Ni–O-redox, oxygen loss and singlet oxygen formation in LiNiO₂ cathodes for Li-ion batteries

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Abstract

Ni-rich cathode materials such as LiNiO₂ achieve high voltages in Li-ion batteries but are prone to structural instabilities and oxygen loss. Mitigating this degradation requires a comprehensive understanding of the cause and mechanism of oxygen loss, also accounting for the formation of singlet oxygen. Using ab initio molecular dynamics simulations, we observe spontaneous O₂ loss from the (012) surface of delithiated LiNiO₂, singlet oxygen forming in the process. We find that the origin of the instability lies in the pronounced oxidation of O during delithiation, i.e., a central role of O in Ni-O redox in LiNiO₂. For LiNiO₂, NiO₂, and the prototype rock salt NiO, a range of computational tools including density-functional theory and dynamical mean-field theory calculations based on maximally localised Wannier functions yield a Ni charge state of ca. +2, with O varying between -2 (NiO), -1.5 (LiNiO₂) and -1 (NiO₂). The O₂ loss route observed here consists of 2 surface O• radicals combining to form a peroxide ion, which is then oxidised to O₂. In leaving the surface, O₂ leaves behind 2 O vacancies and 2 electrons, reducing the 2 nearest surface O⁺ radicals to O⁻ ions: effectively 4 O⁺ radicals disproportionate to O₂ and 2 O⁻ ions, forming 2 O vacancies. The reaction liberates ca. 3 eV. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion, with spin conservation dictating the preferential release of ¹O₂. The strongly exergonic reaction easily provides the free energy required for the formation of ¹O₂ in its excited state.

Keywords: LNO, oxygen loss, singlet oxygen, DFT, DMFT, AIMD simulations.
1 Introduction

Ni-rich layered oxides exhibit excellent performance as high-voltage cathode materials, enabling batteries with high energy densities.\textsuperscript{1,2} They are, however, prone to structural instabilities and degradation involving oxygen loss.\textsuperscript{3-6} Singlet oxygen \(^1\text{O}_2\) has on occasion been captured experimentally\textsuperscript{7} or deduced from the large amount of electrolyte oxidation products found, which are unlikely caused by reaction with unreactive triplet oxygen.\textsuperscript{8,9} Neither the reason for singlet formation nor its concrete fate after evolution from the surface are, to date, well understood.

To understand the role of the surface itself in singlet oxygen formation, Wandt et al. have studied thermally induced \(^1\text{O}_2\) evolution from Ni-rich layered oxides into the gas phase. They report a rise in \(^1\text{O}_2\) evolution around 500 K,\textsuperscript{7} confirming the existence of at least one route for \(^1\text{O}_2\) formation without any electrolyte. Houchins et al. have recently proposed that in metal-air batteries, singlet oxygen forms via a disproportionation reaction of superoxide radicals in solution.\textsuperscript{10} As the superoxide radicals are part of the metal-air electrochemistry and they play no role in Li-ion batteries, it is unlikely or at least unclear if the formation of singlet oxygen in Li-ion batteries with layered oxide cathode materials follows the same mechanism. An attempt to answer these questions will require an atomistic understanding of the surfaces involved. Based on scanning electron microscopy and X-ray diffraction, Zhu and Chen\textsuperscript{11} showed the prevalent surfaces in Ni-rich layered oxide cathodes to exhibit facets of the (012), (001), and (104) families, in line with computational predictions.\textsuperscript{12-14} The facets found to cover the greatest surface area, over a range of particle morphologies, were (012) facets,\textsuperscript{11} which are predicted to be O-terminated at synthesis conditions.\textsuperscript{12} The O-terminated (012) facet is therefore an ideal model system to explore (singlet) oxygen loss in Ni-rich layered oxides.

The redox activity of LiNiO\(_2\) (LNO) involved in battery cycling is generally attributed predominantly to Ni, \textit{i.e.}, it is assumed that in the process of charging and discharging the battery, it is mainly Ni that is oxidised and reduced.\textsuperscript{5,15-18} Within the formal oxidation state model, Ni is considered to be oxidised from +3 to +4 upon delithiating LNO.\textsuperscript{5,18} It is clear that there is Ni–O hybridisation between the Ni \(d\) and O \(p\) states,\textsuperscript{15,19} that the oxidation of Ni also impacts the oxidation state of O and the oxidation states of both species deviate from their formal charge states.\textsuperscript{15,19} The implications of this, however, are usually taken to be that Ni is not solely oxidised/reduced; O is somewhat involved in the Ni-O processes but Ni activity remains dominant.\textsuperscript{5,15,16} Even if O were more redox-active, the hybridisation would lead to a concomitant lowering of the redox activity of Ni, so that the capacity would stay constant irrespective of the relative contributions of Ni and O.\textsuperscript{15} In the light of this, the charge states have not previously been explained in depth, especially as there are numerous technical challenges regarding the quantification of species in hybridised states. Wave-function based charge analyses proposed, for example, by Mulliken\textsuperscript{20} partition the wave function according to atomic orbitals, which is a questionable approach for characterising hybridised states. Determining oxidation
states using density-functional theory (DFT) calculations requires the ground-state electron density to be partitioned and assigned to the individual ions; the resulting ionic charge therefore often depends on the choice of partitioning scheme, the most established being Bader charge analysis.\textsuperscript{21} Reeves and Kanai\textsuperscript{22} as well as Quan and Pickett\textsuperscript{23} suggest that projecting the DFT charge density onto maximally localised Wannier functions yields the most reliable charges of atoms in molecules\textsuperscript{22} and ions in crystals.\textsuperscript{23}

Kong \textit{et al.} have previously reported partial O oxidation upon delithiation of LNO but continue to attribute the main redox activity to Ni.\textsuperscript{15} In a similar vein, Korotin \textit{et al.}\textsuperscript{24} and Foyevtsova \textit{et al.}\textsuperscript{25} invoke ligand holes on oxygen, suggesting a partial charge transfer of oxygen to Ni, but simultaneously propose a disproportionation of the Ni charge states, which has not yet been confirmed experimentally. A greater involvement of O is considered in O-redox materials, where O-redox goes beyond \(\sigma(\text{Ni}–\text{O})\) interactions, \textit{e.g.}, in Li-excess cathode materials,\textsuperscript{19,26–29} in the form of orphaned O states\textsuperscript{19} or stabilising delocalised metal-oxygen \(\pi\) interactions.\textsuperscript{26}

We here re-examine the classic picture of transition-metal centred redox in stoichiometric LiNiO\(_2\) with a variety of computational tools ranging from density functional theory (DFT) to dynamical mean-field theory (DMFT) calculations; we use charge-analysis schemes ranging from a Bader charge analysis to the Wannier transformation and integration over the impurity Green’s functions within DMFT. Employing \textit{ab initio} molecular dynamics (AIMD) simulations, we analyse the spontaneous \(\text{O}_2\) release from the (012) surface of delithiated LNO and for the first time computationally capture singlet oxygen as it forms at the cathode surface. We propose a comprehensive mechanism for the observed route of oxygen loss and singlet oxygen formation.

2 Oxidation states

At a basic level of charge analysis, a Bader partition of DFT densities from PBE+\(U\) calculations (\(U_{\text{eff}} = 6\) eV) shows Ni to exhibit a similar charge state in LiNiO\(_2\) and NiO\(_2\) (see Fig. 1 a, first blue bar in each set). At high states of delithiation, LNO is known to decompose forming surface-reconstruction phases with rock salt-like structures.\textsuperscript{5,30} The prototype material of these rock salt-like phases is NiO, for which a Bader analysis shows Ni to have a similar charge state as in LiNiO\(_2\) and NiO\(_2\). Fig. 1 a shows that the O charge state, on the other hand, changes significantly upon delithiation of LiNiO\(_2\), and even further upon formation of NiO.

The electronic density of states (DOS) (see Fig. 1 b) suggests ferromagnetic behaviour at 0 K. Of particular interest are the states just below the Fermi energy, as these are the states that electrons are removed from upon delithiation of the material. The character of these states can be estimated by projecting the DOS onto spherical harmonics, \textit{i.e.}, local atomic orbitals. They indicate that the states just below the Fermi energy have predominantly O (red) contributions and only to a
small extent Ni (blue) contributions. The charge density of these states (yellow iso
surface in Fig.1 c) confirms pronounced O p contributions and weaker Ni e_g

\[ \text{NiO}_2 \text{ charge states} \]

\[ \text{PBE+U electronic DOS} \]

\[ \text{PBE+U charge densities} \]

\[ \text{DMFT spectral function (ferromagnetic, } T < T_C) \]

\[ \text{paramagnetic, } T > T_C \]

\[ \text{spectral function of the paramagnetic material at } T > T_C \text{ showing good agreement with the small bandgap paramagnetic character seen in experiment.}^{31} \]
contributions just below the Fermi energy (the states are highlighted in the DOS in Fig. 1 b).

Due to the hybridised nature of the states near the Fermi energy, the charges were also analysed at a more advanced level with a wannierisation of the PBE Kohn-Sham orbitals. In the case of LNO, a Ni $d$ wannierisation shows large O $p$ contributions for the nominal Ni $e_g$ states (orbitals shown in yellow and green in Fig. 1 c), confirming that the Ni and O bands are strongly hybridised. The electronic band structure (see SI) suggests that the $d$ and $p$ bands are very close in energy, requiring both the Ni $d$ and O $p$ states to be included in the correlated subspace of the wannierisation. If the O states are explicitly included in the wannierisation using a $d-p$ model, Ni $d$ states are localised on Ni centres and O $p$ states on O centres (see Fig. 1 c). NiO$_2$ also requires a $d-p$ model, while NiO contains $d$ and $p$ bands that are well separated (see band structure in the SI), making a $d$ model sufficient. The resulting ionic charges calculated from Wannier occupancies (see Fig. 1 a, middle bar in each set) have significantly larger values than the Bader charges (by 0.5-0.8 e in the case of Ni and 0.3-0.9 e in case of O), but confirm all trends seen with the Bader analysis of the PBE+$U$ states; the Ni charges are nearly identical in LiNiO$_2$, NiO$_2$, and NiO, while the O oxidation states vary substantially, suggesting pronounced O redox activity. The question arises if this O character just below the Fermi energy and the resulting redox activity of O are an artefact, e.g., of the DFT calculations themselves or of the static Hubbard $U$ treatment of electron correlation, which lowers the energy of the Ni states, potentially causing unphysical O $p$ character just below the Fermi energy. Dynamical mean-field theory (DMFT) calculations were therefore performed which account for electron correlations via a mean-field approach and obtain charge states by integrating over the impurity Green’s functions in a Wannier basis. The DMFT spectral function is shown in Fig. 1 d for the ferromagnetic case, resembling the DFT DOS at 0 K. At temperatures above the Curie temperature, the material becomes paramagnetic, as shown in Fig. 1 e, where the two $e_g$ states are each half occupied (red line). This small band-gap paramagnetic behaviour is in good agreement with experimental findings at battery operating temperatures.\(^{32}\)

Returning to the question of the charge states of Ni and O, Fig. 1 a shows that the DMFT charges (third bar of each set) are nearly identical to the Wannier charges based on the PBE densities (middle bar of each set). DMFT yields a Ni oxidation state of $\sim +2$ in all three materials, LiNiO$_2$, NiO$_2$, and NiO, while the charge of O is ca. $-1.5$ in LiNiO$_2$, $-1$ in NiO$_2$, and assumes its most stable state of $-2$ only in the decomposition product NiO.

3 Surface oxygen loss

As LNO is known to decompose through surface reactions, it is pivotal to understand how the bulk oxidation states discussed above compare to oxidation states at the surface. We explore the prevalent (012) facet,\(^{11}\) where Li is extracted and inserted
during cycling, and we investigate the fully delithiated, unstable material NiO$_2$ (see Fig. 2 a).

The analysis of the oxidation states in the previous section showed a Bader charge analysis to give the correct relative changes of the oxidation states in bulk LiNiO$_2$ and NiO$_2$ without the necessity to assess the suitability of different Wannier models. The surface charges of the (012) facet of NiO$_2$ were therefore evaluated with a Bader charge analysis of the PBE+$U$ charge density, which shows O at the surface to be oxidised even further than in the bulk (see Fig. 2 a). Each Ni-O layer exhibits O species with two slightly different charge states at the surface, both with a lower electron density than in the bulk.

AIMD simulations of this NiO$_2$ surface show a spontaneous loss of O$_2$ molecules and even the formation of singlet oxygen in the process (see Fig. 2 b). O$_2$ evolution occurs spontaneously at simulated temperatures from 300 – 800 K. Fig. 2 b shows the free energy profile of an exemplary PBE+$U$ trajectory at ca. 450 K, suggesting the reaction liberates 3.0 eV. This was confirmed with AIMD simulations including dispersion interactions and based on hybrid functionals (see SI), which also show spontaneous O$_2$ loss to release ca. 3 eV. As seen in Fig. 2 b, the reaction appears barrierless, suggesting that the activation barrier is smaller than the energy fluctuations due to thermal vibrations (<0.05 eV).

At the beginning of the simulation, the O species at the surface of NiO$_2$ are separated by ca. 2.8 Å. An analysis of the magnetic moments yields ca. 1.1 $\mu_B$ per O (see Fig. 2 b), suggesting the presence of unpaired electrons. The magnetisation density shows no unpaired electrons in the bulk, but positive spin density on the surface O that interacts antiferromagnetically with negative spin density on the nearest Ni ions (see SI), suggesting radical character of the surface O, i.e., O$^{\bullet}$•. When lattice vibrations bring 2 O$^{\bullet}$ radicals close together (ca. 1.4 Å) at 369 fs, the electronic character of the surface O changes, causing a steep decrease of the magnetic moments to ca. 0 $\mu_B$, indicative of the formation of a peroxide ion. The charge density and electron localisation function show a covalent O-O bond of the dimer (see SI), in agreement with an O$_2$ dimer predicted by Kong and co-workers.$^{15}$ Fig. 2 b shows the change in electron numbers throughout the reaction, according to a Bader analysis. The O forming the peroxide are oxidised. While some of this charge is transferred to the nearest Ni ions, the majority goes to the nearest surface O$^{\bullet}$ radicals. As the peroxide is oxidised, the O-O distance decreases further to ca. 1.2 Å at 384 fs, typical of an O$_2$ molecule. Fig. 2 d shows a closeup of the free energy profile. The two O$^{\bullet}$ radicals (A) form the peroxide at 369 fs (B), which is oxidised continuously to O$_2$ – in double coordination at 384 fs (C), single coordination at 387 fs (D), and desorbed at 394 fs (E), assuming a Ni-O bond cut-off length of 2.05 Å (based on the charge density and electron localisation function). Most of the oxidation occurs between B and C. The released oxygen molecule vibrates around an average bond length of 1.2 Å and leaves behind two oxygen vacancies and two reduced surface O. The free energy curve shows that ca. 1.7 eV (55%) of the free energy gain is due to the peroxide formation and oxidation, while ca. 1.3 eV (45%)
**Fig. 2 Mechanistic analysis of the observed route of O₂ evolution and the formation of ¹O₂.**

a. Oxidation states of the O ions near the (012) facet of NiO₂ according to a Bader charge analysis of the PBE+U charge density; lighter colours represent higher states of oxidation. Surface O are in a yet more oxidised state than bulk O.

b. Free energy profile (black) and magnetic moments of surface O species (red) of a route of spontaneous O₂ loss, as found in AIMD simulations at ca. 450 K. The reaction occurs around 370-400 fs, where the free energy decreases by ca. 3 eV. The magnetic moments suggest radical character at the beginning of the simulation, μO = 1.1μB, and an abrupt change in electronic character during the reaction.

c. Differences in electron numbers of all ions in the simulation cell between 389 fs (when O₂ just desorbed) and the start of the simulation based on a Bader analysis. d. Closeup of the free energy profile with characteristic points indicated; O²⁻ radicals (A) combine to form a double coordinated peroxide (B), which is continuously oxidised to an O₂ molecule (C-E) and through a single coordinated transition state (D) desorbs as O₂ (E). The charge is transferred to the nearest O²⁻ radicals (see c).

e. Magnetisation density of the peroxide ground-state singlet state and the excited molecular singlet state (yellow isosurfaces).
denote positive spin density and cyan isosurfaces negative spin density, isosurface levels of ± 5.3 × 10⁻⁵ e/Å³.

f. closeup of the magnetic moments of the two O⁺ forming the O₂ molecule as a function of time. The moments exhibit a steep decrease around 369 fs to zero, indicating a singlet ground state of the peroxide ion, and steadily increase from ca. 0.3 μB at 371 fs to ca. 0.8 μB from 500 fs onwards. Once released from the surface, ¹O₂ is no longer a ground state and looks identical to ¹O₂ obtained for the gas phase (¹Δ, see SI).

are due to the remaining oxidation and O₂ desorption. The activation barrier of the desorption is ca. 0.04 eV – easily overcome by thermal energy, especially in the light of the large amount of energy released through the peroxide formation. The rate-determining step is therefore most likely the peroxide formation (with a negligible barrier at 450 K).

4 Singlet oxygen

With this mechanistic understanding of the observed route of oxygen loss from delithiated LNO, we can turn to the question of why singlet oxygen is formed. O₂ molecules in the gas phase have a triplet ground state T₁Σ⁻₀ separated by an energy gap of ca. 0.9 eV from the first excited state (CASSCF, 33 exp₃⁴), i.e., the singlet a¹Δ₀ state. Higher in energy still is the b¹Σ⁺₀ state, which is generally not observed to react chemically as it physically deactivates quickly into the ¹Δ state. It has been a longstanding puzzle why singlet oxygen is formed at layered oxide cathodes. To unravel the mechanism of the singlet formation in our simulations, it is essential to identify the ¹O₂ signatures in the simulations.

The two highest-energy electrons of ¹O₂ are of opposite spin, so the singlet has an overall magnetic moment of zero. Fig. 2 b+d shows that at 369 fs in the AIMD simulations, the magnetic moments of the two oxide radicals forming the peroxide drop and approach zero briefly before steadily increasing from ca. 0.3 μB (at 371 fs) to ca. 0.8 μB (from 500 fs onwards). Albeit briefly, this points towards singlet character of the electronic ground state, and this is the ground state of the peroxide ion. Through constraining the number of unpaired electrons in the simulation cell, we can also enforce the singlet state before the transition, and we see it become degenerate with the AIMD ground state (nearly degenerate ca. 15 fs before the drop in the magnetic moments, and fully degenerate ca. 3 fs before the drop, see the green data points in Fig. 2 d+f). This singlet state forms as the 2 oxide radicals forming the peroxide come close enough together to start interacting with each other but before any oxidation takes place. The magnetisation density of the singlet state is illustrated in Fig. 2 e+f. Two states with strong O p character are seen, one populated with a spin-up electron and the other with a spin-down electron. The lobes of the negative spin state are slightly larger than the lobes of the positive spin state, resulting in a magnetic moment of ca. -0.1 μB.

As the simulation proceeds and the peroxide is oxidised, the negative lobes shrink until they disappear, and the magnetic moments increase to 0.8 μB (see Fig. 2 b+f), suggesting triplet character of the ground state ³O₂ molecule after it has left the surface. Through constraining the number of unpaired electrons, the singlet
state is also obtained for $^{1}\text{O}_2$ after it has left the surface. The magnetisation density seen in Fig. 2 f looks very similar to the singlet seen during the peroxide formation, but in the $^{1}\text{O}_2$ molecule, the planes of the lobes are fully aligned, suggesting a stronger interaction (at a smaller distance; earlier 1.4 Å between the interacting radicals vs. 1.2 Å in the molecule). Fig. 2 d shows that the gas phase singlet is no longer degenerate with the ground state but an excited state.

In a DFT gas phase calculation, $^{1}\text{O}_2$ can also be obtained by constraining the magnetic moments of each O atom to zero. The gas phase $^{1}\text{O}_2$ shows the same magnetisation density as the gas phase $^{1}\text{O}_2$ at the surface of NiO$_2$ (see SI). The highest energy level is degenerate across the two spin channels and occupied by one spin-up and spin-down electron each (see SI), indicating that this type of singlet both in the gas phase and evolving from the NiO$_2$ surface in our simulations corresponds to the $^{1}\Delta$ singlet where the spins are paired, giving the singlet a more closed-shell character.$^{35,36}$

5 Discussion

We propose that a comprehensive understanding of oxygen loss and singlet oxygen formation in Ni-rich cathodes requires a revision of the fundamental understanding of redox processes in LiNiO$_2$. While it is generally assumed that Ni and O states are hybridised, the extent of the O involvement in Ni-O redox seen in Fig. 1 is unexpected. All calculations consistently suggest that what is commonly considered to be Ni-redox chemistry predominantly affects the oxidation state of O (see Figs. 1 a and 3 a). If this effect occurred only in a Bader charge analysis, it might be considered an artefact from rehybridisation, i.e., from differing degrees of overlap, and the O electron density thus contributing more to the Ni charge within the Bader cut-offs. The DMFT calculations based on a Wannier d-p model, however, can separate the d and p contributions, and they confirm the constant oxidation state of Ni$^{2+}$ and the changing oxidation state of O from -1.5 in LiNiO$_2$ to -1 in NiO$_2$ (and -2 in NiO). This suggests effects beyond rehybridisation are at play. Examining the Wannier on-site energies allows for an estimation of the energy levels of the localised states. The on-site energies (see Fig.3 b) show a clear separation between the Ni d and O p states (Mott-type behaviour) only for the prototype rock salt NiO. In LiNiO$_2$, the difference between the O p states and Ni d states is < 1 eV, promoting hybridisation (as directly seen in the charge density in Fig. 1 c). The strong hybridisation leads to pronounced splitting of the energy levels, pushing O states right up to the Fermi energy (as seen in the DOS in Fig. 1 b), resulting in charge-transfer character. As LiNiO$_2$ is delithiated, the O states are raised in energy (see Fig. 3 b). The Ni e$_g$ states and O p states become degenerate in NiO$_2$, maximising the splitting of the hybridised levels. Delithiation thus increasingly pushes the hybridised O states higher in energy, with charge transfer stabilising Ni in the surprising +2 state both in LiNiO$_2$ and NiO$_2$. The charge-transfer nature of LNO is also
predicted according to the criterion proposed by Zaanen, Sawatzky, and Allen,\textsuperscript{24,25,37} namely that the split between $d$ and $p$ states ($\Delta = 2$ eV for LNO) is small

\begin{itemize}
  \item[a] Redox processes during battery cycling
  \begin{itemize}
    \item[formal oxidation state model:]
    \begin{align*}
      \text{+2 NiO} & \rightarrow \text{+3 LiNiO}_2 \rightarrow \text{+4 NiO}_2 \\
      \text{O loss} & \quad \text{battery charge}
    \end{align*}
  \end{itemize}

  \begin{itemize}
    \item[extreme case of new model:]
    \begin{align*}
      \text{-2 NiO} & \rightarrow \text{-1.5 LiNiO}_2 \rightarrow \text{-1 NiO}_2 \\
      \text{O loss} & \quad \text{battery charge}
    \end{align*}
  \end{itemize}

\end{itemize}

\begin{itemize}
  \item[b] Wannier on-site energies
  \begin{itemize}
    \item[Energy (eV):]
    \begin{align*}
      \text{NiO} & \quad \text{LiNiO}_2 \quad \text{NiO}_2 \\
      \text{Energy} & \quad -3 \quad -2 \quad -1
    \end{align*}
  \end{itemize}

\end{itemize}

\begin{itemize}
  \item[c] Mechanism of observed route of O\textsubscript{2} loss
  \begin{itemize}
    \item[combination of 2 O\textsuperscript{2−} radicals to form peroxide ion O\textsubscript{2}\textsuperscript{2−}]
    \begin{align*}
      \text{O}^{2−} + 2 \text{O} & \rightarrow \text{O} - \text{O} \quad \text{2 e}^{-} \quad \text{+ 2 V}_0
    \end{align*}
  \end{itemize}

\end{itemize}

\textbf{Fig. 3 Proposed models of the origin and mechanism of O\textsubscript{2} loss in LNO.}
a, scheme illustrating the differences between the formal oxidation state model of Ni-O redox in LNO and our proposed revision. The standard understanding considers Ni to undergo the greatest changes in oxidation state when a battery is cycled, from +3 in LiNiO\textsubscript{2} to +4 in NiO\textsubscript{2} and +2 in the prototype rock salt NiO during degradation. O is commonly considered to be less affected, mostly assuming a charge state of -2. All our DFT and DMFT simulations instead suggest that O undergoes the greatest changes in oxidation state, from -1.5 in LiNiO\textsubscript{2} to -1 in NiO\textsubscript{2} and -2 in NiO. Ni is less affected and mostly assumes a charge state of +2. b, Wannier on-site energies for NiO, LiNiO\textsubscript{2}, and NiO\textsubscript{2} are a measure of the energies of the localised states. The energies show a small gap $\Delta$ between the Ni $d$ and O $p$ states in LNO, promoting Ni-O hybridisation and charge-transfer behaviour. The gap decreases upon delithiation; in NiO\textsubscript{2}, the Ni $d$ and O $p$ states are degenerate. This causes strong splitting of the levels of the hybridised states, presumably pushing O states close to the Fermi level. This charge-transfer behaviour and O redox activity directly compromise the material’s stability and promote O\textsubscript{2} loss. c, the following mechanism is derived for the route of spontaneous O\textsubscript{2} loss observed in AIMD simulations: (i) 2 oxide radicals O\textsuperscript{2−} combine to form a peroxide ion O\textsubscript{2}\textsuperscript{2−}; (ii) the peroxide is oxidised to an O\textsubscript{2} molecule, desorbs, and leaves behind 2 oxygen vacancies and 2 electrons; (iii) the 2 electrons reduce the closest O\textsuperscript{2−} radicals to O\textsuperscript{2+} ions. In sum, the reaction mechanism thus consists of 4 O\textsuperscript{2−} radicals disproportionateing to form molecular O\textsubscript{2}, 2 O\textsuperscript{2+} ions, and 2 oxygen vacancies. The rate-determining step is the peroxide formation.

compared to the $d$-$d$ split (the Coulomb repulsion $U = 6$ eV). Korotkin et al.,\textsuperscript{24} and Foyevtsova et al.,\textsuperscript{25} also speak of ligand holes on oxygen in LNO, discussing the possibility of charge-transfer behaviour of LNO. It can be concluded that the electrochemical redox activity of LNO stems, to a large extent, from oxidising O, as illustrated in Fig. 3 a. This mechanism does not open routes to enhanced capacities as the overall capacity of the hybridised Ni-O system remains constant – and is also limited by the total content of lithium in the material, but it has central ramifications for the material’s stability at high states of charge. If bulk Ni-O redox in LNO affects
primarily the oxidation states of oxygen and O is oxidised on battery charging, it is not surprising that the material is unstable towards oxygen loss at high states of charge.

Methodologically, we find PBE+$U$ calculations with $U_{\text{eff}} = 6 \text{ eV}$ surprisingly well suited for describing the 0 K electronic structure – particularly with respect to the charge states of LNO, NiO$_2$, and NiO (see Fig. 1 a). DMFT calculations based on a Wannier $d$-$p$ model not only validate the trends seen with a PBE+$U$ Bader charge analysis, and suggest they remain valid at finite temperatures, but also show excellent quantitative agreement with PBE Wannier charges. The wannierisation route for determining charges in hybridised states$^{22,23}$ in our case obtained DMFT-quality oxidation states from PBE when the basis of the Wannier model was chosen carefully ($d$-$p$ for LiNiO$_2$ and NiO$_2$; $d$ for NiO). It promises to be a powerful tool for quantifying charge states in battery materials more generally.

Based on our AIMD simulations of spontaneous O$_2$ loss from the (012) facet in NiO$_2$ (see Fig. 2), we propose the following mechanism for the observed reaction route: (i) 2 oxide radicals O$^\cdot$ combine to form a peroxide ion O$_2$$^2$ (see Fig. 3 c); (ii) upon peroxide formation and desorption, the 2 O$^\cdot$ are oxidised to molecular O$_2$, leaving behind 2 oxygen vacancies and 2 electrons; (iii) the 2 electrons reduce the 2 closest O$^\cdot$ radicals to O$^2_\cdot$ ions. (ii) and (iii) occur simultaneously. In sum, the reaction mechanism thus consists of 4 O$^\cdot$ radicals disproportinonating to form molecular O$_2$, 2 O$^2_\cdot$ ions, and 2 oxygen vacancies. Whereas in metal-air batteries, the superoxide radical O$_2$$^\cdot$ disproportionates$^{10}$ the reaction route we observe in LNO involves the disproportionation of the oxide radical O$^\cdot$; i.e., while there are parallels between the reaction mechanisms, the disproportionating species differ according to the different battery redox chemistries. The oxide O$^\cdot$ disproportionation is likely to be representative of Li-ion batteries with Ni-rich layered oxide cathodes.

The reason for the formation of singlet oxygen, we believe, lies in the ground-state singlet state of the peroxide ion. As the peroxide is oxidised to molecular oxygen, spin conservation rules favour the release of $^1$O$_2$. Given the strongly exergonic nature of the reaction (see Fig. 2 b) liberating 3 eV, $^1$O$_2$ is easily released in its excited state. Singlet oxygen formation in layered oxide cathodes thus follows in the footsteps of the wealth of reports of singlet oxygen formation from (mostly organic) peroxide reactions.$^{38-40}$

The final question concerns the fate of $^1$O$_2$ after its evolution. Does it remain in the singlet state (accounting for $^1$O$_2$ found experimentally$^7$), react with electrolyte components (explaining the vast amounts of electrolyte oxidation products found), or deactivate into its triplet ground state? Both during the reaction and shortly after, the peroxide/O$_2$ molecule strongly interacts with the spins at the surface. Surface interactions, for example, enable the combination of the two O$_2$$^\cdot$ radicals, each with positive spin density, to the singlet peroxide in the first place – a process that would be spin-forbidden for isolated radicals. Interactions of the newly formed singlet $^1$O$_2$ molecule with the surface are therefore expected to also provide routes of the otherwise spin-forbidden relaxation into triplet $^3$O$_2$. We leave these processes for
future study, ideally to be addressed with dedicated multi-reference tools that can fully account for the open-shell character of the isolated O$_2$ molecule and excited states beyond the DFT ground state. In any case, we believe it is the ground state singlet state of the peroxide that causes the release of singlet oxygen.

Mitigating O$_2$ loss and electrolyte degradation in Ni-rich cathodes thus requires a paradigm shift in the understanding of Ni-O redox. Only if the pivotal role of O redox is acknowledged, routes can be sought of suppressing oxidation especially of the surface O or stabilising them to prevent peroxide formation and with that singlet oxygen formation and oxygen release.

6 Conclusion

Through a rigorous charge analysis based on DFT and DMFT calculations, we have shown that the delithiation of LiNiO$_2$ to NiO$_2$ predominantly occurs via the oxidation of O and only causes minor changes in the charge of Ni. The Ni charge remains around +2, whether in LiNiO$_2$, in NiO$_2$, or the prototype rock salt NiO. Instead, the oxygen charge ranges from -2 in NiO to ca. -1.5 in LiNiO$_2$ and -1 in NiO$_2$, and we propose it is the charge-transfer character of LNO and the resulting dominant O redox that cause oxygen loss in Ni-rich layered cathode materials. Our AIMD simulations of the (012) facet of NiO$_2$ show the spontaneous evolution of O$_2$ molecules and the occurrence of singlet oxygen in the process. We proposed the following mechanism for the observed route of O$_2$ loss: (i) 2 O$^*$ radicals combine to form a peroxide ion O$_2$$^{2-}$; (ii) the peroxide ion is oxidised to molecular O$_2$ which then leaves the surface, leaving behind 2 oxygen vacancies and 2 electrons; (iii) the remaining 2 electrons reduce the 2 nearest lattice O$^*$ radicals to O$^{2-}$, steps (ii) and (iii) occurring simultaneously. Overall, this means 4 O$^*$ radicals disproportionate to form O$_2$ and 2 O$^{2-}$ ions. The reaction liberates ca. 3 eV. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion. Spin conservation favours the release of $^1$O$_2$ in the excited state, which is rendered feasible through the strongly exergonic nature of the reaction. The findings presented here not only propose a revised model of redox processes in stoichiometric LNO but also offer a comprehensive atomistic understanding of the cause of oxygen loss and a reaction route forming singlet oxygen, pivotal for mitigating stability issues and degradation phenomena in Ni-rich cathodes.

7 Methods

AIMD simulations and DFT calculations
AIMD simulations and static DFT calculations were performed according to the Generalized Gradient Approximation (GGA) proposed by Perdew, Burke, and Ernzerhof$^{41}$ and the projector augmented wave method (PAW)$^{42}$ as implemented in the Vienna Ab Initio Simulation Package (VASP)$^{43,44}$. The electronic wave functions were expanded with a basis set of plane waves with kinetic energies of up to 500 eV. A supercell with 48 ions (352 electrons) was used. For the $k$-point sampling a
1 x 2 x 1 Monkhorst-Pack mesh\(^45\) was used. The convergence criteria for the electronic and ionic relaxations were set to 10\(^{-6}\) eV and 5 • 10\(^{-3}\) eV/Å, respectively. For Ni, the 4s\(^2\)3d\(^6\) electrons were treated as valence electrons. To account for the strongly correlated \(d\) electrons, a rotationally invariant Hubbard \(U\) parameter was used.\(^46\) The electronic density of states was calculated at varying \(U_{\text{eff}}\) in the range from 0 eV − 10 eV and compared with the density of states obtained with the screened hybrid functional proposed by Heyd, Scuseria, and Ernzerhof (HSE06)\(^47\) with 25% Fock exchange. The best agreement was achieved at \(U_{\text{eff}} = 6\) eV, in agreement with findings by Das \textit{et al.},\(^5\) which was used for all AIMD and DFT calculations. For oxygen, the 2s\(^2\) 2p\(^4\) electrons were considered in the valence.

AIMD simulations were performed for the canonical ensemble (\(NVT\), constant volume, particle number, and temperature). A Nosé-Hoover thermostat was used with a Nosé mass corresponding to a period of 40 fs.

**Dynamical Mean-Field Theory**

Our \textit{ab-initio} dynamical mean-field theory (DMFT) calculations are based on the full-potential augmented plane-wave basis as implemented in WIEN2K.\(^48\) For these calculations, we used the largest possible muffin-tin radii, and the basis set plane-wave cut-off as defined by \(R_{\text{min}} \cdot K_{\text{max}} = 8\), where \(R_{\text{min}}\) is the muffin-tin radius of the oxygen atoms. The consistency between VASP and WIEN2K results has been cross-checked.

We perform the DMFT calculations in a basis set of Maximally Localised Wannier Functions (MLWF) using Wannier90\(^49\) and the wien2wannier\(^50\) interface. DMFT calculations were performed using the TRIQS/DFTTools package\(^51\)-\(^53\) based on the TRIQS libraries.\(^54\) Projective Wannier functions using the DMFTproj module of TRIQS/DFTTools were used to calculate the initial occupancies of the correlated orbitals. DMFT calculations in both MLWF and projective Wannier function (DMFTproj) basis was found to yield consistent results. In both cases a projection window of -8 eV to +2 eV was chosen. For both paramagnetic and magnetic calculations, Ni \(d\) and O \(p\) orbitals have been considered for the DMFT calculation, since the O \(p\) orbitals are higher in energy and closer to Ni \(d\) orbitals and are, thus particularly important in case of LiNiO\(_2\) and NiO\(_2\) where a significant charge transfer is expected. Calculation of \(d\) and \(p\) occupancies using DMFTproj in this energy range yields significantly different occupancies from the expected formal oxidation states for each element which is adjusted only slightly by DMFT calculations on the \(d\) manifold with projections for O \(p\) calculated and made part of the bath.

It is to be noted that Ni \(d\) states strongly hybridise with O \(p\). This hybridisation may also in general be taken into account by considering a downfolded \(d\) only orbital basis, in which O \(p\) degrees of freedom are not thrown away but included in the tail of the \(d\) Wannier functions (as shown in Fig. 1). However, this excludes any charge transfer possibility between Ni \(d\) and O \(p\) orbitals, which is imminent in case of LiNiO\(_2\) and NiO\(_2\) since the \(d\)-\(p\) split \(\Delta\) is smaller than or at best equal to \(U\) and should facilitate charge transfer. It is also to be noted that due to the large \(d\)-\(p\) split \(\Delta\) a
simple downfolded \textit{d only} orbital basis is sufficient to describe NiO. In both NiO\textsubscript{2} and LNO due to the presence of trigonal distortion in the NiO\textsubscript{6} octahedra, the \textit{t\textsubscript{2g}} orbitals are not degenerate, rather they are split into singly degenerate \textit{a\textsubscript{1g}} and doubly degenerate \textit{e\textsubscript{g}}-\pi. The energy difference between \textit{a\textsubscript{1g}} and \textit{e\textsubscript{g}}-\pi is small, hence may be treated as almost degenerate. Wannier90 projects to a local coordinate system, and hence any projections with spherical harmonics correctly identify the orbitals in their projections.

The Anderson impurity problems were solved using the continuous-time quantum Monte Carlo algorithm in the hybridisation expansion (CT-HYB)\textsuperscript{55} as implemented in the TRIQS/CTHYB package.\textsuperscript{56} We performed both one-shot and fully charge self-consistent calculations, with the double-counting correction treated in the fully-localised limit.\textsuperscript{31} A good agreement of both methods is seen. We used the full rotationally-invariant version of the Kanamori interaction.\textsuperscript{57} For our calculations we used \textit{U}\textsubscript{dd} values ranging from 4.5 – 8 eV and \textit{J} varying between 0.5 - 0.75 eV to investigate the whole spectrum of metal-to-insulator transition. We set the intra-orbital interaction to be \textit{U'} = \textit{U} - 2\textit{J}.

Real-frequency results have been obtained using the maximum-entropy method of analytic continuation of the Green’s functions as implemented in the TRIQS/MAXENT module.\textsuperscript{58}

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