Evidence of reversible oxygen participation in anomalously high capacity Li- and Mn-rich cathodes for Li-ion batteries

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ABSTRACT

The reaction mechanism of a high capacity lithium- and manganese-rich metal oxide, $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, has been investigated at the atomic level. High-resolution synchrotron X-ray powder diffraction (HRPD) and X-ray absorption spectroscopy (XAS) were used, respectively, to evaluate the electrochemical charge and discharge reactions in terms of local and bulk structural changes, and variations in the oxidation states of the transition metal ions. Ni K-edge XAS data indicate the participation of nickel in reversible redox reactions, whereas Mn K-edge absorption spectra show that the manganese ions do not participate in the electrochemical reactions. Rietveld refinements of the oxygen occupancy during charge and discharge provide evidence of reversible oxygen release and re-accommodation by the host structure; this unique oxygen participation is likely the main reason for the anomalously high capacity of these electrodes. The HRPD data also show that during the early cycles, characteristic peaks of the Li_2MnO_3 component disappear when charged to 4.7 V, but reappear on discharge to 2.5 V, consistent with a reversible lithium and oxygen extraction process. The results provide new insights into the charge compensation mechanisms that occur when high capacity, lithium- and manganese-rich electrode materials are electrochemically cycled – a topic that is currently being hotly debated in the literature.

KEYWORDS:

Li-rich cathode, electrochemistry, reversible oxygen participation, insertion/extraction mechanism.

1. Introduction

Lithium-ion batteries have served extensively as the green and rechargeable power source in portable electronic devices for almost two and a half decades. This battery technology is now also being targeted for 1) large-scale use in electric vehicles, and 2) energy storage for the electrical grid. However, to dominate in the electric vehicle market and to extend the electric range of hybrid and all-electric vehicles, the energy density, cycle life and safety of the batteries need to be significantly improved. Conventional cathode materials such as layered LiCoO_2 , olivine LiFePO_4 , and spinel LiMn_2O_4 are unable to fulfill the required electric range of vehicles due to their limited capacity.[1] In this regard, the family of layered lithium-rich metal oxides $\text{Li}[\text{Li}_\delta(\text{MnNiCo})_{1-\delta}]\text{O}_2$, which can be regarded as having an intergrown ‘composite’ structure with $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (alternatively, Li_2MnO_3) and $\text{LiMn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$ (NMC) components has been studied intensively because these materials offer a significantly higher capacity than commercial cathode systems, providing 250 mAh g^{-1} or more.[2–4] Researchers at Argonne National Laboratory originally proposed that because the Li_2MnO_3 component, which is electrochemically inactive below 4.3 V, is structurally compatible with LiMO_2 structures, it could be used to stabilize LiMO_2 cathode materials, and therefore enhance their capacity.[5–7]

While the concept of intergrown structures (often referred to as ‘composite’ structures) has been supported by several groups,[8–10] others describe these materials as a solid solution, and being single phase.[11,12] The debate of the atomic structure of these compounds, both in their pristine state and after cycling is ongoing and is being hotly contested in the literature. In particular, HRPD XRD data in which the similarity of the interlayer spacing, d , of two layered components, LiMO_2 ($\text{M} = \text{Mn, Ni}$) with $R\bar{3}m$ symmetry and Li_2MnO_3 with $C2/m$ symmetry, can make it challenging to distinguish the two components from one another.[11,13] Their structural

compatibility allows integration at the atomic level to form a ‘layered-layered’ $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ structure, which can be represented generally, in normalized notation, as $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$. [7] The presence of lithium ions in the transition metal layer results in manganese- and lithium-ion ordering, with characteristic regions of Li_2MnO_3 . The cation ordering between lithium and manganese, particularly for high values of x , is reflected in the X-ray diffraction pattern, in which weak peaks appear at low 2θ angles (typically $20-25^\circ$ with $\text{Cu K}\alpha$ radiation). The complex atomic level ordering in the electrode results in electrochemical behavior that is significantly different from the expected linear sum of these two components.

When initially charged above 4.3 V, cells with lithium- and manganese-rich layered cathodes exhibit a unique voltage profile. This profile can be divided into two regions, 1) a sloping region to 4.4 V and 2) a plateau between 4.4 and 4.7 V. During charge to 4.4 V, lithium is extracted from the LiMO_2 component. [14] The Li_2MnO_3 domains are electrochemically inactive to 4.4 V; at higher potentials, lithium is removed from the structure with concomitant oxidation of the oxygen ions, [12] while the manganese ions maintain their tetravalent oxidation state. Simplistically, this reaction has been represented by the electrochemical removal of lithium and oxygen from the Li_2MnO_3 structure, the net loss being ‘ Li_2O ’; the process results in a significant first-cycle capacity loss. [12,15] The electrochemical extraction of ‘ Li_2O ’ from Li_2MnO_3 therefore generates an active MnO_2 component within the composite electrode structure, thereby increasing the intrinsic capacity of the electrode. Bruce et al. suggested that the extracted lithium from the Li_2MnO_3 component is replaced with H^+ from electrolyte during the activation process. [16] Delmas et al. proposed that the plateau was associated with the migration of the transition metal ions from the surface to the bulk along with oxygen release. [17] Subsequent studies detected the formation of a defect spinel phase at the cathode surface during

the first cycle;[18,19] others have attributed some of the capacity of these lithium- and manganese-rich metal oxide cathodes to electrochemical redox reactions of oxygen at the surface of the electrode.[20] The loss of oxygen gas during the activation process has been reported although its accurate quantification is difficult; in many cases, it does not account for more than 50% of the stoichiometric oxygen release.[17,20,21] A recent X-ray diffraction analysis of a charged $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ (i.e., $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ in normalized layered notation) has revealed vacancies on the oxygen sublattice.[22] The possibility that a peroxide ion (O_2^{2-}) may form as an intermediate species before oxygen is lost from the structure cannot be discounted.[23,24] For example, for $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$, which is isostructural with Li_2MnO_3 , Tarascon et al. have described the electrochemical process as '*a cumulative and reversible cationic ($M^{n+} \rightarrow M^{(n+1)+}$) and anionic ($\text{O}^{2-} \rightarrow \text{O}_2^{2-}$) redox process, due to d-sp hybridization associated with a reductive coupling mechanism*' to account for its high capacity.[25] Of particular significance to this work are recent predictions and evidence that per-oxo ions (O-O dimers) are formed within the lithium layers during the high voltage charge of Li_2MnO_3 and Li_2IrO_3 . [26,27] Oxygen participation in the redox processes of other lithium transition metal oxides is already well known; it depends strongly on the hybridized states of the specific transition metal with the oxygen ligands. In this respect, charge compensation for lithium extraction from LiCoO_2 occurs on cobalt and oxygen simultaneously where the Co:t_{2g} band lies on top of the O:2p band, in contrast to lithium-manganese-nickel-oxide compounds such as $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ where charge compensation occurs predominantly by the oxidation of Ni^{2+} to Ni^{4+} ions.[28,29]

It seems logical to assume that after electrochemical activation and during the initial discharge of these highly complex electrode structures, lithium insertion into MnO_2 regions

created from Li_2MnO_3 ($\text{Li}_2\text{O} \bullet \text{MnO}_2$) nanodomains by lithium and oxygen loss, would occur with the simultaneous reduction of Mn^{4+} to Mn^{3+} ; this is certainly true for pure Li_2MnO_3 electrodes.[30] It may therefore be expected that lithium insertion into these electrode structures would lead to a pronounced shift in the Mn K-edge XANES spectra. In practice, however, the Mn K-edge XANES spectra of fully discharged composite electrode structures, particularly those containing nickel, do not represent reduced Mn^{3+} . [31,32] Moreover, the initial discharge capacity of these electrodes can also exceed the theoretical capacity of a layered LiMO_2 structure.[33] When viewed overall, the charge compensation mechanisms that take place during electrochemical cycling are not yet well understood.

In this study, a lithium-rich manganese-nickel-oxide electrode in the $x\text{Li}_2\text{MnO}_3$ -(1-x) $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ system, in which $x=0.4$, was selected to limit the possibility of peroxide-ion formation to a minimum, and to further probe the anomalously high capacity and electrochemical reaction mechanisms of these high capacity materials. High resolution powder diffraction and X-ray absorption spectroscopy techniques were used to monitor, *ex situ*, structural and electronic changes that occur within the electrodes at different states of charge. The advantage of the *ex situ* approach is the possibility of collecting X-ray diffraction and absorption data of one $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode sample simultaneously. To verify the reversible reaction mechanism, X-ray diffraction and absorption data of the electrode during the second cycle were also analyzed. The study, which includes the identification of a partially reversible oxygen redox reaction in the electrode structure, provides a better understanding of 1) the anomalously high capacity that can be generated by lithium-rich manganese-nickel-oxide electrodes, and 2) the reaction mechanism of the first two activation cycles before the onset of any significant voltage fade induced by the migration of transition metal ions to the lithium-rich

layers.[34] Although our XAS data confirm the existence of localized Li_2MnO_3 configurations within the structure of the pristine electrode powder, $R\bar{3}m$ symmetry was used for crystallographic simplicity and convenience to monitor the variations in lattice parameters and oxygen occupancy during charge and discharge.

2. Experimental Section

The $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ samples were synthesized by a co-precipitation method. A aqueous solution of nickel and manganese sulfates (2.5 M, $\text{NiSO}_4\text{:MnSO}_4 = 3\text{:}7$ molar ratio) was added to a NH_4OH (16 M) and 4 M NaOH solution, leading to the co-precipitation of the nickel and manganese ions. The resulting $(\text{Ni}_{0.3}\text{Mn}_{0.7})(\text{OH})_2$ precursor was dried at 110 °C under a N_2 atmosphere. The required stoichiometric amount of Li_2CO_3 was added to the precursor and heat treated (900 °C for 10 h) in air to obtain the desired electrode composition.

A slurry was prepared by mixing active material (80wt%), carbon black (10wt%, DENKA) to enhance the electronic conductivity of the cathode, polyvinylidene fluoride (10wt%, Solef 6020) as binder, with a N-methylpyrrolidone (NMP) solvent. The slurry was cast and calendered onto an aluminum foil, and dried (120 °C) in air. CR2032 type coins cells were assembled using the laminated cathode, a Celgard separator and 1.3 M LiPF_6 dissolved in a mixture of fluoroethylene carbonate (FEC), dimethyl carbonate (DMC), and fluorinated ether (FE) (FEC:DMC:FE = 45:15:40 by volume). Electrochemical tests were performed at a constant C/10 current rate between 2.5-4.7 V using a WonATech Battery Cycler WBCS3000S. The C-rate was calculated using the weight of the active material and the capacity of the $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode, based on the mass of its starting composition. Electrode samples

were prepared at different states of charge for the *ex situ* experiments by disassembling the coin cells in an Ar-filled glovebox, and washing the cathode films with anhydrous DMC.

HRPD measurements were carried out at the 9B HRPD beamline at Pohang Light Source-II (PLS-II) in South Korea. Electrode samples were scanned from 10 to 130.5° with a step size of 0.01° while rotating the sample to minimize the preferred orientation effects. The incident X-rays were vertically collimated using a mirror and monochromatized to a wavelength of 1.5472 Å using a double-crystal Si (111) monochromator. The detector arm of the diffractometer had soller slits with an angular resolution of 2°, a flat Ge (111) crystal analyzer, an antiscatter baffle and a scintillation detector. Rietveld refinements of recorded HRPD patterns were performed with the GSAS package[35] to obtain structural parameters of the electrode structure at various states of charge and to get quantitative phase information. The X-ray diffraction pattern of the pristine powder was of much better quality compared to those of the electrodes. Therefore, to determine whether there were any significant preferred orientation effects in the HRPD patterns, the diffraction pattern of the pristine powder was compared to that of an uncharged electrode. Diffraction patterns were normalized and background removed for comparison. No noticeable differences in peak intensity ratios were observed as shown in **Figure S1**, confirming that there were no significant preferred orientation effects. Thermal parameters were determined from the refinement of pristine powder patterns using $R\bar{3}m$ symmetry. Because occupancy and thermal parameters are correlated, and the lithium content changes significantly during charge and discharge, thermal parameters obtained from the refinement of the pristine material were held constant during structural refinements of the electrodes. X-ray absorption spectra were collected at the facility installed at beamline 7D and 10C at PLS-II in transmission mode with the N₂ gas-ionization detectors and a Si(111) double crystal monochromator detuned

to ~70% of its original intensity to eliminate higher order harmonics. The storage ring was operated at 2.5 GeV with an injection current of ~125 mA. The spectral energies were calibrated by using the first inflection points in the Mn and Ni metal foil spectra as references. Data pre-processing operations such as deglitching, energy calibration, normalization, and least square fitting with theory was performed as described by Kelly et al.[36] by using IFEFFIT[37] which used the FEFF code.[38]

3. Results and Discussion

The recorded and calculated high-resolution powder diffraction (HRPD) patterns of a pristine, highly crystalline $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ sample are shown in **Figure 1**. The data contain peaks that are characteristic of a typical layered LiMO_2 structure with trigonal ($R\bar{3}m$) symmetry and additional weak peaks, e.g., between 20 and $25^\circ 2\theta$, that are characteristic of Li-Mn ordering in Li_2MnO_3 with lower, monoclinic symmetry ($C2/m$). For simplicity, the Rietveld structural refinements of lattice parameter variations and oxygen site occupancies were conducted using the higher symmetry space group $R\bar{3}m$. The refined unit cell parameters for the trigonal (hexagonal) unit cell are $a = 2.866 \text{ \AA}$ and $c = 14.269 \text{ \AA}$ in which the c/a ratio is 4.978. This ratio is larger than the value of $2\sqrt{6}$ (4.89) for an ideal cubic-close-packed oxygen lattice, which is typical for layered LiMO_2 -type compounds.[39] In addition to the HRPD data, further structural information and the trends in transition metal oxidation state changes during charge and discharge were obtained by X-ray absorption spectroscopy (XAS); these additional data are provided in **Figures 2-10** of this paper, and in supplementary (S) **Tables (S1 to S8)** and **Figures (S2 to S9)**.

Normalized Ni and Mn K-edge XANES and EXAFS spectra of the parent $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ compound were recorded, as shown in **Figure S2** and **S3**. Quantitative crystallographic information obtained from the refinement and fitting of the HRPD and EXAFS data, as presented in Tables S1 to S8, indicate that the manganese and nickel ions adopt oxidation states of $\sim 4+$ and $\sim 2+$, respectively, consistent with compounds in the $x\text{Li}_2\text{MnO}_3$ -(1-x) $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ system.[40]

Stacked HRPD patterns, together with the voltage profile of the initial charge/discharge cycle are shown in **Figure 2a**. The electrochemical data (right) show that the capacity of the first charge to 4.7 V was 287 mAh g^{-1} , whereas that of the first discharge to 2.5 V was 234 mAh g^{-1} , reflecting a first-cycle capacity loss of 53 mAh g^{-1} , consistent with the behaviour of this type of material.[41,42] All the reflections in the HRPD patterns (Figure 2a, left) could be assigned to a composite host structure with components having trigonal $R\bar{3}m$ and monoclinic $C2/m$ symmetry. An enlarged depiction of the (003), (104), (018) and (110) reflections, plotted in the panels **Figure 2b**, **c** and **d**, respectively, and indexed according to $R\bar{3}m$ symmetry, show that these reflections shift significantly during the first charge and discharge cycle. During charge, the (003) reflection (Figure 2b) shifts to lower 2θ values because the increasing lithium deficiency in the lithium layers induces a strong electrostatic repulsion between the close packed oxygen layers and a consequent expansion of the “c” lattice parameter. In contrast, the shift of the (110) reflection (Figure 2d) to higher 2θ values indicates that the “a” lattice parameter shrinks during charge - a consequence of the oxidized Ni^{4+} ions having a smaller ionic radius ($0.48 \text{ \AA}$) than the Ni^{2+} ions ($0.69 \text{ \AA}$) in the parent electrode structure.[43] A close examination of the (003) and (104) reflections (Figures 2b and 2c) shows that there is significant peak broadening and a lowering of the peak height during charge and that these changes are reversed during discharge.

Peak broadening can originate from decreasing crystallite size, strain-induced lattice distortions or the formation of a secondary phase. The volume of the unit cell of lithium-rich metal oxide electrode structures changes typically by about 4% during electrochemical cycling,[44–46] so peak broadening due to crystallite size variations can be readily excluded. Although the formation of a second layered or spinel phase at the end of the charging process has been reported,[23,47,48] no significant peak splitting or the appearance of new, well resolved diffraction peaks was observed in our high resolution diffraction data of the $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode structure during the initial two cycles. The intensity ratio of the (003):(104) peaks remains relatively constant throughout the charge/discharge process, suggesting that the layered character of the structure remained dominant, and that there was no significant spinel formation during the first cycle.[49]

Detailed high-resolution transmission electron microscopy (HRTEM), scanning tunneling microscopy (STM), X-ray absorption spectroscopy (XAS), nuclear magnetic resonance (NMR), and computational studies have been carried out previously on high capacity $x\text{Li}_2\text{MnO}_3$ -(1-x) $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode materials. Some reports have provided evidence of composite structures,[13,50–52] whereas others claim that these materials are rather a solid solution with single phase character.[11,12] If the latter argument were true, then the $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ compound of this investigation would be represented in normalized notation $\text{Li}[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.250}]\text{O}_2$ (using the mathematical equivalence between composite and solid solution phase notations: $x\text{Li}_2\text{MnO}_3$ -(1-x) $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2 = \text{Li}[\text{Li}_{x/(x+2)}\text{Mn}_{(x+1)/(x+2)}\text{Ni}_{(1-x)/(x+2)}]\text{O}_2$. [7]); in this case, the cations in the transition-metal layer $[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.25}]$ would be randomly and homogeneously disordered over the octahedral sites in alternate layers of the structure.

Because our X-ray patterns could be indexed very closely to $R\bar{3}m$ symmetry, we did not attempt to refine the data with a two-phase model, nor with the added complexity of stacking faults [53,54] Instead, we used a simple single-phase model to monitor the oxygen occupancy during charge and discharge, and accounted for the peak broadening by accounting for strain effects, induced by lattice disorder as a result of lithium removal from the transition metal and lithium layers. The fact that all our refinements of the oxygen occupancy showed a consistent trend during the first two charge and discharge cycles lends credence to our data and analyses.

To understand the structural changes that occur during charge and discharge, Rietveld refinements of the HRPD patterns obtained at each state of charge were conducted using the normalized electrode formula $\text{Li}[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.250}]\text{O}_2$ and $R\bar{3}m$ symmetry for the parent electrode, for convenience. Although refinements using $C2/m$ space group symmetry provided an improved fit of the observed and calculated data, they did not significantly change the Li/Ni site disorder in the lithium-rich layer nor the lattice parameter values.[21,55] For the refinements of the Li/Ni site disorder and the Li, Ni, and Mn occupancy parameters, Li and Ni ions were, therefore, placed at the 3b octahedral sites of the $R\bar{3}m$ structure, while Li, Ni, and Mn ions occupied the 3a sites in alternate layers of the close-packed oxygen lattice. During these refinements, the Ni and Li occupancies and the oxygen occupancy were allowed to vary. The Li occupancy was calculated from the state of charge of electrode material whereas the Mn content in the structure was fixed at 0.583, i.e., the value in the normalized formula $\text{Li}[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.250}]\text{O}_2$. For each refinement, the lithium content in the electrode was determined from the amount of electrical current that had passed through the electrode with the assumption there had been no electrolyte decomposition or side reaction product formed as a result of the electrochemical lithium extraction/insertion processes. The variation in the lattice

parameter values, during the initial charge/discharge cycle, as determined from the Rietveld refinement of the HRPD patterns, are shown in **Figure 3a**. The values of “*a*” and “*c*” in the $\text{Li}[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.250}]\text{O}_2$ starting electrode were 2.866 and 14.269 Å, respectively. During charge to 4.4 V, the “*c*” lattice parameter increases, consistent with the shift of the (003) peak to lower 2θ values (Figure 2b). NMR spectroscopy has shown previously that, during the initial charge process, lithium ions in the (3a) octahedral sites of the transition metal layer diffuse to (3b) octahedral sites in the lithium layer via vacant (6c) tetrahedral sites and that these tetrahedral sites can be occupied by lithium if surrounded by vacant neighboring octahedral sites.[18,56] These tetrahedrally-coordinated lithium ions are subsequently removed from the structure by diffusion through the lithium layer. Recent experimental and theoretical studies have suggested that lithium ions are removed from the transition metal layer above 4.4 V.[57,58] The significant increase in the *c* lattice parameter, observed by XRD methods also provides evidence that most of the lithium is extracted from the lithium layer during the early stages of charging,[7,50,59] Therefore, for this study, it was presumed that the lithium ions were first extracted from the lithium layers during the early stages of charge. The “*a*” lattice parameter shrinks during charge to 4.4 V, consistent with the HRPD data in Figure 2d. When charged to higher potentials (4.4 to 4.7 V), when the electrochemical reaction occurs on a 4.6 V plateau, there is a negligible change in the “*a*” and “*c*” lattice parameters, strongly suggesting that the oxidation states of transition metals do not change and, instead, that the oxygen ions participate in the electrochemical oxidation reaction process. From a volumetric standpoint, the lattice parameter changes in Figure 3a indicate that during the initial charge to 4.4 V there is a decrease in unit cell volume from approximately 101.5 Å³ to 100.5 Å³, and that during the activation step to 4.7 V the volume is essentially unchanged; during discharge to 2.5 V, the unit cell expands to

approximately $102.5 \text{ \AA}^3$ as shown in **Figure 3b**. **Tables S3** and **S4** list the refined atomic coordinates and occupancies of the lithium, transition metals and oxygen in the $\text{Li}[\text{Li}_{0.167}\text{Mn}_{0.583}\text{Ni}_{0.25}]\text{O}_2$ unit cell at various stages during the initial charge/discharge process.

Lithium extraction from the $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode to 4.4 V, which corresponds to a capacity of 120 mAh g^{-1} , is compensated predominantly by nickel oxidation, as evident by the prominent shift to higher energies in the Ni K-edge XANES spectra (**Figure 4a**); increasing the voltage to 4.7 V shows no further significant oxidation of the nickel ions. The Ni K-edge data in **Figure 4b** show that the redox reaction on the nickel ions is reversible when the cell is discharged to 2.5 V. In contrast, the Mn K-edge XANES spectra during charge and discharge show only minor changes that are attributed mainly to local structural changes from neighbouring atoms[44] as shown in **Figure 5a** and **5b**, and not to any significant redox of the tetravalent Mn ions. It is therefore concluded that 1) the initial charge reaction to 4.4 V is associated predominantly with the oxidation of Ni^{2+} to Ni^{4+} , and 2) the reaction between 4.4 and 4.7 V occurs with the further extraction of lithium and a concomitant oxidation of the oxygen ions, at least some of which is associated with the irreversible removal of oxygen from the structure.[21]

The changes in the Ni K-edge EXAFS spectra during the initial charge and discharge reactions are presented in **Figure 6a** and **6b**, respectively; **Table S5** provides a structural analysis of the EXAFS data, showing specifically the changes to the Ni-O bond lengths during the first cycle. The Ni-O bond length in the pristine $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure is $2.04 \text{ \AA}$ (Ni^{2+}), which decreases steadily to $1.89 \text{ \AA}$ (Ni^{4+}) during charge to 4.4 V.[60] When charged between 4.4 and 4.7 V, lithium ions are extracted from the Li_2MnO_3 component with charge compensation on the oxygen ions, and with some oxygen loss from the structure.[9,21,55]

In this voltage window, there is no significant change in the Ni K-edge XANES spectra (Figure 4a). However, the intensity of the EXAFS peaks corresponding to Ni-O correlations in Figure 6a changes dramatically during charge to 4.4 V and also during the entire discharge process. Ni^{3+} is a Jahn-Teller active (d^7) ion, and it distorts the octahedral coordination of the nickel site. In the pristine $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ structure, Ni exists as a Ni^{2+} (d^8) ion with perfect octahedral coordination and six equal Ni-O bonds of ~ 2.03 Å, as reflected by a single intense peak in the EXAFS spectrum (Figure 6a). The Jahn-Teller active, Ni^{3+} (d^7) octahedron is distorted with four short Ni-O bonds of ~ 1.87 Å in the equatorial plane and two longer bonds of ~ 2.03 Å [61] that damps the Ni-O peak intensity at an average bond length of 1.94 Å. At 4.4 V, the nickel ions are oxidized to Ni^{4+} and revert to symmetric octahedral coordination with six equal, but shorter Ni-O bonds of ~ 1.89 Å. The Ni K-edge XAS data are consistent with the X-ray diffraction data; when charged between 4.4 and 4.7 V (i.e., after surpassing the charge capacity of 120 mAh g^{-1}), there are no significant changes to the Ni K-edge XAS data nor the lattice parameters, indicating that the cathode structure maintains its layered configuration on the 4.6 V plateau, and providing evidence that lithium removal from Li_2MnO_3 regions and oxygen participation in the electrochemical reaction are predominantly responsible for the charge compensation mechanism above 4.4 V.

The Mn K-edge EXAFS spectra shown in **Figures 7a** and **7b** are significantly different from the corresponding Ni K-edge data in Figures 6a and 6b. In particular, the Mn-O peak intensity is higher than the peak intensity of Mn-M correlations, consistent with recent data reported for materials with varying composition, x , in the $x\text{Li}_2\text{MnO}_3\text{-(}1\text{-}x\text{)LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ system.[40] The difference in peak intensity can be attributed to the difference in the coordination numbers of the transition metals in the Ni- and Mn-rich domains; specifically, both

Ni-O and Ni-M (M = Ni and Mn) correlations are associated with a Ni coordination number of 6 in the layered $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ component of the structure,[28] whereas the Mn-O and Mn-M (M=Mn) correlations in the Li_2MnO_3 component are associated with Mn coordination numbers of 6 and 3, respectively.[8] These observations are consistent with $\text{Li}^{1+}\text{-Mn}^{4+}$ charge ordering in the transition metal layer and indicate the presence of LiMn_6 -like regions, the building blocks of the Li_2MnO_3 component in the parent electrode structure. **Table S6** provides a structural analysis of the Mn K-edge EXAFS data, showing specifically minimal changes to the Mn-O bond length, and therefore the Mn oxidation state, during the initial charge/discharge cycle, consistent with the reasoning that octahedral manganese is unlikely to adopt a higher oxidation state in a cubic close-packed oxygen lattice.[62]

The Mn-O correlation in Figure 7a and 7b maintains its position in the EXAFS data during charge/discharge cycle because no change in the Mn oxidation state is observed. In contrast, the Mn-M correlation (M= Ni and Mn) decreases slightly in magnitude during charge to 4.4 V (120 mAh g^{-1}) and increases back to its original value during discharge. This behavior can be attributed to the change in oxidation state and ionic radius of the Ni ions during cycling, which consequently affects the value of the Mn-Ni bond length. Interestingly, the Mn-O/Mn-M peak height ratio remains higher than 1 after the first charge/discharge cycle, whereas the Ni EXAFS data in Figure 6a and 6b show the opposite trend. These observations provide strong evidence that lithium and manganese ordering (as LiMn_6 units) is maintained during the initial activation cycle, thereby preserving the Li_2MnO_3 character of the structure, at least while there is Li in the transitional metal layer.

The variation of the Ni-O and Mn-O bond lengths during the initial charge and discharge process is summarized in **Figure 8a** and **8b**, respectively. The trends in bond length clearly

support the arguments that 1) there is minimal change to the manganese oxidation state during the full charge/discharge cycle (Figure 8a, 8b), 2) charge compensation occurs predominantly on the nickel ions (Ni^{2+} to Ni^{4+}) when the cell is charged to 4.4 V (120 mAh g^{-1} , Figure 8a), and 3) oxygen participates in the charge reaction above 4.4 V (Figure 8a). Of particular importance is that during discharge (Figure 8b), the Ni-O bond length increases to its original value ($\sim 2.03 \text{ \AA}$) after 180 mAh g^{-1} of capacity has been delivered, and thereafter remains essentially constant for the remainder of discharge to 2.5 V, i.e., while another 54 mAh g^{-1} is delivered. This latter finding is significant; it coincides with the expected reduction reactions of oxygen (O_2) to O^- or O^{2-} in a Li/ O_2 cell, which typically occur at about 2.6 V.[63] The theoretical thermodynamic (open circuit) potentials for these two reactions against a metallic lithium electrode are extremely close, namely, 2.85 V and 2.94 V, respectively.[64] The XAS data therefore provide strong, even though tentative, evidence of a reversible lithium-oxygen reaction during the activation step of high capacity, lithium- and manganese-rich $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ electrode systems.

An accurate explanation of the role that oxygen plays during the initial and subsequent redox reactions of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ electrodes when charged to high potentials is difficult, because it may involve several reactions: 1) oxidation of O^{2-} to O_2^{2-} , 2) the release of oxygen gas (O_2), and 3) oxidizing reactions of O_2^{2-} or O_2 species with the organic solvent at the electrode/electrolyte interface or with neighbouring transition metal ions. Moreover, gas analysis techniques only provide information about gas evolution from the cell and, therefore, do not detect oxygen that remains within the cell or in the proximity of the electrode with which it may react reversibly – at least during early cell cycling. In practice, however, it has been determined that the amount of detectable oxygen is generally significantly less than that expected from the

amount of lithium that can be electrochemically extracted from the structure.[65] This finding, therefore, infers that redox reactions involving oxygen may occur in the solid state.

In order to probe the participation of oxygen in the redox reaction of the $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode, Rietveld refinements of the HRPD patterns were conducted to quantify the possible creation and filling of oxygen vacancies in the electrode structure during the initial charge/discharge process. Despite the relatively small X-ray scattering factor of oxygen, good fits were obtained for all HRPD patterns using the refined structural parameters obtained previously. In the pristine sample, the oxygen occupancy refined to ~ 0.99 (i.e., 99% occupancy) without any restrictions.

The change in oxygen occupancy as a function of the state of charge during the initial activation cycle is shown in **Figure 9a**. The data show that the oxygen content does not change significantly when the electrode is charged to 4.4 V (120 mAh g^{-1}) when lithium is extracted with the concomitant oxidation of Ni^{2+} to Ni^{4+} , as expected. Thereafter, between 4.4 and 4.7 V, there is a significant drop in the oxygen content; at the top of charge (4.7 V, 287 mAh g^{-1}) the occupancy is 0.905. During discharge to 2.5 V, the oxygen occupancy increases to 0.946, indicating that there are about 9.5% and 5.4% oxygen vacancies in the fully charged and subsequently discharged electrode structure, respectively.

The oxygen vacancies can also be estimated by calculating the amount of lithium and oxygen that are removed from the structure during charge and reintroduced into the structure during discharge, assuming that the oxygen ions are fully oxidized to O_2 , i.e., the removal of lithium and oxygen in a 2:1 ratio (Li_2O) during charge. When charged to 4.4 V, the lithium extraction is compensated by the oxidation of Ni^{2+} to Ni^{4+} and accounts for the experimental charge capacity of 120 mAh g^{-1} ; this capacity corresponds to the extraction of 0.39 Li^+ from the

octahedral 3a sites in the lithium layer of the normalized formula $\text{Li}_{(3b)}[\text{Li}_{0.167}\text{Ni}_{0.25}\text{Mn}_{0.583}]_{(3a)}\text{O}_2$. When charged at higher potentials between 4.4 and 4.7 V, the electrode capacity (167 mAh g^{-1}) corresponds to the further extraction of 0.54 Li^+ but, in this case, with the extraction and oxidation of 0.27 O^{2-} ions (assuming that the charging current does not partake in any other side reactions). This process leaves 13.5% oxygen vacancies on the oxygen positions of the structure. The total capacity associated with lithium and oxygen removal is 287 mAh g^{-1} . When discharged to 2.5 V, the delivered capacity (234 mAh g^{-1}) cannot be explained only by the reinsertion of lithium, but rather by the reintroduction of lithium and oxygen. Our calculations show that the reintroduction of 0.75 Li^+ and 0.18 O^{2-} would account for the capacity, leaving 4.5% oxygen vacancies in the discharged electrode structure; these values are close, within experimental error, to values determined from the refined HRPD oxygen occupancy parameters of 9.5% and 5.4% in the charged and discharged electrode, respectively.

Based on the experimental capacity data, and without knowledge of precisely where the released oxygen is accommodated in the electrode structure (i.e., bulk or surface) or the possible role of peroxide or superoxide ion in the electrochemical reactions, it is believed that the initial charge and discharge ('activation') of the lithium- and manganese-rich $\text{Li}[\text{Li}_{0.167}\text{Ni}_{0.25}\text{Mn}_{0.583}]\text{O}_2$ electrode can be described, in general, by the following processes:

Charge to 4.4 V (120 mAh g^{-1}) (1)

assuming that the 0.39Li^+ is extracted from the 3b sites of the lithium layer.

Charge to 4.4-4.7 V (167 mAh g^{-1}) (2)

in which $0 < \Delta < 0.167$ because the precise composition at which lithium is first extracted from the 3a sites in the transition metal layer is unknown. This reaction results in 13.5 % O^{2-} vacancies.

Discharge to 2.5 V (234 mAh g⁻¹) **(3)**

in which $0 < \Delta < 0.167$. This reaction results in 4.5 % O^{2-} vacancies.

The variation in the oxygen occupancy was also monitored by refinement of HRPD patterns during the second charge/discharge cycle to confirm the reversible oxygen extraction and insertion responsible for the abnormal capacity. The stacked HRPD patterns and the electrochemical profile of this cycle are provided in **Figure S4a** (left and right, respectively); enlarged sections of the HRPD patterns in **Figure S4b** to **S4d** show shifts in the (003), (104), (018) and (110) peak positions that reflect the expansion of the “*c*” lattice parameter and contraction of the “*a*” lattice parameter during charge and discharge. The variation of “*a*” and “*c*” during the second cycle is highlighted graphically in **Figure S5**. Although the trends of the lattice parameters are similar to those for the initial cycle (Figure 3a), it is clear that there is less capacity associated with the high voltage region, where there is relatively little change to the lattice parameter values, consistent with the absence of the pronounced voltage plateau at 4.6 V that characterizes the initial charge process (Figure 2a). Nevertheless, refinement of the oxygen occupancy during the second cycle shows a smaller decrease on charge relative to the first charge and that the removal and insertion of oxygen from the close-packed oxygen array is again partially reversible (**Figure 9b**).

Although oxygen diffusion has been widely studied in solid oxide fuel cells that operate at high temperature,[66–69] it has received relatively little attention in lithium-ion cathode

materials when charged to high potentials, although there is a growing interest in this phenomenon.[29,31,60] It has been proposed that, during the charging process, the M-O bond stretches elastically, effectively weakening the bond, thereby decreasing the activation energy barrier and increasing oxygen mobility.[66,67,70,71] Furthermore, during the initial charge of high capacity lithium- and manganese-rich metal oxide electrodes, not all the removed oxygen appears to be evolved as gaseous O_2 , [21,65] suggesting that the oxygen may react with, and oxidize, the electrolyte or remain within the bulk or at the surface of the electrode structure, making it available for reinsertion on the subsequent discharge.[72] Reversible oxygen behaviour has been reported for $Li_{(4-x)/3}Ti_{(2-2x)/3}Fe_xO_2$, $SrCoO_3$, $CaFeO_3$ and $Bi_2Fe_4O_9$ electrodes when used in aprotic lithium or sodium cells.[73–76] Of particular relevance to this study is that manganese-based metal oxide particles are known to adsorb oxygen, thereby stabilizing this species at the electrode-electrolyte surface.[77,78] Furthermore, it has been reported that oxygen radicals released at the electrode surface may react with the electrolyte to generate $C_2O_6^{2-}$ ions prior to the formation of Li_2CO_3 at the cathode surface; during the subsequent charge, the Li_2CO_3 can be electrochemically oxidized to release O_2^{n-} species ($0 \leq n \leq 2$).[72]

Despite the removal of oxygen from the structure during charge, the unit cell of the Li_2MnO_3 -like component maintains its monoclinic symmetry even though the signature Li-Mn ordering peaks become fainter towards the end of charge (**Figure 10**). Of particular significance is the reversible behaviour of the $LiMn_6$ ordering peak at approximately $20.75^\circ 2\theta$ ($\lambda=1.5472 \text{ \AA}$) during charge and discharge for the first (**Figure 10a**) and second (**Figure 10b**) cycles. It is clear from the high-resolution diffraction data that, when both lithium and oxygen are removed from the structure at 4.7 V, the ordering peak disappears and that it reappears on discharge to 2.5 V, confirming the partial reversibility of the oxygen redox reaction for both cycles and giving

credence to the concept of a hybrid Li-ion/Li-O₂ cell.[64] Our data support the outcome of a recent, first principles simulation of the atomic instabilities in high capacity xLi₂MnO₃-(1-x)LiMO₂ electrodes during the initial charge reaction that indicates: 1) “a partial depletion of the oxygen sublattice occupancy” and 2) “that oxygen interstitials, a by-product of the oxygen vacancies, are paired with other oxygen ions with a bond length of 1.3-1.7 Å”. [26] Even more relevant, is a very recent publication by McCalla et al. that reports the identification and visualization (by transmission electron microscopy) of O-O dimers that are formed in the oxygen sub-lattice of Li₂IrO₃ when charged to high potentials; it provides a mechanism that may well account for the reversibility of oxygen observed in the 0.4Li₂MnO₃-0.6LiMn_{0.5}Ni_{0.5}O₂ sample discussed here.[27]

Finally, recent electrochemical, localized scanning transmission electron microscopy, and X-ray absorption studies of Li₂MnO₃ electrodes, when charged to a high potential, have revealed that, on cycling, small domains other than Li₂MnO₃ exist, while the bulk structure maintains the monoclinic identity of the parent material.[79,80] Studies by Hy and Ito et al. and others[81,82] have provided XAS evidence of the reduction of Mn⁴⁺ to Mn³⁺ during the discharge of high capacity lithium-manganese-nickel-oxide and lithium-manganese-nickel-cobalt-oxide composite electrode structures. In contrast, in our study of 0.4Li₂MnO₃-0.6LiMn_{0.5}Ni_{0.5}O₂, there was no convincing evidence of manganese reduction during the initial activation cycle. The differences in redox behavior can be attributed to the relative amounts of Mn, Ni (and Co) in the various electrode structures. To confirm our finding, Ni and Mn K-edge XAS data were recorded during the second charge/discharge cycle; these data are provided in **Figure S6-S9**. As with the first cycle data (Figure 4 to 7), the XAS data of the second cycle clearly show the dominant

participation of nickel ions in the electrochemical reaction without any significant redox participation of manganese during discharge.

3. Conclusions

The structural and electronic properties of electrochemically cycled $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode has been investigated by using a combined X-ray diffraction and absorption spectroscopy approach with high-resolution synchrotron data to study the hotly debated reaction mechanism that occurs during the activation cycle of high capacity, lithium- and manganese-rich materials in rechargeable lithium-ion batteries. The Mn K-edge XAS data clearly show that the manganese ions remain tetravalent and electrochemically inactive during whole charge/discharge activation process. Rietveld refinements of the diffraction patterns and analyses of the XAS spectra show unequivocally that lithium extraction to 4.4 V is compensated by $\text{Ni}^{2+}/\text{Ni}^{4+}$ oxidation and that this process is reversible. At higher potentials, between 4.4 and 4.7 V, lithium extraction is accompanied by the loss of oxygen from the structure, a process that is partially reversible. From the data at hand, it appears that the oxygen is removed predominantly from the Li_2MnO_3 nanodomains of the structure. The participation of oxygen in the redox reactions of these lithium- and manganese-rich composite electrode structures clearly contributes to the anomalously high capacity of the electrode. Indeed, the experimentally obtained electrochemical charge/discharge capacity values determined in this study are, within experimental error, in excellent agreement with the values calculated on the basis of the amount of lithium and oxygen removed from the structure during charge and reinserted during discharge. The results provide new information, which sheds further light on the participation of oxygen in

the redox reactions of high capacity, lithium- and manganese-rich electrode materials, providing valuable guidance for further advances in high energy lithium-ion battery technology.

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Figures Captions

Figure 1. Recorded, calculated and difference plots obtained for pristine $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material from Rietveld refinement of high-resolution powder diffraction patterns.

Figure 2. (a) High-resolution powder diffraction patterns of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material charged to 4.7 V and discharged to 2.5V at C/10 rate along with the voltage profile during the first cycle, and (b-d) selected 2θ ranges shown.

Figure 3. Variation of the (a) lattice parameters and (b) unit cell volume of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material at different states of charge during the first cycle.

Figure 4. Normalized Ni K-edge XANES spectra of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material (a) during charge up to 4.7 V, and (b) during discharge to 2.5 V in the first cycle.

Figure 5. Normalized Mn K-edge XANES spectra of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material (a) during charge up to 4.7 V, and (b) during discharge to 2.5 V in the first cycle.

Figure 6. k^3 -weighted Fourier transform magnitude of Ni K-edge EXAFS spectra of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material (a) during charge up to 4.7 V, and (b) during discharge to 2.5 V in the first cycle.

Figure 7. k^3 -weighted Fourier transform magnitude of Mn K-edge EXAFS spectra of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material (a) during charge up to 4.7 V, and (b) during discharge to 2.5 V in the first cycle.

Figure 8. Variation of the Ni-O and Mn-O bond lengths in $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material at different state of charge (a) during charge up to 4.7 V, and (b) during discharge to 2.5 V in the first cycle.

Figure 9. Variation of the oxygen content in $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material (a) during first cycle and (b) during second cycle.

Figure 10. Selected 2θ range of high resolution powder diffraction patterns of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material during charge up to 4.7 V, and discharge to 2.5 V at C/10 rate (a) in the first cycle, and (b) in the second cycle.

Figure 1

Figure 2

Figure 3

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Figure 10

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