

The role of O₂ in O-redox cathodes for Li-ion batteries

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The energy density of Li-ion batteries can be improved by storing charge at high voltages through the oxidation of oxide ions in the cathode material. However, oxidising O²⁻ triggers irreversible structural rearrangements in the bulk and an associated loss of the high voltage plateau replacing it with a lower discharge voltage, as well as a loss of O₂ accompanied by densification at the surface. Here we consider various models for O-redox proposed in the literature before describing a single unified model involving O²⁻ oxidation to form O₂, which is trapped in the bulk with the balance evolving from the surface. The model extends the O₂ formation and evolution at the surface, which is well-known and well-characterised, into the electrode particle bulk as caged O₂ that can be reversibly reduced and oxidised. This converged understanding allows us to propose practical strategies for avoiding O-redox-induced instability offering potential routes towards more reversible high energy density Li-ion cathodes.

Since the discovery of ‘anomalous’ extra capacity to store charge in 3d transition metal oxide Li-rich cathode materials in the early 2000s,^{1–4} there has been intense research interest seeking to understand the origin of the effect.^{5–9} Over the years, these compounds have grown in number extending to include materials based on 4d and 5d transition metal oxides.^{10–13} In the case of a conventional Li transition metal oxide intercalation cathode, Li⁺ ions are extracted on charging, with charge-compensation by oxidation of the transition metal ion, the process is reversed on discharge, e.g. Li_{1-x}Mn₂O₄ (0 < x < 1). In contrast, the Li-rich cathodes, such as Li_{1.2}Ni_{0.2}Mn_{0.6}O₂, Li_{1.3}Nb_{0.3}Mn_{0.4}O₃, Li₂RuO₃ and Li₂Ir_{0.5}Sn_{0.5}O₃, extend the capacity to store charge by oxidation of the O²⁻ ions.^{10,13–16} The ability of anions to undergo redox reactions is not without precedent, for example the S²⁻/S₂²⁻ reaction in sulphides is well known but the phenomenon was not recognised in oxides until more recently.¹⁷

The oxidation of O²⁻ in cathode materials is typically accompanied by a high voltage plateau (usually ~4.5 V vs Li⁺/Li for 3d cathodes) on charge followed by an S-shaped discharge profile, Fig. 1. Early models posited that the charging plateau was associated completely with the irreversible loss of oxygen from the lattice (O-loss), which alongside extraction of Li⁺ gives rise to the net loss of Li₂O.^{2,4} Online mass spectrometry showed that O₂ gas was released from the surface of the material.¹⁸

Later work showed that there was an insufficient degree of reduction observed of the transition metal ions on re-lithiation to explain the large discharge capacity¹⁹ and quantitative studies also revealed an insufficient amount of evolved O₂ to account for the charging capacity associated with the plateau.^{14,20} Consequently, the idea was developed that reversible oxidation and reduction of O²⁻ ions in the bulk compensate for the extraction and reinsertion of Li⁺ beyond the limit of TM redox.^{5,6,10,19–21}

Some of the charge is still associated with O₂ loss at the surface, although in most O-redox materials this is relatively small. Since, in general, solid state diffusion of O²⁻ is orders of magnitude

slower than cations and it is known that solid/gas reactions such as $\text{Fe}_3\text{O}_4 + 1/4\text{O}_2 = \text{Fe}_2\text{O}_3$ often involved TM diffusion, it was suggested that the TM ions in the structure migrated inwards from the surface to fill some of the empty Li vacancies resulting in a denser TM oxide closer to the stoichiometric composition (TMO_2) near the surface (a core-shell structure). The term ‘densification’ was coined for this process.^{18,22,23}

The nature of oxidised O in the bulk of O-redox cathodes and the process of O oxidation have proved challenging to determine, leading to different models invoking hole states on O^{2-} ,^{20,21} peroxo-like O_2^{n-} species with long O-O bonds,^{7,16} peroxides O_2^{2-} ,^{13,24} or O_2 .^{25,26} Explaining how a reversible bulk O-redox process can accompany the irreversible loss of a 1st charge voltage plateau (voltage hysteresis) has proved difficult but establishing a unified understanding is crucial to inform effective materials design rules.²⁷

In this perspective, we consider O-redox mechanisms proposed in literature and the experimental techniques that have been employed to probe oxidised O^{2-} . We then discuss the recently reported model for O-redox, and the RIXS and NMR data that support it, involving O_2 formation in the bulk and at the surface, i.e. one mechanism that explains simultaneously the bulk and surface processes. On charge, O^{2-} is oxidised to O_2 throughout the material, it is trapped in vacancy clusters within the particles and lost from the particle surface. The trapped O_2 is reduced back to O^{2-} on discharge. The model can explain the voltage hysteresis on the 1st and subsequent cycles. Based on this model we discuss strategies for mitigating voltage hysteresis leading to O-redox cathodes with sustainable high voltage on cycling.

The Nature of Oxidised O^{2-}

Parallel studies published in 2016 by Seo et al. and Luo et al. proposed that oxidation of O^{2-} ions in Li-rich TM oxides generated electron holes in $\text{O}2\text{p}$ orbitals coordinated by Li^+ ions, Fig 2 (a).^{20,21} The ionic $\text{Li}^+ - \text{O}^{2-}$ interactions place these $\text{O}2\text{p}$ states at the top of the O valence band and hence they are the first to be oxidised. The model not only explains which O^{2-} ions are oxidised but also why O-redox is observed dominantly in Li-rich compounds where there is a high degree of coordination of O^{2-} by Li^+ and the location of these $\text{O}2\text{p}$ orbitals places them within the accessible voltage range before electrolyte oxidation. This theory has since been developed by Gent et al. to include partially reversible out-of-plane TM migration to explain the shifting O-redox potential between charge and discharge⁹ and by Yamada and co-workers to involve the participation of π -type back-bonding from the coordinating Mn to stabilise the orphaned $\text{O}2\text{p}$ orbitals.²⁸ Meanwhile, based on findings from the 4d and 5d TM-based Li-rich compounds, Tarascon and co-workers, and Doublet and co-workers proposed a reductive coupling mechanism where over-oxidation of the TM ions triggers O oxidation and formation of peroxo-like O-O dimers O_2^{n-} with long O-O bonds or O_2^{2-} , which is coupled with TM reduction.^{7,10,24} The formation of peroxides (O_2^{2-}) and short TM=O bonds in Sn-substituted 5d-TM based Li_2IrO_3 has also recently been associated with TM migration.¹³ Finally, in a very recent publication, an alternative theory to O oxidation altogether was proposed invoking Mn oxidation beyond +4 to +7 with migration of Mn into tetrahedral sites.²⁹ The various models are summarised in Fig 2.

A wide range of techniques have been deployed in efforts to characterise the nature of O-redox, including, X-ray photoelectron spectroscopy (XPS), hard X-ray photoelectron spectroscopy (HAXPES), electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR) spectroscopy, superconducting quantum interference device (SQUID) magnetic measurements, electron energy loss spectroscopy (EELS), Raman spectroscopy, scanning transmission X-ray microscopy (STXM), soft X-ray absorption spectroscopy (soft XAS) and resonant inelastic X-ray scattering (RIXS). They fall into the

categories of primarily surface and more bulk sensitive techniques. Techniques such as XPS, EELS and shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) are, in general, limited in their ability to probe bulk O states. This problem is compounded by the widely observed near-surface reconstruction/densification associated with some O loss. Conventional Raman which probes deeper than SHINERS, has been used on O-redox compounds including in our previous work which did not detect peroxides in $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and $\text{Na}_{2/3}\text{Mg}_{0.28}\text{Mn}_{0.72}\text{O}_2$.^{14,20,30} However, a recent Raman study on $\text{Li}_{4.15}\text{Ni}_{0.85}\text{WO}_6$ indicates peroxides may form in tungstate compounds inviting further work on the unique stabilising role of W.³¹ Emerging from the range of techniques applied, two are worth specific mention, RIXS and NMR.

RIXS is a photon emission spectroscopy that is being increasingly used to interrogate changes on O in cathodes during O-redox. In the RIXS process, photons are emitted from the relaxation of electrons in the O2p valence band down into O1s core-hole states created by excitation from the incident X-rays. The power of RIXS is that it offers a direct probe of the valence states on O and hence the nature of O-redox. Furthermore, being a photon emission technique, greater bulk sensitivity can, in general, be achieved with RIXS than with electron emission techniques such as XPS. Using RIXS, new spectral features belonging to oxidised O have been observed, which are commonly referred to as the 'signature of O-redox'.^{9,32} More recently, using high-resolution RIXS, we were able to resolve the low energy loss feature in the RIXS spectra of charge O-redox cathodes, previously only seen as a broad shoulder to the elastic peak.^{25,33} High-resolution RIXS shows it is a series of sharp peaks of spacing consistent with the vibrational energy levels of molecular O₂ and not O₂²⁻, longer peroxo-like O-O bonds or hole states on O²⁻. The increase in excitation energy of the O-redox RIXS features by about 0.5 eV relative to gaseous O₂ is consistent with the O₂ molecules being trapped in a condensed environment within the lattice, something also seen in the ¹⁷O NMR.^{33,34}

Solid-state ¹⁷O MAS NMR, unlike the X-ray spectroscopies, is a bulk average probe of the local chemical environment around O and with the potential to provide quantification of the amount of O₂ present in the bulk. We recently showed that by enriching $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode samples with NMR-active ¹⁷O nuclei, a new strongly paramagnetic chemical environment forms during O-redox, which has a consistent paramagnetic shift and anisotropy with that of molecular O₂, but exhibits a sharp, defined sideband manifold indicating it is not gaseous O₂ but, rather, O₂ molecules that are rigidly confined or 'caged' within the crystal structure.³³ Relaxometry analysis of the NMR data show that the quantity of O₂ is commensurate with the amount of charge passed on charging across the plateau.

Relating Structural Change to Voltage Evolution

While mechanisms involving the formation and reduction of O-O diatomics, such as peroxide formation on charge, can give rise to different voltage pathways for charge and discharge, due to the strains induced by the oxide sublattice distortions to accommodate the changes in O-O distances, they do not in themselves lead directly to an understanding of the 1st cycle voltage hysteresis and the smaller residual hysteresis on subsequent cycles.

The voltage profile exhibited by Li-rich cathodes is strongly entwined with the evolution of the bulk crystal structure. Recognising this, TM migration from the TM layer into the lithium layer has been invoked as the key structural change to explain the 1st cycle voltage hysteresis.^{9,13,24,35,36} However, this out-of-plane migration is generally small (~5-6% of the TM ions in the TM layer) and believed to be partially reversible on discharge.^{9,37} If there is no change in structure, or the change is reversible, then the coordination around O would either not change, or would be reformed, respectively, such that the O states would be the same on subsequent cycles and the high voltage plateau would also be

expected on second and subsequent charges, which is not observed experimentally. In fact, the irreversible high voltage plateau necessitates a large-scale, irreversible change in the structure of the bulk and the O coordination environments.

RIXS spectra for $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$, a typical O-redox cathode, taken at different states of the 1st cycle are shown in Fig. 3, demonstrate O_2 formation upon charge and its disappearance on discharge. The low energy fine structure corresponds to the vibrational spectrum for molecular O_2 ,^{9,38} not O_2^{2-} or longer peroxo-like O-O bonds, Fig. 3 (c). In our previous study on the same compound, conventional resolution RIXS identified a broad increase in the elastic peak intensity at 531 eV which was attributed to the formation of localised electron holes on O. Our more recent high resolution RIXS results resolve this broad peak allowing us to assign the electron hole states as being localised on O_2 molecules. The most stable forms of O are O^{2-} in oxides and molecular O_2 , therefore it is not surprising that the former converts to the latter on oxidation.

However, molecular O_2 cannot be formed and trapped in the lattice without significant structural reorganisation. Layered O-redox compounds generally exhibit honeycomb ordering of the TM and Li^+ ions in the TM layer. It has been observed widely that this superstructure is lost on charging across the plateau.²⁵ Detailed Scanning Transmission Electron Microscopy (STEM) and solid-state NMR studies show that the disordering of TM ions occurs largely within the TM layer as Li^+ leaves the layer during charge. Together with the evidence for O_2 formation in the bulk, the creation of vacancies in the TM layer by loss of Li^+ plus the TM in-plane migration, points the way to a mechanism of O^{2-} oxidation. DFT modelling based on the experimental data from Li NMR, STEM and PXRD identifies TM in-plane migration forming small vacancy clusters on the 1st charge that accommodate O_2 , as shown in Fig. 4. As O^{2-} ions are oxidised on charge they disproportionate to form molecular O_2 and O^{2-} ions. Unlike in $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$, which has ribbon ordering of the Li/Mn in the TM layers, where XAS reveals stable hole states on O^{2-} ($\text{O}^{\cdot-}$) at 528 eV,³³ there is no such feature in the XAS data for honeycomb ordered $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ indicating that $\text{O}^{\cdot-}$ does not coexist with O_2 . Once $\text{O}^{\cdot-}$ is formed in the charged structure B, Fig. 4, TM migration takes place, the honeycomb ordering is lost and O_2 is formed, lowering the energy leading to structure C in Fig. 4(a) which is the stable structure in the charged state. The relative energies of the structures on first cycle have been determined by ab initio calculation yielding an average discharge voltage, C to D, of 3.75 V vs Li^+/Li in good agreement with observation.^{9,39}

The high voltage plateau on the 1st charge is an irreversible order-disorder transition, involving TM migration, formation of vacancy clusters and O_2 trapped in these clusters. The O_2 is not bonded to the neighbouring Mn as the vibrational frequency of the O-O bond is a close match to unbound, gaseous O_2 , yet the RIXS and ^{17}O NMR indicate the molecules are physically trapped in a condensed, solid-like environment. Once the highly ordered honeycomb arrangement is lost, it is not recovered, and the disorder is retained explaining the absence of further voltage plateaux. On the 1st discharge, O_2 is reduced back to O^{2-} with the latter located at the centre of the vacancy clusters and the Li^+ ions repopulating the TM layer but crucially not in their original sites, since these are now occupied by TM ions, but within the vacancy clusters and coordinating the newly formed O^{2-} , Fig 4 (a) structure D. The 1st discharge is not the reverse of the 1st charge in accord with the irreversible change in voltage. The coordination environment around O^{2-} at the centre of the vacancy clusters in the TM layer at the end of the 1st cycle has changed from O- Li_4Mn_2 in the pristine material, to O- Li_6 , at the end of the 1st discharge Fig. 4(c, d). The greater degree of ionicity of the $\text{Li}^+/\text{O}^{2-}$ interactions raises the energy of these $\text{O}2p$ states hence lowering the voltage on the 1st discharge compared with the 1st charge (voltage hysteresis). More precisely, the average voltage on charge is related to the differences between the free energies of the unrelaxed charged (B) and pristine (A) materials and for discharge the average voltage is the difference between the relaxed charged (C) and discharged (D) materials. Once the

ordered honeycomb structure has been lost on the 1st cycle it remains disordered from the 2nd cycle onwards. After the 1st cycle, molecular O₂ can be formed and cleaved at lower voltages without TM migration and encountering only the strain associated with the formation of O₂ and its reformation to O²⁻ on discharge. This explains why there is much reduced hysteresis and no plateau and why the RIXS signature appears and disappears on charge and discharge. Studies by others suggest that O₂ persists for hundreds of cycles.^{9,39} The formation of voids has been recently evidenced in materials subjected to long duration cycling.^{40,41}

While disorder in the charged state is favoured for compounds such as Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ and Na_{0.75}Li_{0.25}Mn_{0.75}O₂ due to the electronic stabilisation of oxidised O, conversely, honeycomb ordering would be favoured in the fully discharged state due to the minimisation of Coulombic charge repulsion between highly charged TM ions. However, there appears to be no evidence of dynamic reordering of the TM layer during discharge in these cases. Nevertheless, recent evidence shows that, when annealing cycled Li-rich cathodes at moderate temperatures, the honeycomb superstructure is recovered and, consequently, the high voltage charging plateau re-emerges.^{42,43} This shows the honeycomb arrangement is more stable in the discharged state. In the case of the disordered rocksalt and spinel O-redox materials, such as Li₂MnO₂F, which already possess a disordered structure in the pristine state, they do not exhibit a high voltage O-redox plateau and instead bear closer resemblance to the sloping voltage profile of the second cycle of layered Li-rich compounds.^{44,45} In other disordered rocksalts such as Li_{1.2}Mn_{0.4}Ti_{0.4}O₂ and Li_{1.3}Mn_{0.4}Nb_{0.3}O₂,¹⁵ the O-redox process does proceed via a high voltage plateau on charge, indicating that TM migration and O₂ formation could be possible by either what appears to be single phase or two phase mechanism in this class of material. Recent results indicate that the same O-redox behaviour also pertains to ordered layered cathodes based on 4d and 5d transition metals such as Ru and Ir, as well as the disordered rocksalts, offering a model that unifies a diverse range of O-redox materials.⁴⁶

Converging Surface and Bulk Behaviour

Although it has become common to regard the O-redox behaviour at the surface and the bulk of Li-rich cathodes as different, our results show that, in fact, the same charge compensation process is occurring throughout the particle. Molecular O₂ is formed both at the particle surface and in the bulk. The difference is that at the surface O₂ is released leading to densification which self-limits further surface O₂ loss, whereas in the bulk the O₂ remains trapped in the vacancy cluster defects, Fig. 5. The outcome is a core-shell structure that can be cycled many times supported by TM and O²⁻/O₂ redox in the core. O₂ loss and densification are not completed within the 1st cycle. The repeated formation of minor amounts of surface O₂ on charging on each cycle provides one possible explanation for the small but continuous shift in the voltage on extended cycling, the so-called voltage fade.

Surface O₂ loss leads to lower Coulombic efficiencies since the charge passed cannot be recovered. In contrast, O₂ trapped in the bulk can contribute capacity to the discharge process through reduction to O²⁻. Although most O-redox materials exhibit only minor O loss this is not universally true. In the case of the archetypal O-redox cathode on which most materials are based, Li₂MnO₃, all the capacity is associated with O loss as evidenced by quantitative online mass spec. measurements leading to poor Coulombic efficiency.^{47,48} Accompanying this prolific loss of O, extensive Mn migration occurs from surface to bulk, forming a core-shell structure where a high proportion of the material is shell. Substitution of Ni and Co into the TM layer of Li₂MnO₃ to form less Li-rich LiTMO₂-Li₂MnO₃ compositions suppresses the degree of O-loss observed by a greater extent than that expected from the lower mole fraction of Li₂MnO₃.⁴⁹ Ni is more effective than Co at suppressing O loss. It has been shown that Ni segregates preferentially at the surface and Ni is known to favour anti-site disorder between layers, i.e. formation of a rocksalt like structure. As a result, Ni doping may be particularly

effective in inhibiting TM migration from surface to bulk and suppressing O loss leaving the formation of trapped O₂ in the bulk as the dominant process and hence reversible O₂/O²⁻. The same argument also extends to explain why reduced surface O-loss is observed in 4d and 5d Li-rich systems where the migration of larger, heavier elements Ru, Ir and Sn may be less facile and surface passivation would occur relatively easily. Interestingly, Co doping of Li₂MnO₃ does not lead to Co segregation at the surface and this may explain why it is less effective at suppressing O₂ loss.⁴⁹

Strategies for Harnessing O-redox.

A deeper understanding of the fundamental mechanisms of O-redox is important in informing strategies to mitigate the current limitations of such cathodes. Eliminating 1st cycle voltage hysteresis and hence retaining high voltage and high capacity depends on suppressing TM migration and O₂ formation such that O-redox involves the formation of hole states on O²⁻. If this is not possible then exploiting the O²⁻/O₂ redox mechanism in the bulk of the cathode to increase capacity albeit at lower voltage is possible by starting with disordered materials. Surface coating or surface modification can also be exploited to suppress O₂ loss at the surface. Several of these approaches are described below:

Different TM layer Ordering Schemes

Recently, we investigated two Na intercalation compounds with very similar crystal structure and composition, Na_{0.75}[Li_{0.25}Mn_{0.75}]O₂ and Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂, but which show respectively the presence and absence of voltage hysteresis, in order to understand better how to suppress the former.²⁵ Na_{0.75}[Li_{0.25}Mn_{0.75}]O₂ possess the honeycomb superstructure ordering of TM ions that dominates conventional layered Li-rich compounds exhibits extensive in-plane TM migration when the Li⁺ ions in the TM layer are extracted on charge leading to O₂ formation. In contrast, the superstructure in Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂, exhibits a ribbon like (non-honeycomb) arrangement of TM and Li⁺ ions in the TM layer, Fig. 5(a). This ribbon-like superstructure inhibits TM migration when the Li⁺ ions are removed on charge suppressing the formation of vacancy clusters and O₂, favouring the generation of electron-holes on the oxide sublattice and preserving a reversible high voltage plateau, Fig 5(a). Future research efforts to discover materials with ordering schemes in which Li⁺ ions are further spaced apart from one another than in the honeycomb superlattice (such as ribbon ordering) offer a possible way forward.

Non-Li-rich Layered Compounds

In order to suppress in-plane TM migration it may prove necessary to use non-lithium-rich compositions with fully dense TM layers. To ensure O-redox activity at potentials accessible within the stability window of liquid electrolytes it would be necessary to maintain a sufficiently ionic coordination environment around O by using non-redox active ions. Of course, this strategy reduces the capacity compared with Li-rich compositions, but it does shift the capacity to higher voltages. Provided that the TM layer remains dense and out-of-plane migration is prevented, voltage hysteresis would be avoided.

Pillaring

Even if in-plane migration is suppressed, such as in non-Li-rich compounds, for some cations out-of-plane migration could occur leaving behind vacancies in the TM layer and hence indirectly triggering in-plane migration to form vacancy clusters. One strategy to prevent this is pillaring, in which large, immobile cations such as Ca²⁺, are introduced into the alkali metal layer thus forcing the TM layers further apart making the occupation of alkali layer sites by TM ions less favourable. Of course, only a fraction of the alkali metal layer sites should be occupied to preserve diffusion pathways

for the mobile ions. This strategy may find useful application in Na intercalation cathodes where the mobile cation size is compatible with the pillar (e.g. Ca^{2+}). It would also prevent layer gliding transitions which are commonly observed in Na-ion cathode materials. Maintaining P-type stacking over the entire intercalation range would avoid formation of octahedral sites (O stacking) in the alkali metal layers further disfavours out-of-plane TM migration.

Ordered 3D structures

Moving away from layered compounds altogether to other ordered systems where TM migration is less favoured also presents many new interesting opportunities. This is exemplified by the recently reported $\beta\text{-Li}_2\text{IrO}_3$ system, which is a 3-dimensionally-ordered Li-rich phase able to support near complete Li extraction reversibly reaching beyond $\text{Ir}^{5.5+}$.¹¹ There are many other ordered systems besides the layered phases, such as spinel, olivine and polyanionic materials, where O-redox is completely unexplored. These phases may prove to have much greater structural integrity against TM migration and O_2 formation than layered counterparts and thus better support high voltage O-redox.

Li-rich Disordered Structures

A different approach is to accept disorder and embrace the O^{2-}/O_2 redox couple, which is the case in the family of so-called disordered rocksalt compounds. It means accepting lower voltage capacity (i.e. around 3.5 V rather than 4.5 V) and a degree of path-dependent hysteresis. In this context, there has been rapidly growing interest in Li-rich disordered rocksalt intercalation compounds, such as $\text{Li}_2\text{MnO}_2\text{F}$,⁴⁴ $\text{Li}_4\text{Mn}_2\text{O}_5$,⁵⁰ $\text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_2$,¹⁵ $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ ⁵¹ and, more recently the disordered spinel oxyfluorides,⁴⁵ which all cycle over a large composition range utilising reversible O-redox. These compounds, being in an inherently disordered state, avoid the order-disorder transition in honeycomb layered O-redox compounds and already possess many Li-rich local environments for O_2 formation with minimal TM rearrangement.⁵² This avoids the need to charge to high voltages to perform the formation cycle potentially opening up options for electrolytes which do not need to be stable to these voltages. Solutions to improve surface instability, which has been linked with the poor capacity retention over long-term cycling that these materials commonly exhibit, must be sought for these to become viable alternatives.

Surface Modification

Returning to layered Li-rich compounds, surface instability is well-known to be a key issue in O-redox cathodes. Oxygen loss is prevalent in almost all known materials and, as exemplified by Li_2MnO_3 ,^{47,48} can result in damage to the electrode particles leading to densification and poor capacity retention. We showed recently that $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ possesses stoichiometric surfaces in the as-prepared materials, which explains why Ni doping of Li_2MnO_3 suppresses O-loss.⁴⁹ The use of stoichiometric surfaces has been employed widely, for example, in gradient cathodes with epitaxial, near-stoichiometric surfaces and Li-rich bulks thereby alleviating O-loss and voltage fade.⁵³ Other surface modifications such as coatings, fluorination and oxygen vacancy treatments⁵⁴ have also proven to be highly effective. These methodologies all allow TM reorganisation and O_2 formation to take place in the bulk but suppress O_2 being formed at the surface.

Conclusions

In this perspective, the various models put forward to explain the process of O-redox in cathode materials were considered. A recently proposed model that unifies O-redox and is supported by RIXS and NMR evidence, was then discussed in detail. The model describes oxidation of O^{2-} in terms of the formation of O_2 in the bulk and at the surface of the particles, the latter is evolved while the

former is trapped in voids in the bulk of the particles. Subsequent reduction of bulk O₂ on discharge reforms O²⁻ but in a different coordination: O-Li₆ instead of O-Mn₄Li₂ on charge, increasing the energy of the O2p states and rationalising the lower voltage on discharge than on charge (voltage hysteresis). O₂ formation in the bulk occurs again on the 2nd cycle returning to O²⁻ on subsequent discharge but without the major structural change in cycle 1 and commensurate with the lower 2nd cycle hysteresis. The model has been shown to apply to a wide range of cathodes, including those based on 4d and 5d-transition metals and disordered rocksalt cathodes. It is noteworthy that O²⁻ ions and molecular O₂ are, the 2 most stable forms of O found in nature. Using this understanding of the O-redox process, strategies are discussed that may allow new O-redox cathodes with suppressed hysteresis to be implemented.

References

1. Lu, Z., Beaulieu, L.Y., Donaberger, R.A., Thomas, C.L. & Dahn, J.R. Synthesis, Structure, and Electrochemical Behavior of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂. *Journal of The Electrochemical Society* **149**, A778–A778 (2002).
2. Lu, Z. & Dahn, J.R. Understanding the Anomalous Capacity of Li/Li[Ni_xLi_(1/3-2x/3)Mn_(2/3-x/3)]O₂ Cells Using In Situ X-Ray Diffraction and Electrochemical Studies. *Journal of The Electrochemical Society* **149**, A815–A815 (2002).
3. Johnson, C.S. *et al.* The significance of the Li₂MnO₃ component in ‘composite’ xLi₂MnO₃·(1-x)LiMn_{0.5}Ni_{0.5}O₂ electrodes. *Electrochemistry Communications* **6**, 1085–1091 (2004).
4. Kim, J.-S. *et al.* Electrochemical and Structural Properties of xLi₂M’O₃·(1-x)LiMn_{0.5}Ni_{0.5}O₂ Electrodes for Lithium Batteries (M’ = Ti, Mn, Zr; 0 ≤ x ≤ 0.3). *Chemistry of Materials* **16**, 1996–2006 (2004).
5. Koga, H. *et al.* Different oxygen redox participation for bulk and surface: A possible global explanation for the cycling mechanism of Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂. *Journal of Power Sources* **236**, 250–258 (2013).
6. Oishi, M. *et al.* Direct observation of reversible charge compensation by oxygen ion in Li-rich manganese layered oxide positive electrode material, Li_{1.16}Ni_{0.15}Co_{0.19}Mn_{0.50}O₂. *Journal of Power Sources* **276**, 89–94 (2015).
7. Saubanère, M., McCalla, E., Tarascon, J.-M. & Doublet, M.-L. The intriguing question of anionic redox in high-energy density cathodes for Li-ion batteries. *Energy Environ. Sci.* **9**, 984–991 (2016).
8. Muhammad, S. *et al.* Evidence of reversible oxygen participation in anomalously high capacity Li- and Mn-rich cathodes for Li-ion batteries. *Nano Energy* **21**, 172–184 (2016).
9. Gent, W.E. *et al.* Coupling between oxygen redox and cation migration explains unusual electrochemistry in lithium-rich layered oxides. *Nature Communications* **8**, (2017).
10. Sathiya, M. *et al.* Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. *Nature materials* **12**, 827–835 (2013).
11. Pearce, P.E. *et al.* Evidence for anionic redox activity in a tridimensional-ordered Li-rich positive electrode beta-Li₂IrO₃. *Nature Materials* **16**, 580–586 (2017).

12. Perez, A.J. *et al.* Approaching the limits of cationic and anionic electrochemical activity with the Li-rich layered rocksalt Li_3IrO_4 . *Nature Energy* **2**, 954–962 (2017).
13. Hong, J. *et al.* Metal-oxygen decoordination stabilizes anion redox in Li-rich oxides. *Nature Materials* **18**, 256–265 (2019).
14. Luo, K. *et al.* Anion Redox Chemistry in the Cobalt Free 3d Transition Metal Oxide Intercalation Electrode $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$. *Journal of the American Chemical Society* **138**, 11211–11218 (2016).
15. Yabuuchi, N. *et al.* Origin of stabilization and destabilization in solid-state redox reaction of oxide ions for lithium-ion batteries. *Nature Communications* **7**, 13814 (2016).
16. McCalla, E. *et al.* Visualization of O-O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries. *Science (New York, N.Y.)* **350**, 1516–1521 (2015).
17. Hansen, C.J. *et al.* Multielectron, Cation and Anion Redox in Lithium-Rich Iron Sulfide Cathodes. *Journal of the American Chemical Society* **142**, 6737–6749 (2020).
18. Armstrong, A.R. *et al.* Demonstrating oxygen loss and associated structural reorganization in the lithium battery cathode $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$. *Journal of the American Chemical Society* **128**, 8694–8698 (2006).
19. Koga, H. *et al.* Reversible Oxygen Participation to the Redox Processes Revealed for $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$. *Journal of The Electrochemical Society* **160**, A786–A792 (2013).
20. Luo, K. *et al.* Charge-compensation in 3d-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nature Chemistry* **8**, 684–691 (2016).
21. Seo, D.-H. *et al.* The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials. *Nature Chemistry* **8**, 692–697 (2016).
22. Tran, N. *et al.* Mechanisms Associated with the “Plateau” Observed at High Voltage for the Overlithiated $\text{Li}_{1.12}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.88}\text{O}_2$ System. *Chemistry of Materials* **20**, 4815–4825 (2008).
23. Weill, F., Tran, N., Martin, N., Croguennec, L. & Delmas, C. Electron Diffraction Study of the Layered $\text{Li}_y(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.88}\text{O}_2$ Materials Reintercalated after Two Different States of Charge. *Electrochemical and Solid-State Letters* **10**, A194–A194 (2007).
24. ben Yahia, M., Vergnet, J., Saubanère, M. & Doublet, M.-L. Unified picture of anionic redox in Li/Na-ion batteries. *Nature Materials* **18**, 496–502 (2019).
25. House, R.A. *et al.* Superstructure control of first-cycle voltage hysteresis in O-redox cathodes. *Nature* **577**, 502–508 (2020).
26. Chen, H. & Islam, M.S. Lithium extraction mechanism in Li-rich Li_2MnO_3 involving oxygen hole formation and dimerization. *Chemistry of Materials* **28**, 6656–6663 (2016).
27. Gent, W.E., Abate, I.I., Yang, W., Nazar, L.F. & Chueh, W.C. Design Rules for High-Valent Redox in Intercalation Electrodes. *Joule* **4**, 1369–1397 (2020).
28. Okubo, M. & Yamada, A. Molecular Orbital Principles of Oxygen-Redox Battery Electrodes. *ACS Applied Materials & Interfaces* **9**, 36463–36472 (2017).

29. Radin, M.D., Vinckeviciute, J., Seshadri, R. & van der Ven, A. Manganese oxidation as the origin of the anomalous capacity of Mn-containing Li-excess cathode materials. *Nature Energy* **4**, 639–646 (2019).
30. Maitra, U. *et al.* Oxygen redox chemistry without excess alkali-metal ions in $\text{Na}_{2/3}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. *Nature Chemistry* **10**, 288–295 (2018).
31. Taylor, Z.N. *et al.* Stabilization of O-O Bonds by d^0 Cations in $\text{Li}_{4+x}\text{Ni}_{1-x}\text{WO}_6$ ($0 \leq x \leq 0.25$) Rock Salt Oxides as the Origin of Large Voltage Hysteresis. *Journal of the American Chemical Society* **141**, 7333–7346 (2019).
32. Xu, J. *et al.* Elucidating anionic oxygen activity in lithium-rich layered oxides. *Nature Communications* **9**, (2018).
33. House, R.A. *et al.* First cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O_2 trapped in the bulk. *Nature Energy* **5**, 777–785 (2020).
34. Meng, Y. *et al.* Inelastic x-ray scattering of dense solid oxygen: Evidence for intermolecular bonding. *Proceedings of the National Academy of Sciences of the United States of America* **105**, 11640–11644 (2008).
35. Croy, J.R. *et al.* First-charge instabilities of layered-layered lithium-ion-battery materials. *Physical Chemistry Chemical Physics* **17**, 24382–24391 (2015).
36. Mohanty, D. *et al.* Correlating cation ordering and voltage fade in a lithium-manganese-rich lithium-ion battery cathode oxide: A joint magnetic susceptibility and TEM study. *Physical Chemistry Chemical Physics* **15**, 19496–19509 (2013).
37. Croy, J.R., Balasubramanian, M., Gallagher, K. G. & Burrell, A. K. Review of the U.S. Department of Energy’s “deep Dive” Effort to Understand Voltage Fade in Li- and Mn-Rich Cathodes. *Accounts of Chemical Research* **48**, 2813–2821 (2015).
38. Weill, F., Tran, N., Martin, N., Croguennec, L. & Delmas, C. Electron Diffraction Study of the Layered $\text{Li}_y(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})_{0.88}\text{O}_2$ Materials Reintercalated after Two Different States of Charge. *Electrochemical and Solid-State Letters* **10**, A194–A194 (2007).
39. Dai, K. *et al.* High Reversibility of Lattice Oxygen Redox Quantified by Direct Bulk Probes of Both Anionic and Cationic Redox Reactions. *Joule* **3**, 518–541 (2019).
40. Yan, P. *et al.* Injection of oxygen vacancies in the bulk lattice of layered cathodes. *Nature Nanotechnology* **14**, 602–608 (2019).
41. Hu, E. *et al.* Evolution of redox couples in Li- and Mn-rich cathode materials and mitigation of voltage fade by reducing oxygen release. *Nature Energy* **3**, 690–698 (2018).
42. Singer, A. *et al.* Nucleation of dislocations and their dynamics in layered oxide cathode materials during battery charging. *Nature Energy* **3**, 641–647 (2018).
43. Qiu, B. *et al.* Metastability and Reversibility of Anionic Redox-Based Cathode for High-Energy Rechargeable Batteries. *Cell Reports Physical Science* **1**, 100028 (2020).
44. House, R.A. *et al.* Lithium manganese oxyfluoride as a new cathode material exhibiting oxygen redox. *Energy & Environmental Science* **11**, 926–932 (2018).

45. Ji, H. *et al.* Ultrahigh power and energy density in partially ordered lithium-ion cathode materials. *Nature Energy* **5**, 213–221 (2020).
46. House, R.A. *et al.* Covalency does not suppress O₂ formation in 4d and 5d Li-rich O-redox cathodes. *submitted*.
47. Rana, J. *et al.* Quantifying the Capacity Contributions during Activation of Li₂MnO₃. *ACS Energy Letters* **5**, 634–641 (2020).
48. Guerrini, N. *et al.* Charging Mechanism of Li₂MnO₃. *Chemistry of Materials* **32**, 3733–3740 (2020).
49. Boivin, E. *et al.* The Role of Ni and Co in Suppressing O-Loss in Li-Rich Layered Cathodes. *Advanced Functional Materials* 2003660 (2020) doi:10.1002/adfm.202003660.
50. Freire, M. *et al.* A new active Li–Mn–O compound for high energy density Li-ion batteries. *Nature Materials* **15**, 173–177 (2015).
51. Yabuuchi, N. *et al.* High-capacity electrode materials for rechargeable lithium batteries: Li₃NbO₄-based system with cation-disordered rocksalt structure. *Proceedings of the National Academy of Sciences of the United States of America* **112**, 7650–7655 (2015).
52. Sharpe, R. *et al.* Redox Chemistry and the Role of Trapped Molecular O₂ in Li-Rich Disordered Rocksalt Oxyfluoride Cathodes. *Journal of the American Chemical Society* jacs.0c10270 (2020) doi:10.1021/jacs.0c10270.
53. Zhu, Z. *et al.* Gradient Li-rich oxide cathode particles immunized against oxygen release by a molten salt treatment. *Nature Energy* **4**, 1049–1058 (2019).
54. Qiu, B. *et al.* ARTICLE Gas–solid interfacial modification of oxygen activity in layered oxide cathodes for lithium-ion batteries. *Nature Communications* **7**, (2016).
55. Arhammar, C. *et al.* Unveiling the complex electronic structure of amorphous metal oxides. *Proceedings of the National Academy of Sciences* **108**, 6355–6360 (2011).

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Competing Interests

The authors declare no competing interests.

Figure 1. Layered Li-rich Cathodes: (a) Parent crystal structure of layered Li-rich O-redox cathodes, Li_2TMO_3 ($\text{Li}[\text{Li}_{1/3}\text{TM}_{2/3}]\text{O}_2$) pale blue atoms are Li, dark blue atoms are the TMs. (b) Typical first and second cycle load curves for archetypal 3d Li-rich compound $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$.³³ (c) Typical first cycle load curves for other Li-rich cathodes based on 3d, 4d and 5d TM ions each exhibiting a high voltage O-redox plateau and S-shaped discharge curve. Panel b reproduced with permission from ref. 33, Springer Nature Ltd.

Figure 2. Previously Proposed Forms of Oxidised O: Schematic illustrations of the main theories proposed to explain the nature of oxidised O in Li-rich cathodes. Purple atoms represent TM ions (i.e. Mn), blue, lithium, and red, oxygen. (a) Electron holes in orphaned O2p orbitals. (b) Partially reversible out-of-plane migration inducing band reshuffling. (c) Back-bonding interaction between Mn and orphaned O2p orbital through π -type molecular orbitals. (d) Reductive coupling mechanism distorting TMO_6 octahedra to form peroxo-like $(\text{O}_2)^{n-}$ species with long O-O bonds. (e) Mn over-oxidation to form tetrahedral Mn^{7+} as the source of excess capacity. (f) Point-defect model forming short $\text{TM}=\text{O}$ and bridging peroxide bonds after TM migration.

Figure 3. Experimental Evidence for Molecular O_2 : (a) High resolution resonant inelastic X-ray scattering (RIXS) data collected at the O K-edge at an excitation energy of 531 eV for $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ at different states of charge and discharge (adapted from ref. 33), along with the spectrum for O_2 collected at 530.3 eV (reproduced with permission from ref. 55). (b) The peak progression at the low energy loss region of RIXS spectrum at full charge, FC, arises from transitions between different vibrational energy levels of O_2 diatomics. (c) STEM images before and after the charging plateau along the [010] direction showing loss of clearly defined TM-TM dumbbells arising from honeycomb ordering within the TM layer. (d) *Operando* PXRD showing the irreversible loss of superstructure peaks when charging across the plateau. The decrease in peak area shows this is primarily due to in-plane TM disorder, not stacking faults. Panels b, c and d are adapted from ref. 33.

Figure 4. Relationship between Structural Change and Voltage Hysteresis: (a) First cycle hysteresis mechanism. Blue Li, purple TM and red O. Starting from pristine structure A on charge Li^+ lost from TM layer (B) followed by structural relaxation and loss of honeycomb ordering across the plateau through in-plane TM migration driven in part by the energy stabilisation gained by O_2 formation to reach structure C. Disorder remains on discharge with Li^+ returning to the TM layer but populating sites in the vacancy clusters to form D. Honeycomb ordering may be recovered in the lithiated state through moderate heating D to A. (b) Voltage hysteresis mechanism for the second cycle onwards. TM layer disorder remains throughout, strain release from O_2 formation and reduction could explain path dependent hysteresis. Although the structural representations show O_2 forming part of the coordination sphere around Mn there is little bonding interaction between O_2 and Mn seen by NMR or RIXS. (c) Local coordination environment around O in pristine honeycomb ordered $\text{O-Li}_4\text{Mn}_2$ (structure A) and (d) local coordination around O in disordered Li-rich cluster O-Li_6 (structure D) after the 1st cycle. O2p states belonging to O with 6 coordinating Li are higher in energy than those with 4 resulting in the observed lower voltage on the 1st discharge compared with 1st charge. Also, the persistence of the disorder and hence O-Li_6 coordination leads to the lower potential oxidation on the 2nd cycle.

Figure 5. Surface and Bulk O_2 Formation: Formation of molecular O_2 is the primary O-redox charge compensation mechanism at the surface and in the bulk of Li-rich cathodes. However, while O_2 is irreversibly evolved from the surface, it is retained within the bulk for reversible O^{2-}/O_2 redox. There is net TM migration inwards from the surface to compensate for the loss of O_2 . Evidence for rocksalt like structure at the surface indicates TM in lithium and TM layers in the shell.

Figure 6. Strategies for Developing Stable O-redox Materials: Schematics illustrating potential strategies for mitigating the structural instability induced by O-redox. (a) Suppressing in-plane TM migration through new TM layer superstructure ordering schemes. (b) Substituting other electropositive and redox-inactive elements into the TM layer to eliminate in-plane TM migration. (c) Introducing large, immobile cations into the Li layer acting as pillars to prevent out-of-plane TM migration. (d) Exploring other, 3-dimensional crystal structure systems with improved stability. (e) Embracing structural disorder and O_2 formation with disordered Li-rich cathodes. (f) Suppressing the loss of O_2 and structural reorganisation at the surface and allowing bulk O_2 formation.