

The Role of Ni and Co in Suppressing O-Loss in Li-Rich Layered Cathodes

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Lithium-rich transition metal cathodes can deliver higher capacities than stoichiometric materials by exploiting redox reactions on oxygen. However, oxidation of O^{2-} on charging often results in loss of oxygen from the lattice. In the case of Li_2MnO_3 all the capacity arises from oxygen loss, whereas doping with Ni and/or Co leads to the archetypal O-redox cathodes $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ and $Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O_2$, which exhibit much reduced oxygen loss. Understanding the factors that determine the degree of reversible O-redox versus irreversible O-loss is important if Li-rich cathodes are to be exploited in next generation lithium-ion batteries. Here it is shown that the almost complete eradication of O-loss with Ni substitution is due to the presence of a less Li-rich, more Ni-rich (nearer stoichiometric) rocksalt shell at the surface of the particles compared with the bulk, which acts as a self-protecting layer against O-loss. In the case of Ni and Co co-substitution, a thinner rocksalt shell forms, and the O-loss is more abundant. In contrast, Co doping does not result in a surface shell yet it still suppresses O-loss, although less so than Ni and Ni/Co doping, indicating that doping without shell formation is effective and that two mechanisms exist for O-loss suppression.

1. Introduction

Cathode materials for Li-ion batteries are typically transition metal (TM) layered oxides, such as $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$.^[1] However, new cathode materials are required to achieve substantial gains in energy density. Lithium rich compounds, where

additional Li is substituted into the TM layer, are a promising solution as they introduce extra capacity due the activation of oxygen redox.^[2,3] However such compounds suffer from different degrees of O-loss at the particle surface when the O^{2-} ions are oxidized on charge.^[2–5] Li-rich 3d cathodes are based on the parent compound Li_2MnO_3 ($Li[Li_{1/3}Mn_{2/3}]O_2$). All of the charge capacity exhibited by Li_2MnO_3 is accounted for O-loss,^[6] whereas substitution in Li_2MnO_3 with Ni and/or Co to form compositions, such as $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ and $Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O_2$ suppresses O-loss and promotes reversible O-redox.^[2,3] Understanding the role of Ni and Co on the degree of reversible O-redox versus irreversible O loss in Li-rich cathodes is important in order to exploit new materials which suppress O-loss.

The ternary phase diagram for Ni and Co substitution into Li_2MnO_3 is shown in Figure 1. Within this diagram we explore

two tie-lines (Li_2MnO_3 – $LiNi_{1/2}Mn_{1/2}O_2$ and Li_2MnO_3 – $LiCoO_2$) giving particular attention to compositions which have the same degree of Li-richness (i.e., $x = 0.2$ in $Li[Li_xTM_{1-x}]O_2$) and therefore the same amount of TM capacity: $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (LNMO) and $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ (LMCO). The commonly studied composition with mixed Co and Ni substitution is also investigated: $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ (LNMCO).

The results show that Ni substitution in Li_2MnO_3 leads to as-prepared materials in which the particles exhibit a core-shell morphology, with a rocksalt shell being Ni-rich and Li-poor compared with the core. This dense, less Li-rich (nearer stoichiometric) rocksalt shell acts as a protective layer inhibiting O-loss and further densification, favoring reversible bulk O oxidation. In contrast, substituting Li_2MnO_3 with solely Co preserves a layered surface structure having the composition of the bulk yet it still suppresses O loss. The suppression, although less effective than Ni doping, indicates that forming solid solution materials also inhibits to some extent O-loss. At Co contents above 0.25, local segregation into well-dispersed $LiCoO_2$ and $Li_{1.25}Co_{0.25}Mn_{0.5}O_2$ domains occurs throughout the particles and the fraction of O-loss is reduced only by diluting the O-redox active phase with $LiCoO_2$.

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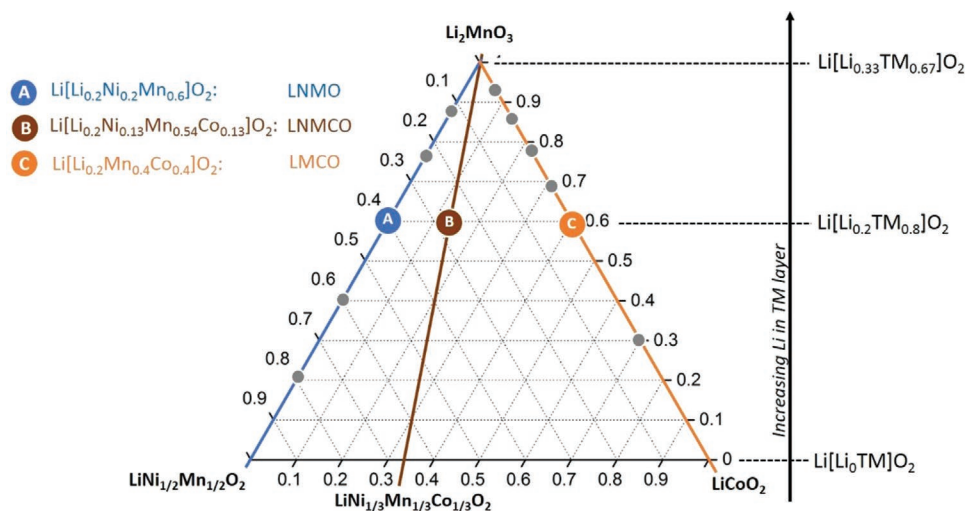


Figure 1. Li_2MnO_3 – $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ – LiCoO_2 ternary diagram mapping the phase space that includes Li_2MnO_3 substituted with Ni and/or Co and showing all compositions studied (gray dots). Particular attention has been given to three compositions that exhibit the same degree of Li-richness and TM redox capacity: $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (A, LNMO), $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ (B, LNMCO), and $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ (C, LMCO).

2. Results

The compositions, structures, and particle sizes of the materials were determined using Ion coupled plasma (ICP), X-ray diffraction (XRD), neutron diffraction (ND), Brunauer–Emmett–Teller (BET), and pycnometry. All compounds possess the O3 layered structure and with similar primary particle sizes and surface areas of ≈ 110 nm and ≈ 13 m² g^{−1}, respectively (Table S1 and Figure S1a, Supporting Information). Although, LNMO and LNMCO can be refined using single phase models (Figure S2a,b, Supporting Information), at high Co content ($>\text{Co}_{0.2}$) along the Li_2MnO_3 – LiCoO_2 tie line, an additional LiCoO_2 component has to be used as secondary phase, as reported previously.^[7] For LMCO this additional phase corresponds to 25.3(2) wt% (Figure S2c, Supporting Information).

Figure 2 shows the first cycle of LNMO, LNMCO, and LMCO. Each material exhibits a sloping region corresponding to TM-redox capacity and a plateau corresponding to O-redox and O-loss. However, the plateau at ≈ 4.55 V versus Li^+/Li varies in length between the materials. During the first discharge, the materials all show the familiar S-shaped voltage profile which is maintained over extended cycling.

2.1. O-Loss Behavior

Operando electrochemical mass spectrometry (OEMS) was employed to establish the amount of O-redox activity that is associated with O-loss and to distinguish the impact of Ni and/or Co substitution on this process (Figure S3, Supporting Information). It has been shown previously that singlet O_2 generated directly from oxidized oxide ions at the cathode surface either self-quenches to form the more stable triplet O_2 or attacks the electrolyte forming CO_2 .^[8,9]

The capacity associated with O-loss from each material was calculated from the O_2 and CO_2 evolved during the charge, using the procedure described previously.^[2,3] It has been previously shown that the gas evolution arising from the direct oxidation of

the electrolyte solvent is negligible below 5 V.^[3,10] The ^6Li NMR (at Figure 4; and Figure S5, Supporting Information) does not show any evidence of diamagnetic Li_2CO_3 with a detection limit

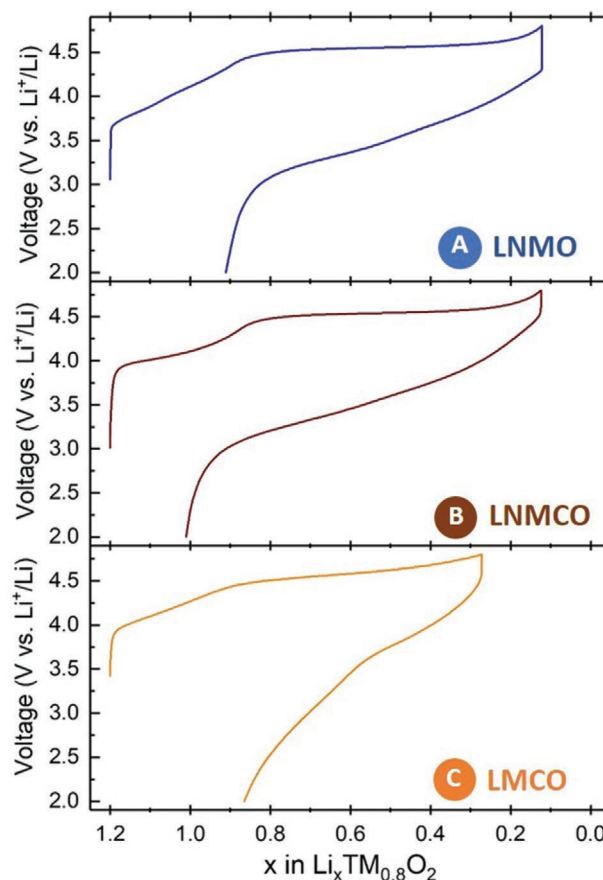


Figure 2. First galvanostatic cycle of LNMO (blue), LNMCO (brown), and LMCO (orange) at 50 mA g^{−1}.

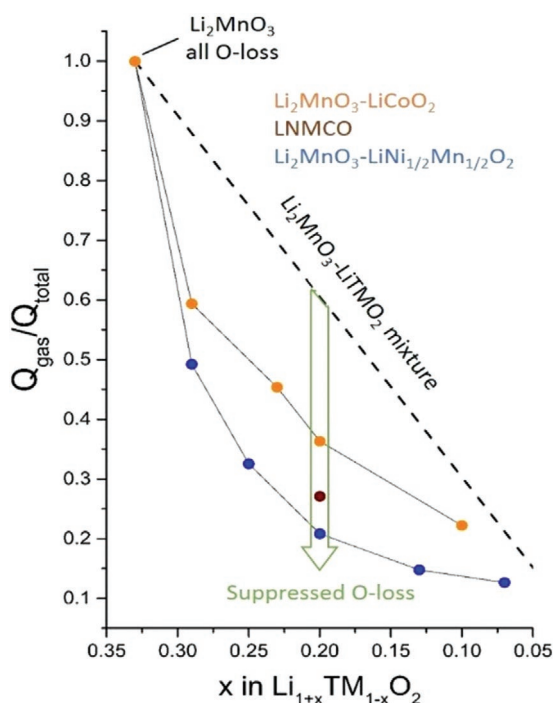


Figure 3. Fraction of the total capacity associated with gas evolution ($Q_{\text{gas}}/Q_{\text{total}}$) during 1st charge of materials belonging to the $\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (blue), $\text{Li}_2\text{MnO}_3\text{--LiCoO}_2$ (orange) tie-line, and LNMCO (brown) as a function of Li-richness. While in Li_2MnO_3 , all the capacity is charge compensated with O-loss, Ni and/or Co substitution in Li_2MnO_3 progressively decreases the fraction of O-loss compared to a mechanical mixture of the end member phases but to different extents: Ni suppresses O-loss more efficiently than Co substitution and to a lesser extent than Ni and Co cosubstitution.

of about 0.1 mol%, ruling out any significant capacity associated to surface carbonates decomposition. The gas evolved therefore arises primarily from the lattice of the material according to the equation provided in the Experimental Section; O_2 and CO_2 each consuming 4 electrons. The results are presented in **Figure 3**; and **Figure S3** (Supporting Information). As reported previously,^[6,11,12] decreasing the Li-richness leads to a clear decrease in the proportion of capacity associated with gas release, from exclusively O-loss for Li_2MnO_3 to mainly reversible O-redox for compositions close to LiTMO_2 . The quantity of gas released is dependent on the surface/volume ratio of the cathode particles which was kept close to constant across the materials used in this study. Previous studies^[2,3] reported somewhat lower $Q_{\text{gas}}/Q_{\text{total}}$ ratios for LNMCO arising from the larger particle sizes used in that study. Along the $\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line, the charge compensation associated with gas loss drops significantly, even at high degrees of Li-richness, with the almost complete suppression of O-loss by $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.57}\text{O}_2$. However, along the $\text{Li}_2\text{MnO}_3\text{--LiCoO}_2$ tie-line, the suppression of O-loss relative to the mechanical mixture between the end-members is much less pronounced and for LNMCO the O-loss lies between that of the Ni and Co substituted Li_2MnO_3 alone. This contrast between Ni and Co substitution indicates that Ni suppresses O-loss and hence stabilizes reversible O-redox much more effectively than Co substitution. However, the fact that LNMCO shows a

smaller irreversible capacity than LNMCO despite a higher level of O released indicates that the underlying mechanism governing the capacity retention is complex and that O-loss from the lattice is not the sole factor.

2.2. Impact of Ni and/or Co Substitution on the Structure

The Synchrotron X-ray diffraction patterns of LNMCO, LNMCO, and LMCO (**Figure S1a**, Supporting Information) possess the familiar additional peaks arising from honeycomb ordering within the TM layer.^[13] Li_2MnO_3 , exhibits perfect honeycomb ordering with Li surrounded by 6 Mn. As Ni-substitution into Li_2MnO_3 involves 3 Ni^{2+} substituting for 2 Li^+ and 1 Mn^{4+} , while for Co, 1 Li^+ and 2 Mn^{4+} are replaced by 3 Co^{3+} , the location of TM ions on the Li and Mn sites means that the perfect honeycomb superstructure cannot be preserved. The results of Rietveld refinement of the structures based on synchrotron XRD and ND data (shown for LNMCO, LNMCO, and LMCO in **Figure S2**, Supporting Information) confirm the solid solution mechanism, with Li and Mn substitution by Ni or Co in LNMCO and LMCO, respectively. Whereas, in the case of Ni and Co cosubstitution they are located on the Li and Mn sites, respectively. It is also known that Ni and Li exhibit site exchange in layered oxides,^[14] for LNMCO 3.6(2)% of Li sites in the alkali metal (AM) layer are occupied by Ni (see **Figure S1b**, Supporting Information). As the overall Ni content is increased, the proportion of Ni engaged in antisite defects remains constant (around 20%) and hence the amount of Li sites occupied by Ni increases. For the LNMCO, the fraction of Ni in the AM layer significantly decreases (0.5(1)% of Li sites in the AM layer occupied by Ni) and along the $\text{Li}_2\text{MnO}_3\text{--LiCoO}_2$ tie-line, a negligible amount of Co/Li antisite defects is observed (0.2(1)% of Li sites in AM metal layer occupied by Co).

In order to characterize the local cation distribution, TM K-edge extended X-rays absorption fine structure (EXAFS) was employed. The EXAFS spectra (**Figure S4**, Supporting Information) show a first shell corresponding to Ni, Mn, or Co coordinated by 6 oxygen atoms and a second shell associated with the TM–TM (and TM–Li which has a negligible contribution) scattering. Therefore, the intensity ratio between the 2nd and the 1st shell gives insight into the local TM/Li distribution. For the Mn K-edge EXAFS, this intensity ratio has a much stronger dependency on the composition along the $\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line than is the case for $\text{LiCoO}_2\text{--Li}_2\text{MnO}_3$, consistent with the substitution of 2 Li^+ and 1 Mn^{4+} by 3 Ni^{2+} for the former and 1 Li^+ and 2 Mn^{4+} by 3 Co^{3+} in the latter case. For LNMCO the significantly higher Ni and lower Co 2nd/1st shell ratio compared to that observed for Ni-substituted and Co-substituted materials respectively confirm the presence of Ni on the Li and Co on the Mn sites.

To further probe the local structure ^6Li magic angle spinning nuclear magnetic resonance (MAS NMR) was employed. The spectra of LNMCO, LNMCO, and LMCO are shown in **Figure 4** and of the $\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ and $\text{Li}_2\text{MnO}_3\text{--LiCoO}_2$ tie-lines in **Figure S5** (Supporting Information). The spectrum for Li_2MnO_3 reveals three sharp isotropic peaks, centered at 770, 810, and 870 ppm, corresponding to the three lithium sites in the

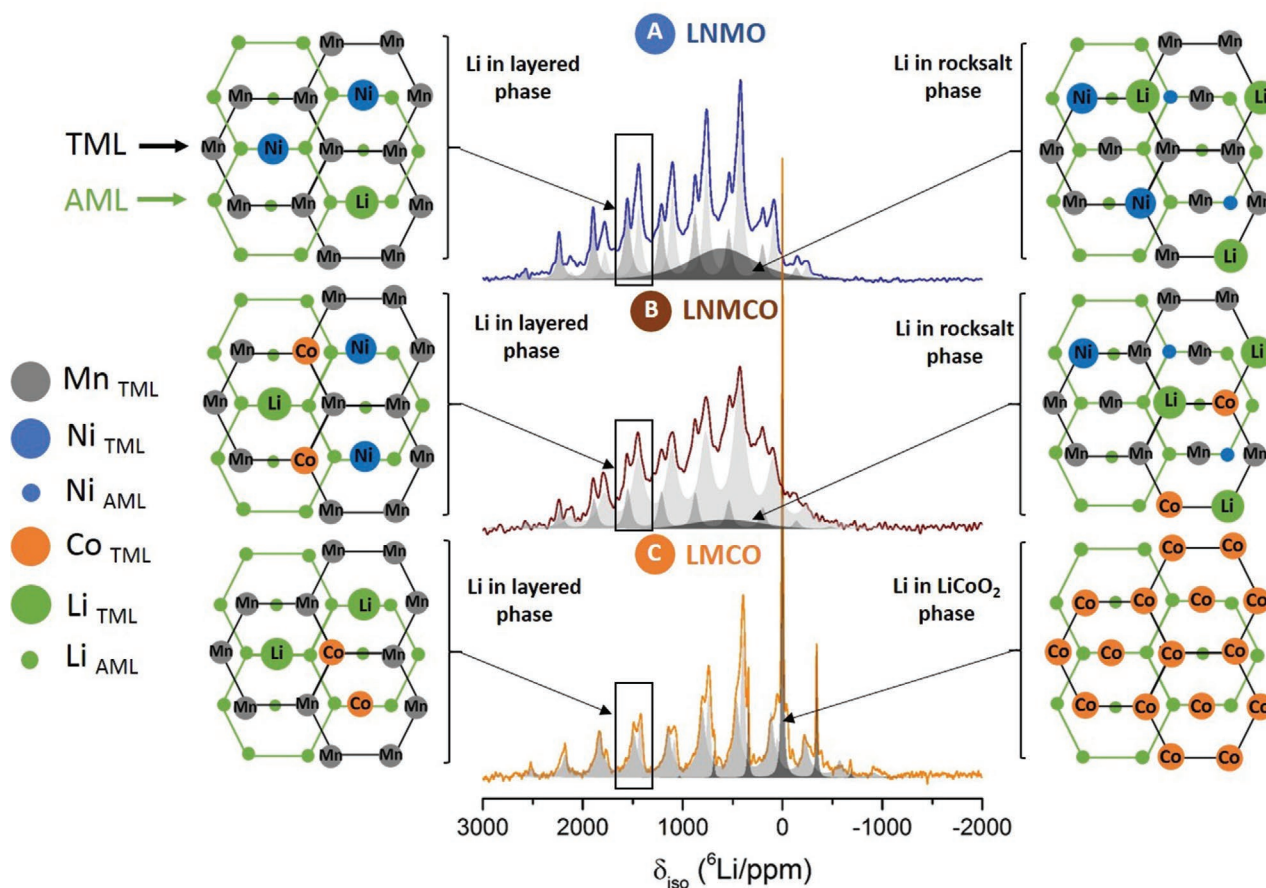


Figure 4. ^6Li MAS NMR spectra of A) LNMO, B) LNMCO, and C) LMCO with their corresponding deconvolutions showing the different phase segregation occurring in these materials. In addition to the Li_2MnO_3 -like component observed in all spectra, LNMO and LNMCO possess a rocksalt contribution while a LiCoO_2 peak is seen for LMCO. The Li environments associated with these NMR contributions are represented by the schematics of the local cation distribution in the transition metal layer (TML, black hexagons, and large circles) and in the alkali metal layer (AML, green hexagons, and small circles).

structure which have been assigned previously to two lithium sites in the AM layer and the lithium in the TM layer, respectively.^[15] The spectra of LNMO and LNMCO can be fitted well using a combination of this Li_2MnO_3 reference spectrum with an additional broad contribution consistent with Li in a disordered phase, Figure 4. For LNMO, about 23% of the lithium in the material is in a highly disordered environment, whereas for LNMCO the proportion is only 6%. This trend of increasing proportion of lithium in a disordered environment with higher Ni contents is also seen right across the Li_2MnO_3 – $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line, Figure S5 (Supporting Information). Turning to the Li_2MnO_3 – LiCoO_2 tie-line, a different trend is seen (see Figure S5, Supporting Information). A progressive broadening of the Li_2MnO_3 -like components is observed with increasing Co substitution until, at high Co contents, a new, sharp, diamagnetic peak appears. Since Co^{3+} does not possess any unpaired electrons, this diamagnetic contribution is likely to correspond to Li in a Co-rich and Mn-free environment, i.e., LiCoO_2 , consistent with phase segregation involving formation of LiCoO_2 as reported previously^[7] and also observed by XRD. The $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ (LMCO) spectrum comprises 23% LiCoO_2 (vs 25.3(2)% from XRD), the other phase should have the composition $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.50}\text{O}_2$, which would correspond to the high Co concentration threshold

for the Li_2MnO_3 – LiCoO_2 solid solutions. The position of this threshold is consistent with the ^6Li NMR data in Figure S5 (Supporting Information) showing the growth of the LiCoO_2 peak between $\text{Co}_{0.2}$ and $\text{Co}_{0.3}$ compositions.

2.3. Surface Structure

In order to characterize the near surface structure and composition of these compounds, we employed annular dark field scanning transmission electronic microscopy (ADF-STEM) imaging, electron energy loss spectroscopy (EELS) and X-ray photoemission spectroscopy (XPS). The STEM image of pristine LNMO, Figure 5, reveals a distinct core-shell structure with a well-ordered layered bulk (high contrast between the Li layer and the TM layer) and a rocksalt shell (very little contrast difference between the Li layer and TM layer) extending up to 4 nm into the particle. This shell thickness corresponds to $\approx 20\%$ of the volume of the 100 nm particle which is in good agreement with the 23% of Li in a disordered environment seen by NMR for LNMO indicating that the Li/Ni disorder is located at the edge of particles. Furthermore, EELS mapping across the particles indicates that this disordered surface is Ni-rich and

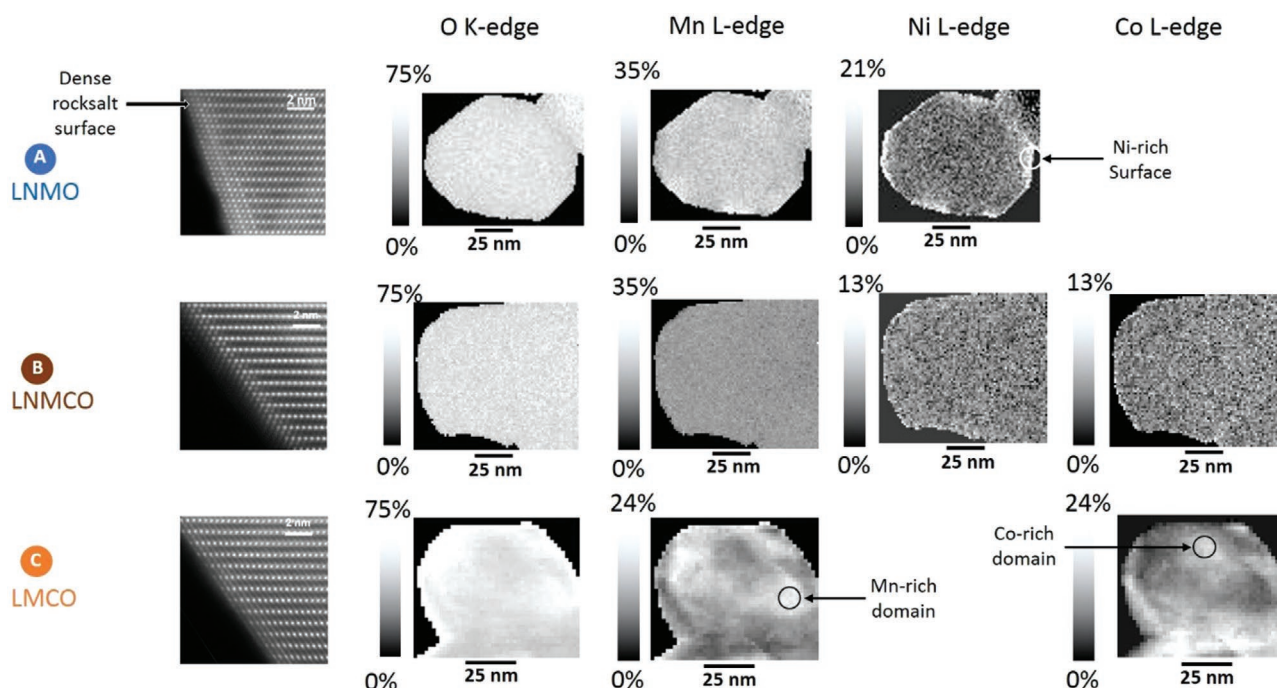


Figure 5. ADF-STEM images of the materials surface and relative O, Mn, Ni, and Co intensity ratios obtained from EELS mapping of A) LNMO, B) LNMCO, and C) LMCO particles. The rocksalt surface observed for LNMO and LNMCO is Ni-rich/Mn-poor compared to their respective bulk, while for LMCO the phase segregation occurs into randomly distributed Mn-rich/Co-poor ($\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$) and Co-rich/Mn-poor (LiCoO_2) domains preserving a layered structure at the surface.

Mn-deficient (Figure 5). For LNMCO, STEM, and EELS evidence a significantly thinner Ni-rich rocksalt shell compared to LNMO. For LMCO, while STEM suggests a well-ordered layered structure throughout the particle (i.e., an almost total absence of disordered surface), EELS reveals a clear segregation between randomly distributed Mn-rich/O-rich ($\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$ solid solution) and Co-rich/O-poor (LiCoO_2 phase) domains.

XPS was also employed to determine the surface composition. The TM ratios are compared with the bulk compositions in Figure 6a–c. The overlap of the Li 1s core level with the Mn 2s does not allow for direct lithium quantification. However, it can be estimated from the Ni, Co, and Mn assuming each metal is in divalent, trivalent, and tetravalent state, respectively. The plot of lithium content versus composition, is also included in Figure 6d. The data show that for Ni containing compounds (Li_2MnO_3 – $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line and LNMCO) the surface is Ni-rich, Mn, and Li-deficient. Whereas, there is very little difference between the surface and bulk compositions along the Li_2MnO_3 – LiCoO_2 tie-line.

For $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ this estimation leads to a surface composition of $\text{Li}_{1.12}\text{Ni}_{0.32}\text{Mn}_{0.56}\text{O}_2$ from XPS and $\text{Li}_{1.07}\text{Ni}_{0.39}\text{Mn}_{0.54}\text{O}_2$ from EELS (averaged on 10 particles). We therefore conclude that the rocksalt surface observed for the Ni containing materials is denser (Li deficient) and more Ni-rich than the corresponding bulk.

2.4. Suppressing O-Loss

Comparing the effect of Ni and Co substitution into Li_2MnO_3 on the oxygen loss is instructive in understanding compositional control of oxygen redox. The schematic in Figure 7 summarizes the

situation. Lithium extraction from Li_2MnO_3 is charge compensated exclusively by the oxidation of O^{2-} to O_2 , which is evolved from the surface.^[6] This is necessarily accompanied by migration of Mn toward the bulk into vacancies left behind by the extracted Li.^[5] In Ni substituted Li_2MnO_3 , the relatively thick surface shell with extensive Li/Ni antisite defects, i.e., a rocksalt coating, which is less Li-rich (nearer stoichiometric) than the core exhibits a small amount of oxygen loss. For LNMCO, as Co inhibits the Ni/Li antisite defects and as the composition is closer to the bulk than for Ni doping, the thinner rocksalt protective layer does not suppress O-loss to the same extent as Ni substitution, but is still more effective than Co substitution alone. Indeed, in the case of the Li_2MnO_3 – LiCoO_2 compositions, it might have been anticipated that the absence of a surface layer would lead to no suppression of O-loss. However, this is not the case; suppression is less effective than Ni doping or Ni/Co codoping but still significant. The suppression of O-loss for Co doping up to $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$ taken together with the results for Ni doping, demonstrate that forming a solid solution also inhibits O-loss. Indeed, at higher Co content, the material segregates into $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$ and LiCoO_2 domains that appear to be well dispersed throughout the particles and the dilution of $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$ by LiCoO_2 , which does not lose oxygen, continues to suppress O-loss but much less effectively than a solid solution.

3. Conclusion

Introduction of Ni and/or Co into Li_2MnO_3 suppresses O-loss on charging but to different extents and by different mechanisms. Along the Li_2MnO_3 – $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line, which

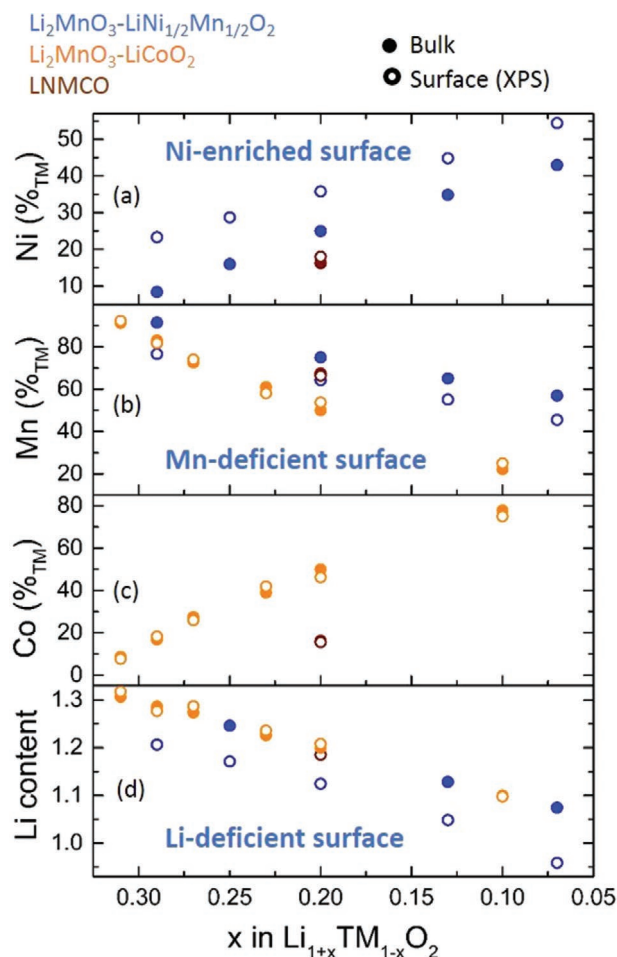


Figure 6. Surface Ni a), Mn b), Co c) contents as percentage of TM, and the Li content d) obtained from XPS (open circles) compared to the bulk (filled circles) for $\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (blue), $\text{Li}_2\text{MnO}_3\text{--LiCoO}_2$ (orange) tie-line and LNMCO (brown). While the surface composition of Co-substituted materials appears to be similar to their bulk composition, all Ni containing compounds ($\text{Li}_2\text{MnO}_3\text{--LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ tie-line and LNMCO) show Ni-rich, Mn-poor, and Li-poor surface compared to their bulk.

includes $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, the materials adopt a core-shell morphology in which the rocksalt shell is Ni-rich and Li-poor compared with the layered core. The Li-poor surface phase acts as a protective layer inhibiting O-loss. Simultaneous doping of Ni and Co in Li_2MnO_3 , giving $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$, also results in a rocksalt shell, but this shell is much thinner and less effective at suppressing O-loss than Ni doping alone. Up to $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.50}\text{O}_2$, Co substitution leads to a solid solution that does not induce a core-shell morphology, the surface composition and structure are that of the bulk, but it does suppress O-loss, although less effectively than Ni and Ni/Co doping. At higher Co content, it segregates into randomly distributed $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.50}\text{O}_2$ and LiCoO_2 domains and O-loss continues to be suppressed only by diluting the mole fraction of the former. Overall, combining the results from Ni and Co doping shows that there are two mechanisms of O loss suppression: i) substituting Ni and/or Co ions for Mn and Li forming a solid solution material and/or ii) forming a core-shell structure whereby the Li-excess is mitigated at the surface relative to the bulk.

4. Experimental Section

Stoichiometric amounts of $\text{Li}_2\text{CH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$ (99.0%, Sigma-Aldrich), $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (>99.0%, Sigma-Aldrich), and $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (99.0%, Sigma-Aldrich) and $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (99.0%, Sigma-Aldrich) were dissolved in 50 mL of water with 0.25 mmol of Li_2CO_3 (99.0%, Sigma-Aldrich) as lithium excess. 0.1 mol of resorcinol (99.0 %, Sigma-Aldrich) were dissolved in 0.15 mol of formaldehyde (36.5% w/w solution in water, Fluka). The resulting solution was subsequently heated at 80 °C until formation of a homogeneous gel. The gel was finally calcinated at 450 °C for 10 h and the resulting powder annealed at 800 °C for 20 h under air. The electrodes for electrochemical tests were composed of a mixture of active material, carbon Super P, and polyethylene tetrafluoride in an 8:1:1 mass ratio, respectively. The powder mixture was homogenized in a mortar, roll pressed down to a thickness of 100 μm , cut into disks ($\Phi = 10$ mm) and dried overnight under dynamic vacuum at 80 °C before being stored in Ar filled glovebox. The electrodes were assembled into coin cells under an inert argon atmosphere inside a glove box (O_2 and $\text{H}_2\text{O} < 1$ ppm) with ≈ 20 mg of active cathode material, a metallic lithium disk as negative/reference electrode, two glass fiber discs ($\Phi = 22$ mm) as separator, soaked with 0.2 mL of LP30 electrolyte (1 M LiPF_6 in 1:1 w/w ethylene carbonate: dimethyl carbonate). Cells were cycled on a BioLogic VMP3 potentiostat/galvanostat at 30 °C in a thermostatically controlled oven. A constant current corresponding to 50 mA g^{-1} was applied to the cells in the 2.0–4.8 V versus Li^+/Li range.

ICP-OES elemental analysis of the as-prepared samples was carried out using a PerkinElmer Optima 7300DV ICP-OES. BET analysis was conducted using a Micromeritics Gemini VII surface area analyzer using nitrogen as the adsorbate at liquid nitrogen temperature. All samples were degassed at 200 °C under flowing nitrogen overnight prior to analysis.

Pycnometry densities have been obtained using a Micromeritics Accupyc II 1340 pycnometer and helium as gas.

XRD patterns were recorded on 11BM diffractometer. Approximately 20 mg of powder were placed in kapton capillary, data were collected for 1 h using X-ray radiation of $\lambda = 0.4128$ Å. Time of flight ND patterns have been collected in POLARIS at ISIS, Harwell, UK. Approximately 1 g of powder were placed in a 6 mm diameter vanadium tube, data were collected for 1 h and converted using Mantid-plot.^[6] The diffraction data were analyzed using the Rietveld refinement method as implemented in the Fullprof software.^[7] A detailed refinement procedure used is provided in Supporting Information.

EXAFS measurements were undertaken at beamline B18 at the Diamond Light Source, Harwell, UK.^[8] The X-ray adsorption spectroscopy spectra were collected in transmission mode and the intensities of both the incident and transmitted X-ray beams were measured using gas-filled ionization chambers. To correct for any drift in monochromator, Mn/Ni or Co metal foils were placed in front of a third ionization chamber. Using the Athena program,^[9] for each sample the three scans collected were summed, calibrated, background subtracted, and normalized, then the EXAFS oscillation was extracted using a similar k -range of $\approx 2.5\text{--}11.5$ Å⁻¹ for all edges and k^2 weighted data for the Fourier Transform. In order to extract the normalized intensities, the area of the first and the second shells were integrated and the normalized second shell intensity have been obtained dividing the second shell intensity (metal-metal scattering) by the first one (metal-oxygen scattering).

MAS NMR experiments were performed in a 3.2 mm probe-head on a 400 MHz Bruker Avance HD III spectrometer at the ^6Li Larmor frequency of 58.9 MHz. MAS of 20 kHz was applied. The spectra were recorded with rotor-synchronized Hahn-echo pulse sequence; the applied $\pi/2$ pulse length and the delay between $\pi/2$ and π pulses were 3.5 and 44.8 μs . The MAS probe-head temperature was controlled at 268 K (the real sample temperature in the rotor was about 298 K during spinning at 20 kHz). The ^6Li spectra were externally referenced with 1 M LiCl aqueous solution at 0.0 ppm.

XPS spectra were recorded using a Thermo Scientific K-alpha instrument equipped with microfocused monochromated Al X-ray source and a 180° double focusing hemispherical analyzer-128-channel detector. The samples were attached onto Cu adhesive tape and transferred in

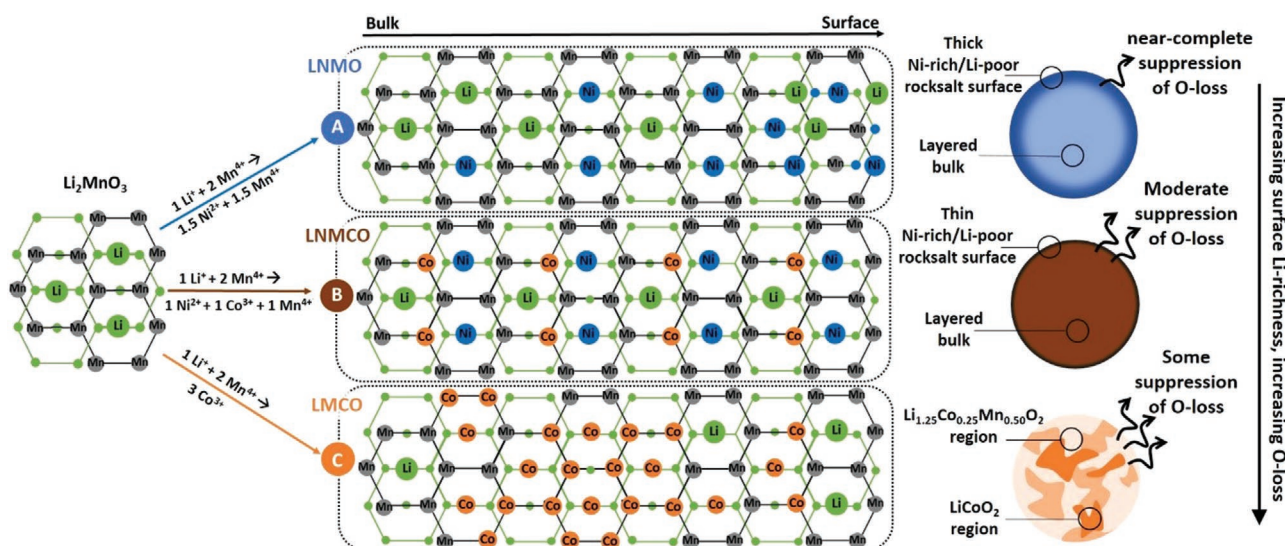
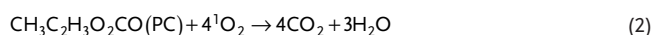


Figure 7. Schematic representation of the local cation distribution in the TM layer (black hexagons and large circles) and in the AM layer (green hexagons and small circles) from the bulk to the surface and of the associated microstructure at the particles scale along each tie-line. The Li deficient and Ni rich rocksalt shell (high degree of Li/Ni out of plane antisite defects) present in LNMO suppresses O-loss. This occurs to a lesser extent for LNMCO. In LMCO, a phase segregation into randomly distributed LiCoO_2 and $\text{Li}_{1.25}\text{Co}_{0.25}\text{Mn}_{0.5}\text{O}_2$ domains occurs and significant O-loss is observed.

the ion-pumped ultrahigh-vacuum chamber for analysis. CasaXPS software was used to fit the data. The background subtracted Ni/Mn/Co 2p and O 1s core levels signals were fitted using a combination of contributions whose the area were integrated and normalized according to the corresponding X-ray photoemission cross-section. According to the equation provided,^[20] the electron inelastic mean free path in all the materials studied in this article varies from 2.8(1) to 3.0(1) nm and hence the fraction of the of volume of particles probed is $\approx 15 \pm 2\%$. Moreover, the beam diameter of 200 μm (3 orders of magnitude larger than the particles) averages the signal over many particle surfaces allowing for an accurate surface composition quantification.

EELS and ADF-STEM data were collected on an aberration corrected JEOL ARM 200F operated at 200 kV and equipped with a Gatan GIF Quantum 965 ER. The convergence semiangle used was 22 mrad, and the collection semiangle was 69.6–164.8 mrad (ADF). EELS maps were collected with a step size of 0.3 nm and energy dispersion of 0.25 eV per channel. Plural scattering was removed to account for thickness effects.

OEMS analysis was conducted to detect the gases generated during charging and discharging. The operando mass spectrometry system was built in-house and employed a commercial quadrupole mass spectrometer (Thermo Fischer) with a turbo molecular pump (Pfeiffer Vacuum). The setup was based on a previously described design.^[21] The operando mass spectrometry measurements were carried out using a Swagelok electrochemical test cell. The cell consisted of a lithium anode, electrolyte (1 M LiPF_6 in PC), and the same cathode as described above. According to Gasteiger and co-workers, the oxygen released from the lattice is in the form of singlet oxygen ($^1\text{O}_2$) which attacks the PC electrolyte leading to the formation of carbon dioxide, as follows^[8,9]



$^1\text{O}_2$ that does not have time to react with the solvent before it is self-quenched into its stable triplet oxygen ($^3\text{O}_2$) is detected as O_2 in the MS



In both cases (O_2 or CO_2 release) the associated reaction involves a 4 electrons mechanism permitting calculation of the capacity associated to the gases evolved. The raw data were first background subtracted and then integrated over the whole charge/discharge process allowing to obtain the number of moles of gas evolved per mole of material. This value was then multiplied by 4 and converted into specific capacity.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathodes, Li-ion batteries, Li-rich layered oxides, oxygen loss, oxygen redox

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