most Li-rich rock salt oxides, including Li-rich NMC,²⁵ which could be related to a rearrangement of cations or oxygen release from the material. To understand the origin of the irreversibility, several cells were cycled with different maximum cutoff voltages, as shown in Figure 6d, with the corresponding differential capacity curves in Figure S6 in SI. For a 4 V cutoff, less than 100 mV polarization is observed between the oxidation and reduction processes and the discharge capacity of 100 mAh/g slightly exceeds the charge capacity of 85 mAh/g, suggesting that extra lithium is inserted upon reduction of the material at low voltage. Excess electrochemical insertion of lithium is not uncommon in rock salt oxides^{3,26,27} and can be expected here due to the partial oxidation of nickel in the pristine material ($\text{Li}_{4.15}\text{Ni}^{3+}_{0.15}\text{Ni}^{2+}_{0.7}\text{WO}_6$), which upon reduction can lead to the insertion of 0.15 extra Li^+ . After charging at 4.5 V with a capacity of 225 mAh/g, several broad reduction peaks are spread between 3.4 and 4.4 V, and an intense peak appears at 1.7 V corresponding to the low voltage plateau described previously. The modification is even more obvious when the material is fully charged to 5 V, with only a broad reduction feature left at 4 V and most of the capacity recovered on the 1.7 V plateau. One can note the appearance of two small features at 2.2 and 2.8 V (see inset of Figure S6 in SI) when the sample is charged at 4.5 V, which could indicate a small fraction of cations (Ni or W) in different coordination environments. More importantly, it clearly appears that the irreversible capacity on the first cycle is due to the redox process at 4.2 V.

Ex situ samples were prepared along the first two cycles and their XRD patterns measured to look for structural changes during cycling (Figure 7b). In addition to significant broadening of the peaks, a

reversible shift of the peak positions is observed upon charge and discharge. Superstructure peaks are preserved, suggesting that the W ordering is not affected, and all patterns can be indexed with the same Cm space group as the pristine material using the LeBail method, with the refined lattice parameters shown in Figure 7a and listed in Table S8 in SI. At 4 V, the slight decrease of the in-plane lattice parameters a and b and increase of the out-of-plane parameter c are consistent with the contraction of the honeycomb layer containing the majority of Ni (layer 1 in Figure 2) upon Ni oxidation and removal of Li^+ from the interlayer space. When charged further, all parameters decrease, with a large jump between 4.5 and 5 V, leading to a total contraction of the unit cell volume of 7%. The cell size increases back to close to its initial value on the next discharge, with slight differences in cell parameters that reflect the non-reversibility of the redox process at 4.2 V on initial charge. A similar evolution is observed on the second cycle with however a less pronounced contraction at 5 V. Surprisingly, the most drastic volume change happens between 4.5 and 5 V on charge and between 5 and 3 V on discharge, whereas this corresponds to less than 0.5 Li^+ (de)inserted from the material, suggesting that another structural process participates in the substantial contraction of the unit cell.

Charge compensation mechanism

The high initial charge capacity (270 mAh/g) and reversible discharge capacity (200 mAh/g) cannot be explained solely by the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple, which can only provide up to 116 mAh/g on the first cycle (Ni is partially oxidized in the pristine $\text{Li}_{4.15}\text{Ni}^{3+}_{0.15}\text{Ni}^{2+}_{0.7}\text{WO}_6$) and 127 mAh/g on the next cycles. To understand the role played by Ni, W and O in the different electrochemical processes, we measured selected *ex situ* samples by several spectroscopic techniques. X-ray absorption spectroscopy at the W L_3 -edge (Figure 8a) shows a very slight change in shape of the absorption peak from 4 to 4.5 V that cannot be assigned to a change of oxidation state but rather to a distortion of the W local environment. This is consistent with an irreversible transformation of the material associated with the 4.2 V process, as the double peak initially observed seems to coalesce and remains unchanged on further cycling. The Ni K-edge was used to probe the activity of Ni, with NiWO_4 and LiNiO_2 as standards for +2 and +3 oxidation states, respectively. The edge position of the pristine sample is similar to that of the NiWO_4 standard (see Figure 8b), as expected based on the predominance of the Ni^{2+} oxidation state in the starting material. Upon charging to 4 V, the edge gradually shifts to higher energies and finally reaches the edge position of the LiNiO_2 standard at 4.5 V, indicating oxidation of Ni^{2+} to Ni^{3+} . Slight changes can be more easily visualized by plotting the difference between two successive spectra (Figure S7 in SI). Further oxidation to 5 V does not affect the edge, which suggests that the Ni oxidation is limited to Ni^{3+} , making $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ a rare example of a cathode material where the average oxidation state of nickel is considerably less than +4 after charging to 5 V. This limitation cannot be attributed to reduced sensitivity of the Ni K-edge to oxidation states higher than 3+ as several studies have shown a clear shift between trivalent and quadrivalent nickel compounds,^{28,29} including an *in situ* study of the $\text{Li}_{1-z}\text{Ni}_{1+z}\text{O}_2$ ($z \leq 0.02$) cathode.³⁰ On discharge, Ni is partially reduced back to an oxidation state between

Ni²⁺ and Ni³⁺ at 3 V, and to Ni²⁺ when discharged to 1 V. During the second cycle, the oxidation of Ni seems to start at a higher voltage, between 4 and 4.5 V (Figure 8c), but does not reach the full Ni³⁺ oxidation state. This is possibly a consequence of structural reorganization during the first cycle that leaves some Ni²⁺ ions inactive in the material, resulting in a broadening of the Ni K-edge maximum but no clear shifts of the edge position.

At this point, it is very surprising that only the Ni²⁺/Ni³⁺ redox couple is active in the material, as it should theoretically account for about 64 mAh/g whereas the reversible capacity reaches 200 mAh/g, leaving two-thirds of the capacity unexplained. To investigate the possible participation of oxygen redox in the charge compensation mechanism, O1s XPS spectra were collected to probe the presence of oxidized oxygen species. Figure 9b compares the XPS results for samples charged and discharged at different voltages on the first cycle. Up to 4.5 V, the spectra are dominated by the signal of oxygen O²⁻ at 530.6 eV and show little variation, with only a weak contribution at higher binding energy for 4 and 4.5 V. This feature appears very clearly for the sample charged at 5 V as an intense contribution at higher binding energy (532.2 eV), which can be explained by the formation of oxidized oxygen species, written as Oⁿ⁻ (0 ≤ n < 2) until more information about their chemical nature is obtained as discussed below. Other contributions arising from deposited species are also very intense for this sample (~ 534 eV), as we expect some electrolyte decomposition at the cathode surface at high voltage. Upon discharge, the relative intensity of the Oⁿ⁻ peak decreases compared to that of the O²⁻ one but does not fully disappear, suggesting that some of the Oⁿ⁻ species formed are not reduced back to oxide. On the second cycle (Figure S8 in SI), the contribution at 532.2 eV increases again at 4.5 V, a lower voltage compared to the first cycle. The same observations can be made by monitoring the W 4f doublet position, which is very sensitive to changes in local environment of W ions (see Figure 9b). At 5 V, the doublet shifts to higher binding energy suggesting an increase of ionicity of W-O bonds with decreasing Li content, and a new doublet appears, whose evolution closely follows that of the Oⁿ⁻ peak on the O1s spectra. This new doublet is therefore assigned to a new W environment coordinated by the oxidized Oⁿ⁻ species, and its relative intensity is correlated with the amount of oxidized oxygen next to the surface of the sample. To strengthen this assignment, we measured the XPS spectra of two reference samples with W⁶⁺ cations in different coordination environments, namely WO₃ and WO₂(O₂)H₂O,³¹ the latter containing a peroxo (O₂)²⁻ ligand (see Figure 9a). The position of the O1s peak (530.7 eV) and W4f doublet (35.9-38.0 eV) of WO₃ are in good agreement with the corresponding O²⁻ (530.7 eV) and W-(O²⁻) (35.5-37.6 eV) peaks of the fully charged sample, whereas the position of the O1s peak (532.7 eV) and W4f doublet (36.9-39.0 eV) of WO₂(O₂)H₂O correspond to the Oⁿ⁻ (532.4 eV) and W-(Oⁿ⁻) (36.9-39.0 eV) peaks in the fully charged sample. Finally, the 2.14 eV splitting of both W-(O²⁻) and W-(Oⁿ⁻) doublets remains constant at any state of charge, confirming that W is in the +6 oxidation state at all points along the charge/discharge curves. It is quite unexpected that most oxidized oxygen species appear above 4.5 V on the first charge, whereas Ni does not oxidize beyond +3 according to XAS,

leaving a gap in our understanding of the charge compensation mechanism between OCV and 4.5 V. As XPS is a surface-sensitive technique, it is possible that oxygen is oxidized at lower potential in the bulk of the material, as is suggested by the low intensity contribution in the 4 and 4.5 V samples which are consistent with the Oⁿ⁻ peak at 532.2 eV, whereas the oxygen species oxidized close to the surface evolve as oxygen gas and are therefore not observed.

Formation of stable O-O bonds

If anionic redox can explain the high reversible capacity of Li_{4.15}Ni_{0.85}WO₆ (200 mAh/g on first cycle) despite the minor participation of Ni in the charge compensation mechanism, the low voltage of the reduction plateau at 1.7 V highlights the difficulty in reducing back the oxidized Oⁿ⁻ species formed during charge. Because of its d⁰ electronic configuration and associated π acceptor character, W⁶⁺ is prone to stabilize peroxy (O₂)²⁻ ligands in aqueous media through the formation of coordination complexes,³² similarly to other d⁰ transition metal species such as Ti⁴⁺. WO₂(O₂)H₂O is such an example, with an O-O bond of 1.46 Å, and shows clear signature peaks between 900 and 1000 cm⁻¹ in both infrared³¹ and Raman spectroscopies (light green in Figure 10b). The most intense peak at 983 cm⁻¹ is generally assigned to the short W-O bond stretching mode,³³ and the less intense peak at 920 cm⁻¹ to the stretching of the peroxy O-O bond. Computed Raman spectra (dark green) using DFT calculations can fairly well reproduce these two features (961 and 939 cm⁻¹, respectively), and further demonstrate that both peaks correspond to combinations of stretches of the short W-O and peroxy O-O bonds. This result shows that the presence of a peroxy bond does not necessarily result in one but possibly several vibration modes - this is the case for Na₂O₂, MgO₂ and ZnO₂³⁴ - and that DFT calculation can provide decisive insight for the correct assignment of the Raman peaks.

To check the formation of O-O bonds in the bulk structure of Li_xNi_{0.85}WO₆, we measured Raman spectra of *ex situ* samples at different states of charge (Figure 10a) and compared them to those obtained by DFT calculations on two model systems Li₃Ni³⁺WO₆ and Li₃Ni²⁺WO₅(O₂²⁻)_{1/2} with delithiation mediated by Ni redox and O redox respectively (see Note 4 and Figure S9 in SI). The pristine material has one main broad Raman band at 810 cm⁻¹ corresponding to the W-O stretching mode and less intense peaks (327, 460, 515 cm⁻¹) at lower frequency, where one expects bending and deformation modes. Upon charging to 4 V, the intensity of the main peak decreases and a sharper peak appears at 930 cm⁻¹, joined by a second peak at 910 cm⁻¹ at 4.5 V. Finally, the fully charged sample (5 V) shows a very well defined Raman spectrum, with relatively sharp and intense peaks, suggesting that the local structure of the fully charged sample is fairly ordered. Focusing on the peaks in the 800-1000 cm⁻¹ region in the fully charged sample, we observe a very intense peak at 890 cm⁻¹ and a second peak at 930 cm⁻¹ that appears as a shoulder. The peak at 930 cm⁻¹ is then present in all subsequent spectra, including the fully discharged samples, whereas the most intense band progressively disappears again upon discharge and is replaced at 1 V by a broader band centered at 830 cm⁻¹. On the second cycle, a perfectly reversible evolution is observed, consistent with the improved electrochemical reversibility after the first cycle.

The position of the peak at 930 cm^{-1} is in excellent agreement with that at 920 cm^{-1} in $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$, and could result from the formation of a peroxo bond. Calculation of the Raman modes was therefore performed with DFT to confirm the assignment of the peaks, using the pristine structure and two models of delithiation mediated by Ni redox (blue spectra in Figure 10b) and O redox (red spectra) respectively, the latter being characterized by the formation of a peroxo $(\text{O}_2)^{2-}$ unit ($d_{\text{O-O}} = 1.46 \text{ \AA}$, Figure S10 in SI). The calculated spectra are shown in Figure 10b, with the contributions of the short W-O and O-O vibration to the different peaks of the peroxo-containing model highlighted in orange and purple, respectively. It is important to note that the O-O vibration resulting from the peroxide formation in the $\text{Li}_3\text{Ni}^{2+}\text{WO}_5(\text{O}_2^{2-})_{1/2}$ model is again not associated with just one, but several vibrational modes, including the most intense peak at 877 cm^{-1} , with a major contribution from the short W-O stretching mode, and a smaller peak at 923 cm^{-1} . These two peaks predicted by the DFT model are in excellent agreement with the intense peak (890 cm^{-1}) and shoulder (930 cm^{-1}) observed experimentally in the fully charged sample. If the $\text{Li}_3\text{Ni}^{2+}\text{WO}_5(\text{O}_2^{2-})_{1/2}$ model does not perfectly represent the structure of the material charged at 5 V, it does capture the effect of forming a peroxo bond on the calculated Raman spectra. By comparison, the model with oxidation of nickel results in a single peak above 800 cm^{-1} which is inconsistent with the experimental observations. The observed values for O-O stretching frequencies (880-930 cm^{-1}) are higher than the Raman signals previously reported for $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and Na_3RuO_4 (850 cm^{-1}),^{35,36} and closer to the frequencies encountered for MgO_2 (864 and 934 cm^{-1}) and ZnO_2 (847 and 944 cm^{-1}) compared to those of Li_2O_2 (790 cm^{-1}) and Na_2O_2 (736 and 791 cm^{-1}).³⁴ Such differences are likely to arise from different O-O bond orders, which may greatly vary depending on the metal center. The agreement between experimental and calculated Raman spectra, and more importantly the comparison with the hydrated tungsten peroxide $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$, provide strong evidence for the formation of localized peroxo oxygen-oxygen single bonds upon full charge of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. This is consistent with the oxidized oxygen signal obtained from XPS, which also agrees with measurement on the same peroxide-containing $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$ standard, and shows that the redox of oxygen is not only happening at the surface but is indeed a bulk effect. The formation of quasi-molecular $(\text{O}_2)^{2-}$ species explains the shift of the W 4f doublet at higher binding energy (Figure 9b) with the increased ionicity of W- $(\text{O}_2)^{2-}$ bonds compared to W- O^{2-} bonds. This can also explain the strong contraction of the unit cell observed by diffraction at the end of charge (Figure 7a), as the formation of peroxo bonds would be expected to strongly perturb interatomic distances in the material. Finally, the fact that the peak at 930 cm^{-1} does not completely disappear at the end of the first cycle is also consistent with the XPS data and indicates that some peroxo species are formed irreversibly and maintained through subsequent cycling, thus explaining some of the irreversible capacity of the first cycle.

Discussion

By combining different techniques, we have obtained some insights into the electrochemical behavior of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. One of the most surprising results is the impossibility of accessing the $\text{Ni}^{3+}/\text{Ni}^{4+}$

redox, which suggests close competition between the redox activities of Ni and O. This results stand out from the behavior of the related $\text{Li}_4\text{NiTeO}_6$, which uses the full $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple with less than 200 mV hysteresis between charge and discharge.²² Moving from a main group cation (Te^{6+}) to a d^0 cation (Mo^{6+} , W^{6+}) as non-redox-active elements not only affects the cation ordering in the structure but also drastically changes the electrochemical properties of the material. Here, the activation of redox of oxygen-based states is demonstrated by alignment of both Raman and XPS spectra of electrochemically delithiated samples with the tungsten peroxide standard $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$. DFT calculations were carried out to investigate the electronic structure of delithiated Li_4NiWO_6 using both the VASP PBE+U and HSE06 total energies (see Note 4 in SI for details on the calculation). An idealized cation-ordered Li_4NiWO_6 structure was used for the calculations, with the experimental tungsten positions fixed and Ni/Li ordering with the lowest energy configuration. The two models of delithiation previously described were then explored (Figure S11 in SI), mediated by Ni redox and O redox respectively. The computed voltage for $x = 1$ in $\text{Li}_{4-x}\text{NiWO}_6$ is found 0.2-0.4 V higher for the anionic redox compared to the cationic $\text{Ni}^{2+}/\text{Ni}^{3+}$ model (Table S9 in SI), which is consistent with our observation of Ni oxidation at 3.7 V, and highlights the small difference in energy between cationic and anionic redox in this material. The stabilization of peroxide upon further oxidation could prevent the activation of the $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couple, or else be mediated by removing electrons from Ni e_g states to form transient Ni^{4+} species, according to the reductive coupling mechanism proposed for Ru-based materials.^{1,37} However, no change in the oxidation state of Ni beyond 3+ is observed experimentally so that this second hypothesis cannot be confirmed. As irreversibility increases when charging above 4 V, the material probably undergoes some irreversible oxidation of oxygen and gas release from the surface, corresponding to the process at 4.2 V on the first charge. This would explain why oxidized oxygen species are not observed by XPS in *ex situ* samples until 5 V. Nevertheless, the reversible formation of peroxo (O_2)²⁻ species on the second cycle, measured by Raman and XPS, proves that the large reversible capacity on discharge (200 mAh/g) is due to both cationic and anionic redox, contributing respectively to 1/3 and 2/3 of the capacity. If we assume that the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox is fully used, 1.75 e^- are to be accounted for by oxygen, *i.e.*, 0.29 e^-/O after normalizing by the number of oxygen in the formula unit, which is 16% higher than Li-rich NMC (0.25 e^-/O) according to Luo et al.,³⁸ reflecting the possibility of attaining considerable reversible anionic redox capacity from localised O-O bond formation.

Turning to the large voltage hysteresis observed upon activation of oxygen redox, it should be underlined that this is a true concern for the development of Li-rich cathode materials,³⁹ as it results in a large penalty on the round-trip energy efficiency (< 90% for Li-rich NMC). Such hysteresis has been correlated with oxygen redox activity and cationic migrations,^{13,15,40} which both result in different thermodynamic pathways on charge and discharge. One pending question is how the choice of transition metal affects the bond order and reversibility of O-O bond formation upon charge and discharge. The use of high-valence d^0 cations to increase the lithium content leads to higher capacities, thanks to the

combined participation of cationic and anionic redox. However, the XPS and Raman evidence on $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ suggests that high-valence d^0 cations also stabilize the formation of localized O-O bonds with a bond order n close to 1, which results in a large energy penalty associated with breaking the bonds upon reduction. It is well illustrated by density of states calculations that the empty antibonding (σ^*) states of quasi-molecular $(\text{O}_2)^{2-}$ species in the model derived from Li_4NiWO_6 by oxidation of oxygen are difficult to reduce back, as they lie well above the Fermi level (Figure S11c in SI). Such reduction is possible in $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$, at a very low discharge voltage of 1.7 V that makes the energy efficiency drop dramatically to 50%. The same redox processes are observed in the stoichiometric Li_4NiWO_6 (Figure S5 in SI), showing that the presence of isolated WO_6 octahedra is enough to stabilize $(\text{O}_2)^{2-}$ species whereas the long range cation ordering does not impact the electrochemical behavior. The local coordination of oxygen atoms is comparable in both materials with every oxygen coordinated by one W cation, as well as one Ni and four Li cation on average, although the imperfect ordering of Ni/Li will also result in other local coordination configurations around oxygen and a distribution of environments for Ni and Li which could explain why we do not see well-defined delithiation steps. Both materials also offer high dimensional diffusion pathways for Li diffusion. Similar voltage hysteresis has been observed in the disordered rock salt $\text{Li}_{1.2}\text{Ni}_{1/3}\text{Ti}_{1/3}\text{Mo}_{2/15}\text{O}_2$,⁴¹ as well as the $\text{Li}_4\text{NiMoO}_6$ phase reported by Yabuuchi et al.,¹² suggesting that a stabilization of O-O bonds by d^0 cations could be present in these materials as well. Among all cathode materials showing anionic redox, those containing late 4d/5d transition metals such as Ru/Ir form O-O pairs with much lower bond-order ($d_{\text{O-O}} \sim 2.4 \text{ \AA}$) and almost certainly differing extents of oxygen hole localization compared to the $3d^n/5d^0$ system studied here. This would lead to less destabilized antibonding σ^* states, thus improving the reversibility of the process and resulting in relatively low voltage hysteresis because of the reduced energy penalty to occupy these less antibonding states.^{26,37,42} To take full advantage of the high capacity of d^0 -based Li-rich rock salt oxides, one needs to facilitate the reduction of the O-O bonds. This could be done by stabilizing intermediate O-O distances ($1.4 < d_{\text{O-O}} < 2.4 \text{ \AA}$) through optimisation of the extent of delocalization of charges over the oxygen atoms in the structure, or lowering the barrier to electron transfer into the antibonding states. Both these scenarios are likely to be achieved by a careful selection of cations to minimize hysteresis and maximize anion redox capacity accessible from the formation of O-O bonds, *i.e.*, by optimizing the extent of localization of the oxygen holes.

Conclusion

In this work, the structural and electrochemical properties of a family of Li-rich rock salt oxides $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ were explored. The cation ordering is very sensitive to the Li/Ni ratio and generates two new structure types derived from $\text{Li}_3\text{Ni}_2\text{TaO}_6$ for $\text{Li/Ni} = 4$ and Li_5ReO_6 for $\text{Li/Ni} > 4$. Similar electrochemical processes were found regardless of the cation ordering, but a higher reversible capacity was measured for the $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ sample compared to the stoichiometric one. Surprisingly, Ni could not be oxidized beyond Ni^{3+} even at high voltage (5 V), accounting for only 64 mAh/g, *i.e.*, one third

of the total reversible capacity (200 mAh/g), thus leaving the large reversible capacity mostly unexplained by a classical cationic redox mechanism. The capacity associated with oxygen redox in this material is thus considerably larger than that obtained from the oxidation of the $3d^n$ cations. Raman spectroscopy combined with DFT calculation on the cycled material and a known tungsten peroxide standard compound represent definitive evidence of the formation of true peroxo $(O_2)^{2-}$ anions with localized O-O single bonds, stabilized by the presence of $5d^0 W^{6+}$ cations consistent with the solution coordination chemistry of d^0 peroxo complexes. This results in a good reversibility of the anionic redox process after the first activation cycle, with however a very large voltage hysteresis between charge and discharge that we attribute to the difficulty in reducing the stabilized $(O_2)^{2-}$ species, highlighting the importance of balancing electrochemical access to oxygen oxidation with enabling its reversal. The electronic structure and bonding characteristics of both redox active (Ni) and inactive (W) components of the structure play key roles in controlling the capacity accessible by stabilizing localized O-O bonds and the reversibility of the bond formation that defines the efficiency of the energy storage process. Such findings can be generalized to other d^0 containing Li-rich rock salt oxides, which also struggle with large voltage hysteresis and low energy efficiency, although the origin of this issue had not been investigated until now. Having clarified this point, we expect that this work will help in defining new strategies to decrease the voltage hysteresis and bring high capacity rock salt oxides closer to potential applications.

Methods

Synthesis. Pale green powder samples of Li_4NiWO_6 were prepared by a conventional ceramic route. A stoichiometric mixture of Li_2CO_3 (99.997%, Sigma Aldrich, dried at 250 °C for 12 h), NiO (99.999%, Sigma Aldrich, dried at 250 °C for 12 h) and WO_3 (99.995%, Sigma Aldrich, dried at 250 °C for 12 h) was ball-milled in propanol for 2 h, dried, pressed into a pellet and loaded into an alumina crucible to produce ~1 g of material. Part of the precursor mixture was used as a sacrificial powder in order to minimize the effects of Li volatility. The samples were fired twice at 1000 °C for 24 h with heating/cooling rates of 5 °C/min, with intermediate hand grinding of the pellet and sacrificial powder between firings. Brown-black powder samples of $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($0 \leq x \leq 0.25$) were prepared as above but with a 10% molar excess of lithium in the appropriate ratio of starting materials (e.g. $\text{Li}:\text{Ni}:\text{W} = 4.51:0.9:1$ for $x = 0.1$). For the neutron powder diffraction (NPD) experiments, both Li_4NiWO_6 and $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ were enriched with ^7Li using $^7\text{Li}_2\text{CO}_3$ (99% ^7Li atom, Sigma Aldrich dried at 250 °C for 12 h), with the synthesis scaled up to 4 g of product. $\text{WO}_2(\text{O}_2)\text{H}_2\text{O} \cdot n\text{H}_2\text{O}$ was prepared following the method described by Pecquenard et al.,³¹ followed by a thermal treatment at 120°C for 12 hours to prepare the reference sample $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$.

Diffraction. Phase identification of the $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ samples was conducted using laboratory powder X-ray diffraction data obtained using a PANalytical X'Pert Pro diffractometer ($\text{Co } K\alpha_1$) in Bragg-Brentano geometry. This instrument was also used for the determination of lattice parameters in the $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($0 \leq x \leq 0.25$) series by inclusion of crystalline Si as an internal standard. For detailed structural analysis of the as-synthesized materials, synchrotron X-ray powder diffraction (SXRD) data were collected at the I11 beamline at Diamond Light Source (Oxfordshire, UK), with an incident wavelength of 0.82588(1) Å using five multi-analyzer crystal detectors. The samples were loaded into borosilicate capillaries of 0.1 mm diameter, to minimize the absorption cross-section of the sample, and mounted on a capillary spinner during data collection. High-resolution time-of-flight (ToF) neutron powder diffraction (NPD) data were collected at room temperature using the HRPD instrument at ISIS (Oxfordshire, UK). The structural models were refined by the Rietveld method^{43,44} using the TOPAS software.

Electrochemical Testing. To evaluate the performance of $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($x = 0.15$) as a Li-ion battery cathode material, composite electrodes were fabricated by casting a mixture of active material/Super C carbon/polyvinylidene fluoride (PVDF) binder (Kynarflex, Arkema) (80:10:10 by wt) onto an aluminium foil current collector. Coin cells (CR2025) were assembled in an argon-filled glove box using 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (BASF) 1:1 by volume as the electrolyte, impregnated onto a glass fiber separator (Whatman) with a lithium metal counter electrode. Electrochemical characterization was carried out with a Maccor Series 4000 battery cycler, at 25°C, using a C-rate of C/10 (defined as 1 Li^+ exchanged in 10 h) between 1-5 V. For preparation of *ex situ*

samples, electrodes were cycled to different charge/discharge states, the electrodes were recovered and washed with DMC in the glovebox and dried.

Ex Situ PXRD of Charged Cathodes. Samples mixed with Super C carbon (80:20 by wt) were cycled to different states of charge/discharge in Swagelok cells. They were recovered, washed with DMC and dried under vacuum before being loaded in borosilicate tubes (0.3 mm diameter). The capillaries were sealed with wax prior to removal from the glove box, then heat sealed with a blowtorch. PXRD of the samples was collected at the I11 beamline with an incident wavelength of 0.826212 Å using a wide-angle position sensitive detector.

X-ray Absorption Spectroscopy (XAS). The X-ray absorption spectra were measured at the B18 beamline at Diamond Light Source (Oxfordshire, UK). X-ray absorption near edge structure (XANES) spectroscopy was used for analysis of the nickel and tungsten oxidation states, near the Ni K- and W L_{III}-edges. The data was calibrated using Ni/W metal foil references and normalized with the Athena software.⁴⁵ Electrodes for *ex situ* XAS were prepared by pressing a pellet (~60 mg) of active material with super C carbon and PVDF binder (74:13:13 by wt). After washing the samples, the active electrode pellets were mixed with an appropriate amount of cellulose (Sigma Aldrich), pressed with the appropriate density and sealed into polyethylene-lined foil bags (Sigma Aldrich) to prevent air exposure. Samples of uncycled active material were prepared in an analogous way including the carbon and binder. Materials used as reference standards including NiWO₄ (Ni²⁺ and W⁶⁺ standard), WO₃ (W⁶⁺ standard) and WO₂ (W⁴⁺ standard) were prepared by mixing appropriate masses of each with cellulose and pressed as pellets, but were not sealed in polyethylene foil bags.

X-ray Photoelectron Spectroscopy (XPS). Measurements were performed in a standard ultrahigh vacuum surface science chamber consisting of a PSP Vacuum Technology electron energy analyser (angle integrating ± 10°) and a dual anode Mg Kα (1253.6 eV) X-ray source. The base pressure of the system was 2 × 10⁻¹⁰ mbar, with hydrogen as the main residual gas in the chamber. The spectrometer was calibrated using Au 4f_{7/2} at 83.9 eV. All spectra were calibrated by aligning the main peak in the O1s region to that measured from the reference WO₃ compound at 530.6 eV. XPS spectra were fitted using Voigt functions (30% Gaussian – 70% Lorentzian) after Shirley background removal. The analysis was done with the minimum number of components required to explain the data. In the case of W 4f spectra, the relative intensities of the 4f_{5/2} and 4f_{7/2} peaks were constrained from the ratio found for the pristine spectra. Samples were transported from the glovebox to the instrument using a dedicated transfer chamber to avoid contact with air.

Raman Spectroscopy. Ex-situ measurements were performed at different stages of galvanostatic cycling. To avoid oxygen and moisture contamination, an air-tight Raman cell (ECC-Opto-STD, El-Cell, GmbH) was assembled inside an argon-filled glove box. Raman spectra were collected with a 633 nm wavelength laser using a Raman system (Renishaw inVia Reflex) with a microscope focused

through a 50x objective lens (Leica). The estimated power on the sample was 0.43 mW with 200 s exposure time and two accumulations. The baseline of the spectra were corrected for clarity purposes.

Computational methods. Plane-wave based density functional theory (DFT) calculations were performed with VASP,⁴⁶ using the PBE functional⁴⁷ augmented by an on-site Hubbard correction (PBE+U) using a rotationally invariant scheme⁴⁸ with an U_{eff} of 7 eV applied to the Ni 3d states. Core electrons were treated using the projected augmented wave approach,⁴⁹ with the Li 1s, Ni 2p and W 5s and 5p semi-core states treated as valence states. A 700 eV plane-wave cutoff energy was used for calculations of final structures and properties, with a $7\times 7\times 4$ k -point grid. A 600 eV plane-wave cutoff and a reduced k -point grid of $5\times 5\times 3$ was used when screening the energies of many configurations, which was sufficient to obtain relative energies within 20 meV of those obtained using the more accurate settings. In general the unit cell and atomic positions of structures were optimised until all forces were below 0.01 eV/Å, with a tighter convergence of 0.001 eV/Å used for the equilibrium structures of normal mode calculations.

Raman spectra are computed using the vasp_raman.py code.⁵⁰ A full normal mode calculations was performed at the Γ point using finite differences with displacements of 0.01 Å and the harmonic approximation. Following this, the change in the macroscopic dielectric tensor for each mode was calculated using density functional perturbation theory, and used to compute the Raman activity of the mode. Projection operators were evaluated in reciprocal space for these calculations to provide a high enough accuracy.

Hybrid DFT calculations were performed with a Gaussian basis set using CRYSTAL14.⁵¹ The HSE06 functional⁵² was used to obtain a better prediction of delithiation potentials. The pob-TZVP triple-zeta valence with polarisation basis functions were used for Li, Ni and O,⁵³ and a modified Hay–Wadt double-zeta basis set was used for W which had previously been shown to perform well for WO_3 .⁵⁴ A k -point grid of $7\times 7\times 4$ was used for each model, and the unit cell and atomic positions were optimised until forces were below 0.01 eV/Å.

Associated content

Supporting information

Supporting Information is available free of charge on the ACS Publications website.

Supplementary text on composition/structure analysis and computational summary. Tables with structural parameters, evolution of cell parameters upon cycling and calculated delithiation potential. Figures with structural information, SEM images, differential capacity plots, XPS on the second cycle of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$, result of calculated structure and associated DOS.

Crystallographic Information File for Li_4NiWO_6 (CSD 1884635) and $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ (CSD 1884637).

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Notes

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Figures

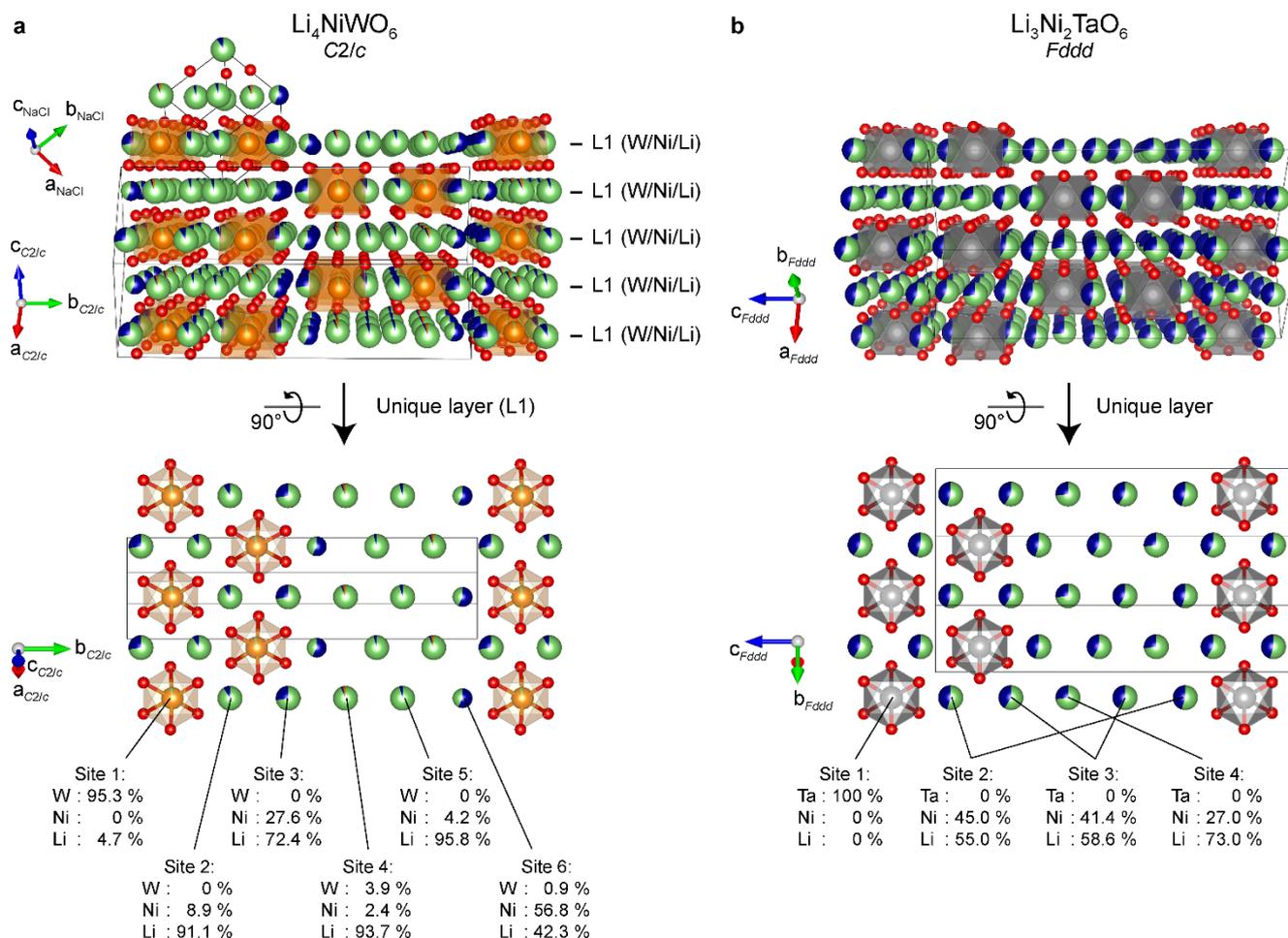


Figure 1: Structure of Li_4NiWO_6 . Comparison of the $C2/c$ structure of stoichiometric Li_4NiWO_6 (a) and the $Fddd$ structure of the archetype $\text{Li}_3\text{Ni}_2\text{TaO}_6$ (b) phases. For Li_4NiWO_6 , the cubic unit cell of the NaCl structure is shown in addition to the $C2/c$ cell to highlight the rock salt ordering of the structure. Both structures can be described by a staggered stacking sequence of a unique layer with a similar ordering of the highest oxidation state cation (W^{6+} in orange and Ta^{5+} in grey). The unique layer for each structure is rotated by 90° and displayed in the lower part of the figure. The different content of Ni (blue) and Li (green) coupled with off-centre displacement of W^{6+} results in different orderings of the remaining cation sites in the two materials, with site 2 (site 3) of the $Fddd$ structure being split into sites 2 and 6 (sites 3 and 5) of the $C2/c$ structure. The partial occupation of the different cation sites is indicated in the figure.

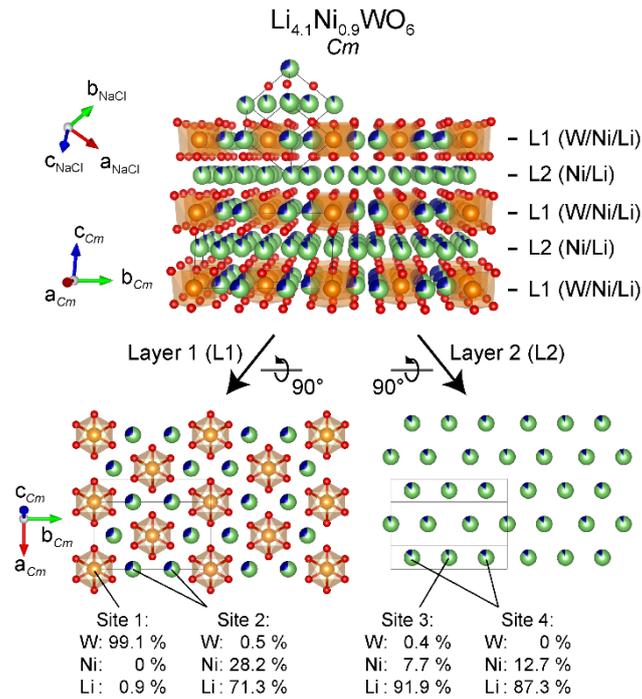


Figure 2: Structure of $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$. Phases with $x > 0$ in $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$, including $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$, adopt a *Cm* structure with an alternate stacking of two different layers, which are rotated by 90° and displayed in the lower part of the figure. W atoms (orange) form a honeycomb pattern in layer 1, while Ni (blue) and Li (green) occupy the other sites, with a majority of Li in the layer 2 (sites 3 and 4). The partial occupation of the different cation sites is indicated in the figure. The cubic unit cell of the NaCl structure is shown in addition to the *Cm* cell to highlight the rock salt ordering of the structure.

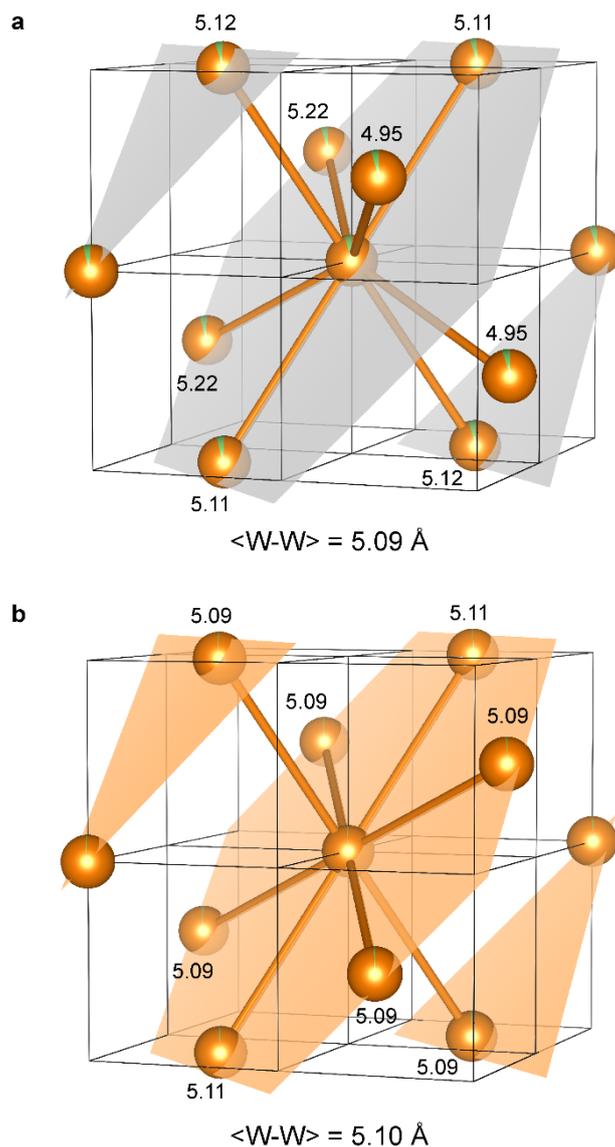


Figure 3: W ordering. The arrangement and distances between W atoms in Li_4NiWO_6 (a) and $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ (b). The distances (in \AA) from the central W atom are indicated next to each atom. The two structures have similar W-W distances, corresponding to the translation vector $\mathbf{T}_3 = (a, a/2, a/2)$, where a is the dimension of the rock salt cubic cell shown in the figure. However, the ordering differs between the two structures, resulting in a layered W ordering in $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ (b), highlighted by the orange planes, and a tridimensional W ordering for Li_4NiWO_6 (a), with some of the W atoms situated between the grey planes.

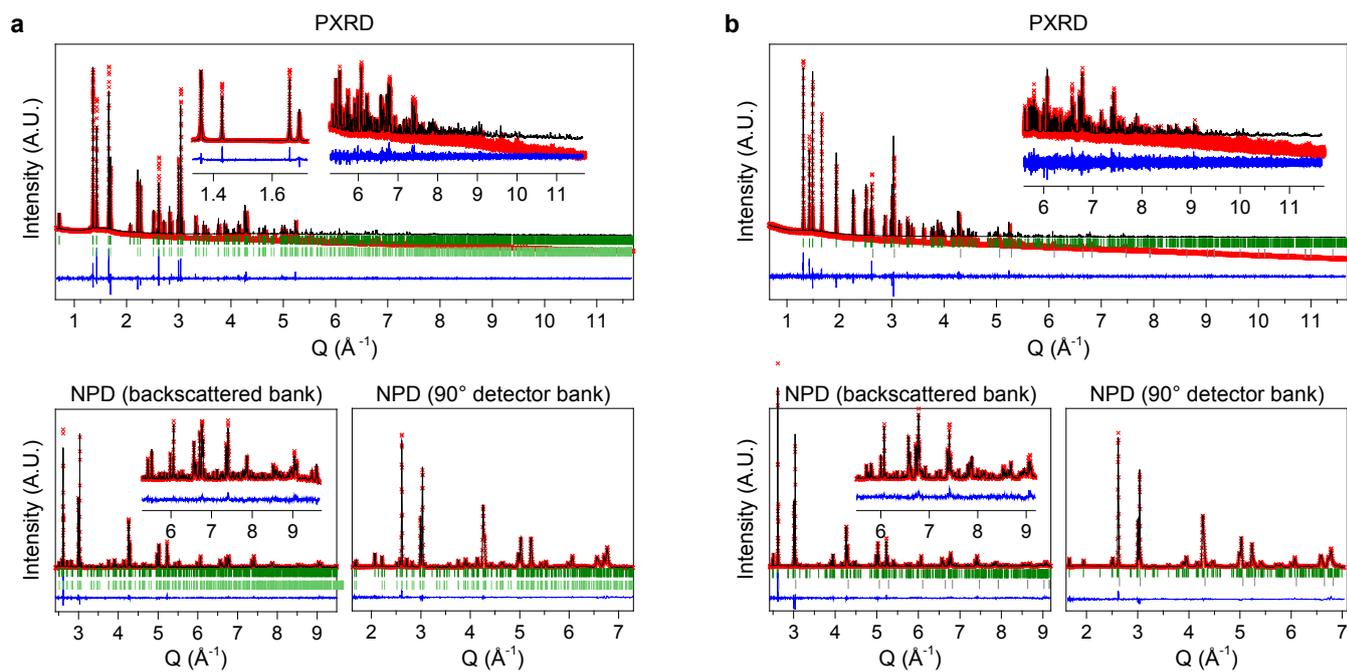


Figure 4: Combined Rietveld refinement of Li_4NiWO_6 (a) and $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ (b) using synchrotron powder X-ray diffraction ($\lambda = 0.82588(1)$ \AA) data and high resolution neutron powder diffraction banks: 168° bank and 90° detector bank. Experimental points are in red, calculated patterns in black, difference lines in blue, hkl ticks are dark green for the main Li_4NiWO_6 ($C2/c$) phase and light green for the minor Li_4NiWO_6 ($Fddd$) phase in (a); dark green for the main $\text{Li}_{4.1}\text{Ni}_{0.9}\text{WO}_6$ (Cm) phase and grey for the cubic impurity $\text{Li}_{0.3}\text{Ni}_{0.7}\text{O}$ phase in (b).

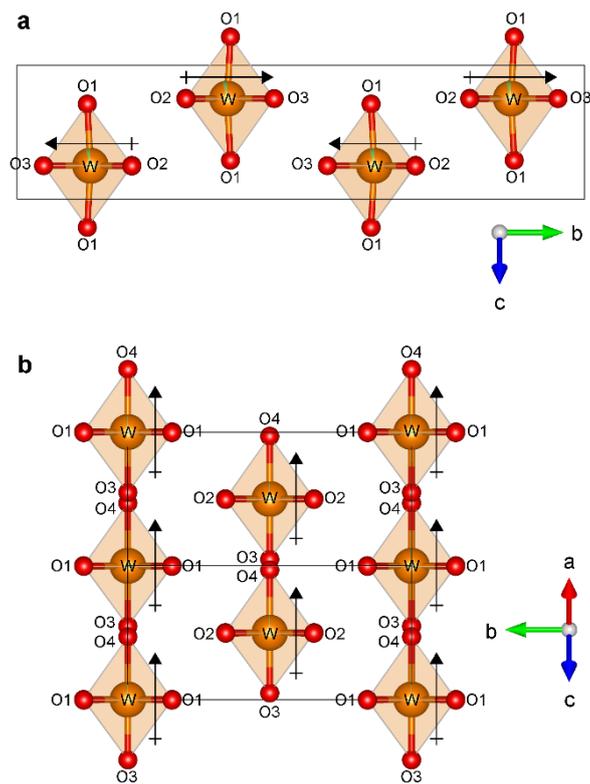


Figure 5: Displacement of W atoms due to second order Jahn-Teller effect in the two structures, resulting in overall polarization for Cm $Li_{4.1}Ni_{0.9}WO_6$ (b) but not for $C2/c$ Li_4NiWO_6 (a).

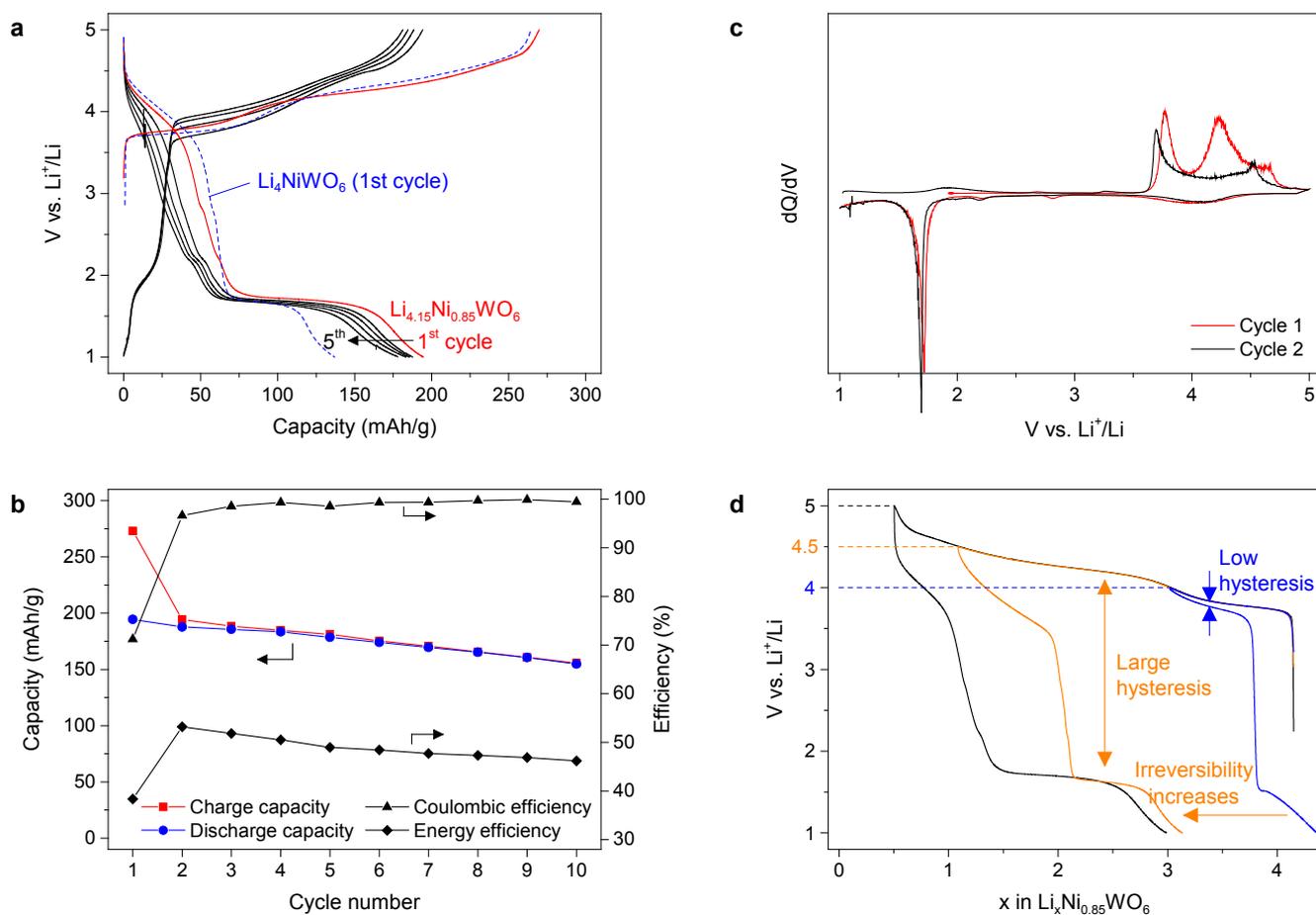


Figure 6: Electrochemical performance of $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ as a cathode material. (a) First 5 cycles of the $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ cathode. The first cycle of the stoichiometric Li_4NiWO_6 is plotted as a comparison (dashed blue line). Similar redox features are observed but a higher reversible capacity is found for the non-stoichiometric $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ phase. (b) Capacity retention, Coulombic efficiency and energy efficiency for $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. (c) Differential capacity curve for the first two cycles of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. (d) Voltage opening experiment. Charging to 4 V results in a good reversibility of the capacity and low hysteresis whereas activation of the 4.2 V process leads to irreversible capacity and high voltage hysteresis on discharge.

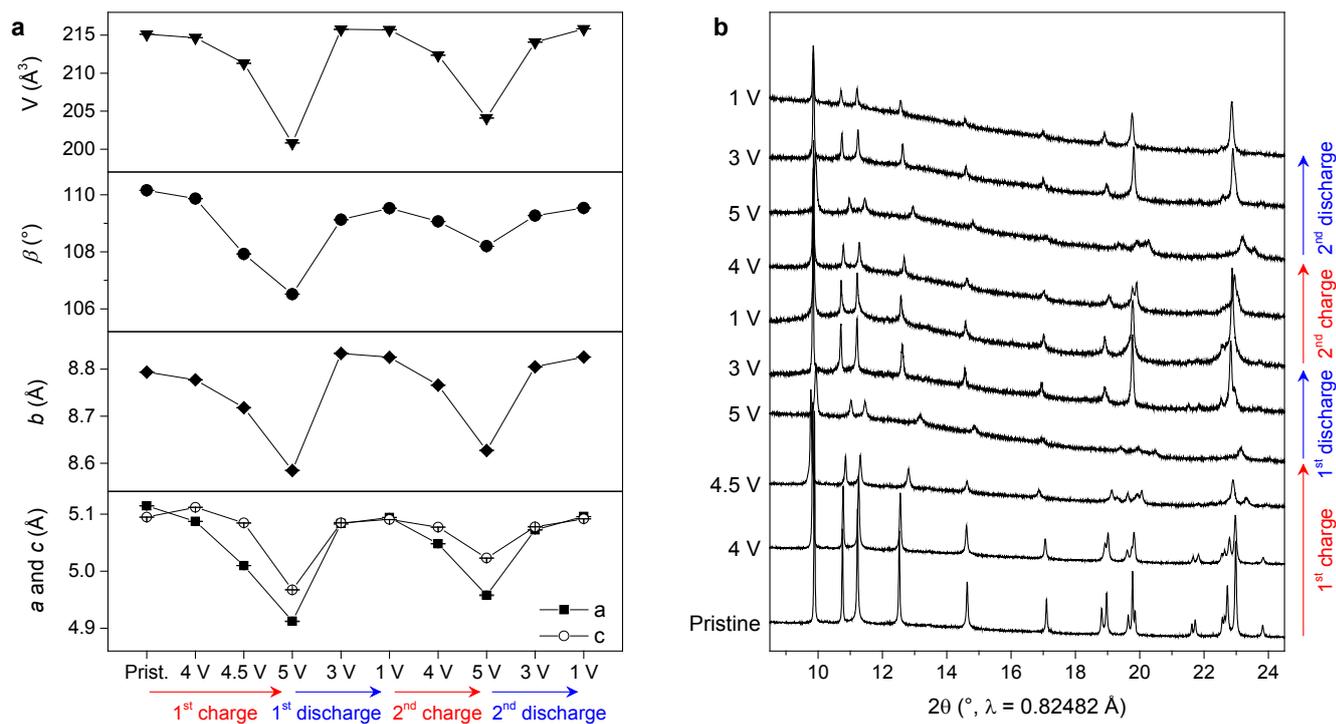


Figure 7: *Ex situ* X-ray diffraction study of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ on the first two cycles. (a) Evolution of cell parameters from pattern matching using the Cm space group of the pristine material. The unit cell contracts by 7% upon the first full charge and 5% on the second charge, suggesting an important modification of interatomic distances at high voltage. (b) Diffraction patterns at different states of the charge and discharge cycles. The conservation of superstructure peaks between 10° and 18° confirms that the honeycomb ordering of W cations is preserved upon cycling.

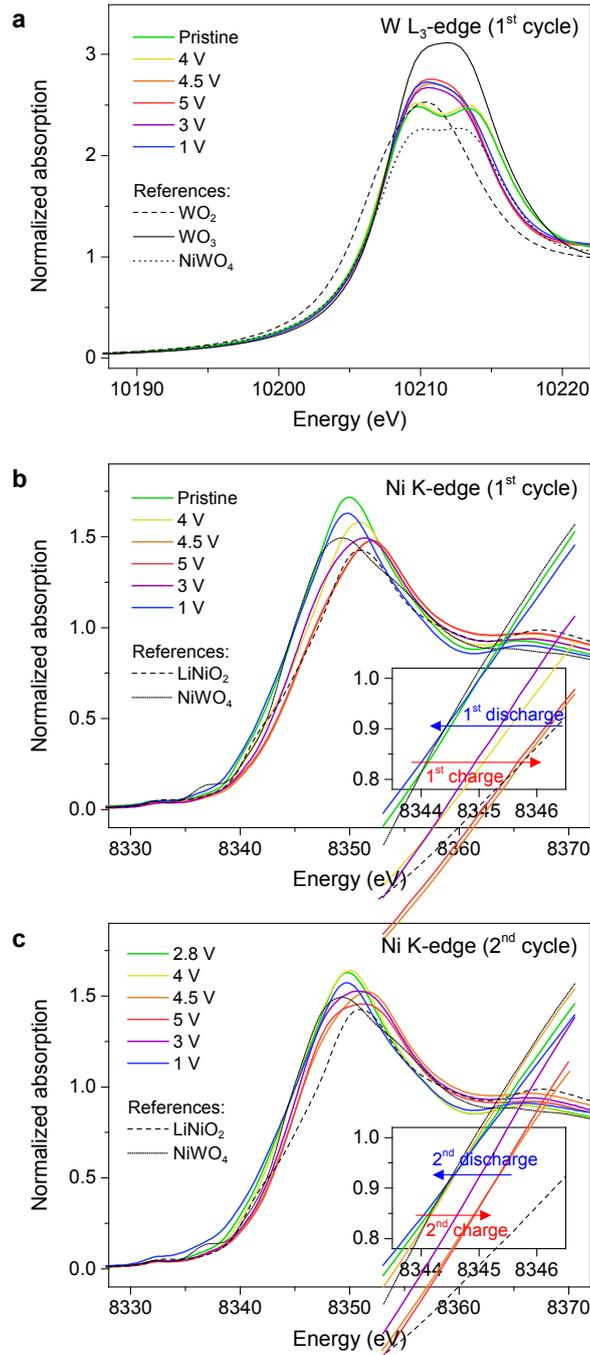


Figure 8 : X-ray absorption spectroscopy data of cycled $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. *Ex situ* spectra at W L₃-edge on the first cycle (a) and Ni K-edge on the first (b) and second (c) cycles were measured for cycled samples at different states of charge/discharge. The spectra for W^{4+}O_2 , W^{6+}O_3 , $\text{Ni}^{2+}\text{W}^{6+}\text{O}_4$ and $\text{LiNi}^{3+}\text{O}_2$ are given as references.

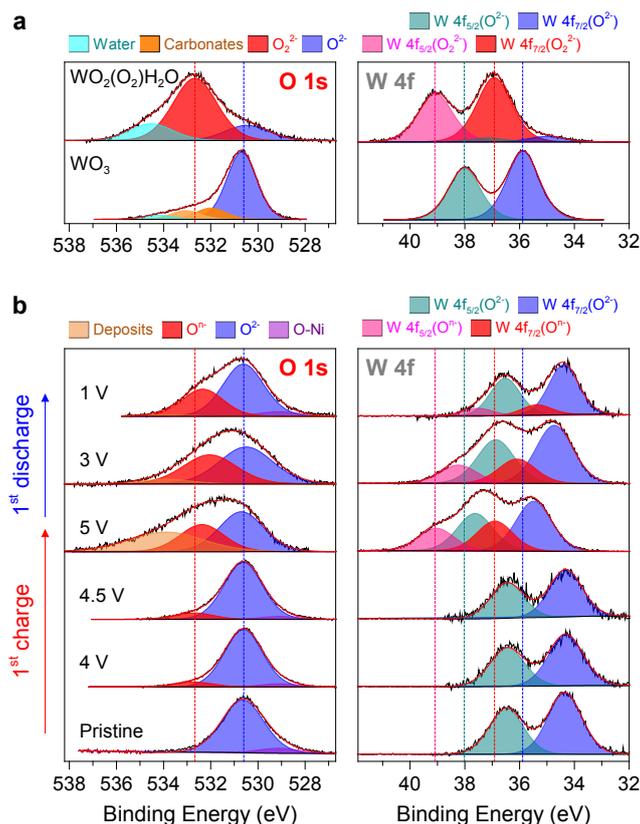


Figure 9: O 1s and W 4f X-ray photoemission spectroscopy data collected on standard W compounds (a) and during the first charge/discharge cycle of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ (b). The black and red lines are the experimental points and the result of the fit, respectively. In the O1s spectra, the contributions of O^{2-} and $\text{O}^{\text{n-}}$ (or $(\text{O}_2)^{2-}$ for $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$) are shown in blue and red, respectively. Surface deposits from decomposition products of the carbonate-based electrolyte are in orange and a small contribution at lower binding energy that we attribute to an oxygen environment rich in nickel is shown in purple. Some contribution of water is also shown in cyan for $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$. The W4f doublet is shown in blue ($4f_{7/2}$) and dark cyan ($4f_{5/2}$) for the contribution with non-oxidized oxygen environment and in red ($4f_{7/2}$) and pink ($4f_{5/2}$) for the contribution with oxidized oxygen $\text{O}^{\text{n-}}$. Dashed line are guides to compare the position of the different peaks to those in the standard samples.

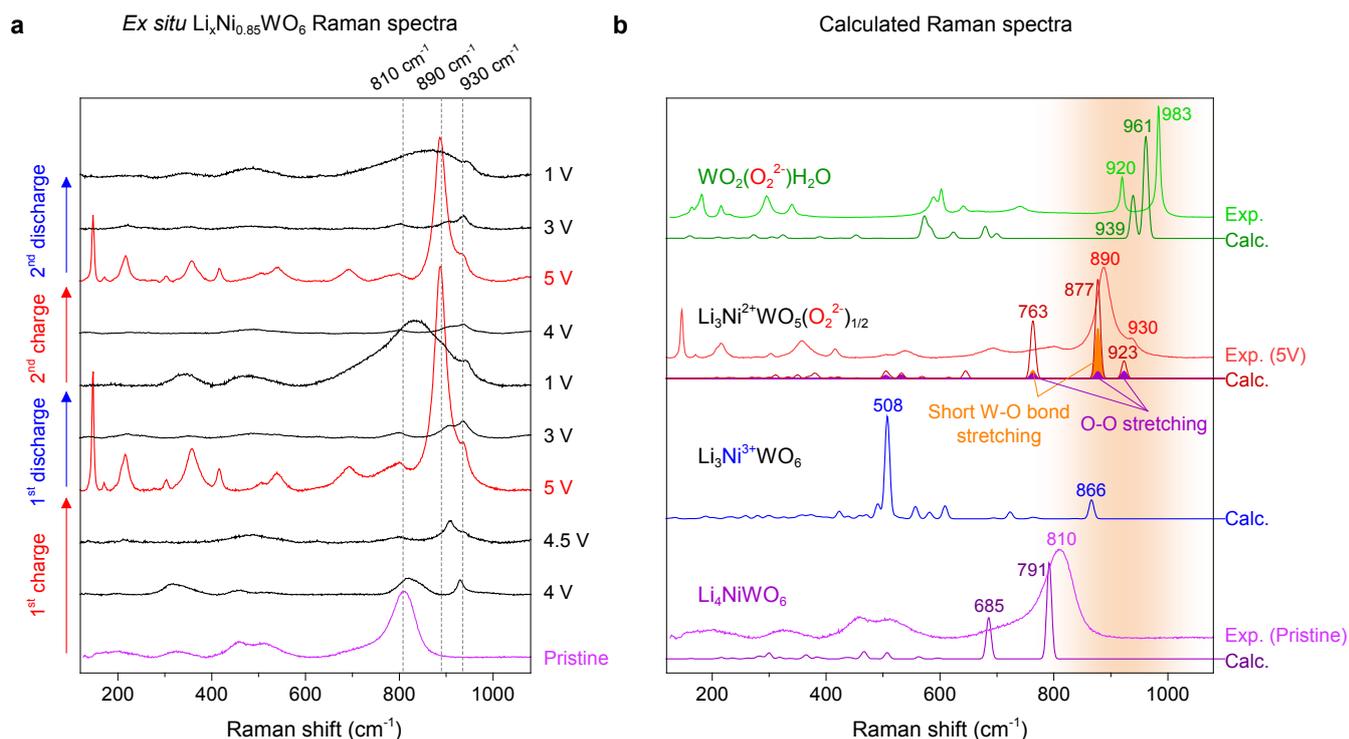


Figure 10: Experimental and calculated Raman spectra. (a) *Ex situ* Raman spectra for different states of charge/discharge of $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$. The pristine and fully charged spectra are highlighted in light purple and red, respectively. (b) Calculated Raman spectra for the pristine Li_4NiWO_6 (purple), two models of delithiation assuming cationic ($\text{Li}_3\text{Ni}^{3+}\text{WO}_6$, blue) and anionic redox ($\text{Li}_3\text{Ni}^{2+}\text{WO}_5(\text{O}_2^{2-})_{1/2}$, red) and the reference sample $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$ (green). Experimental spectra of the pristine material (light purple), charged to 5 V (light red) and $\text{WO}_2(\text{O}_2)\text{H}_2\text{O}$ (light green) are also plotted for comparison with the calculated ones. The typical range of frequencies for peroxide O-O stretching mode is shaded on the figure from 800 to 1000 cm^{-1} .

TOC

