Thermodynamically-Favoured Bulk O_2 Formation on Charging in $LiCoO_2$ and $LiNiO_2$ Cathode Materials

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(Dated: November 27, 2024)

The formation of O_2 molecules within the bulk of $LiCoO_2$ and $LiNiO_2$ cathode materials during charging has been reported experimentally, but the validity and significance of these observations remain debated. Using density functional theory calculations, we demonstrate that at high states of charge, layered $LiNiO_2$ and $LiCoO_2$ are thermodynamically unstable with respect to both O_2 gas release and internal decomposition forming bulk-confined O_2 molecules, indicating that, from a thermodynamic perspective, the oxygen chemistry of these stoichiometric layered oxides parallels that of Li-rich oxides, and may likewise limit their long-term cycling stability.

The useful energy density of transition metal (TM) oxide lithium-ion cathodes over repeated charge-discharge cycles is limited by their oxygen chemistry. At high voltage, TM-oxide cathodes release gas-phase O_2, with this process linked to structural degradation, capacity loss, and gas build-up in cells [1]. It has recently been observed that in some TM-oxide cathodes, O_2 molecules also form within the bulk [2]. This bulk O_2 formation is linked to the formation of voids [3–7], and results in energy-density loss that cannot be prevented through surface engineering only.

Bulk O_2 formation was first identified in Li-rich ($Li_{1+x}M_{1-x}O_2$) cathodes (where M = Mn, Co, Ni), from resonant inelastic X-ray scattering (RIXS) data, magnetic probes, and neutron diffraction [2, 8]. The standard explanation for O_2 formation in Li-rich cathodes is that the full charge capacity of these materials cannot be accounted for by formal TM redox alone [2], assuming a maximum accessible TM oxidation state of 4+. The additional capacity then is attributed to partially reversible bulk O_2 formation [2], associated with oxidation of O^{2-} ions with collinear Li–O–Li coordination [9].

Recently, bulk O_2 formation has been reported in Ni-rich Li-stoichiometric ($LiMO_2$-based) cathode materials, suggesting possible similarities with the oxygen chemistry of Li-rich cathodes and raising questions about their internal degradation processes. However, the interpretation of the characteristic RIXS signature of molecular O_2 in charged $LiNiO_2$ [4, 10] as evidence for bulk O_2 has been contested [11].

The possibility of bulk O_2 formation in $LiMO_2$ cathodes could be considered surprising when considered in the context of prevailing explanations for O_2 formation in Li-rich cathodes. In $LiMO_2$ cathodes, TM oxidation to a formal 4+ oxidation state can fully account for the theoretical capacity at the top of charge, seemingly negating the need for O oxidation to charge-balance Li^+ extraction. Moreover, in non-defective layered $LiMO_2$ cathodes, the collinear Li–O–Li coordination proposed as necessary for O^{2-} oxidation [9] is absent.

An alternative view of possible O_2 formation is provided by considering the corresponding chemical reaction from a thermodynamic perspective. For a fully delithiated cathode material MO_x, the thermodynamic driving force for forming O_2 is governed by the reaction

$$MO_x \rightarrow MO_y + \frac{x - y}{2}O_2 \quad (y < x). \qquad (1)$$
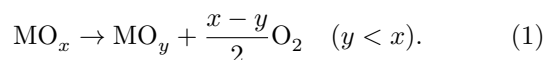
O_2 release from charged $LiNiO_2$ and $LiCoO_2$ can be rationalised if this reaction has a negative free energy change when the O_2 product is gas-phase [12]. Consequently, delithiated CoO_2 and NiO_2 are metastable and, if possible, will decompose into molecular O_2 and a more metal-rich oxide, MO_y, with the O_2 released as gas. Their ability to be cycled without decomposing is due to kinetic stability, specifically a combination of self-limiting oxygen release from the surface and kinetically slow TM cation diffusion in the bulk [12].

From a thermodynamic perspective, O_2 release and bulk O_2 formation differ only in the location and degree of confinement of the resulting O_2 [13]. Bulk O_2 forms at internal surfaces rather than at the external surface and is confined to a small volume within the cathode, resulting in a higher molar free energy. In Li-rich cathodes (e.g., Li_2MnO_3-based), reaction (1) has a negative free energy change for both O_2 release [14] and bulk O_2 formation [7], consistent with experimental observations of both phenomena in these systems. This established behaviour in Li-rich systems provides a valuable point of comparison for thinking about the oxygen redox chemistry in stoichiometric $LiMO_2$ cathodes.

To assess the thermodynamic drive for $LiMO_2$ (M = Co and Ni) cathodes at high states of charge to form trapped O_2, we computed formation energies of structures along the O_2–MO_2–MO tie-line for each system using density functional theory. These calculations employed the r^2SCAN+rVV10 functional due to its accuracy describing O–O bonding energies (Methods). For the O_2 end-member, we considered both gas-phase O_2
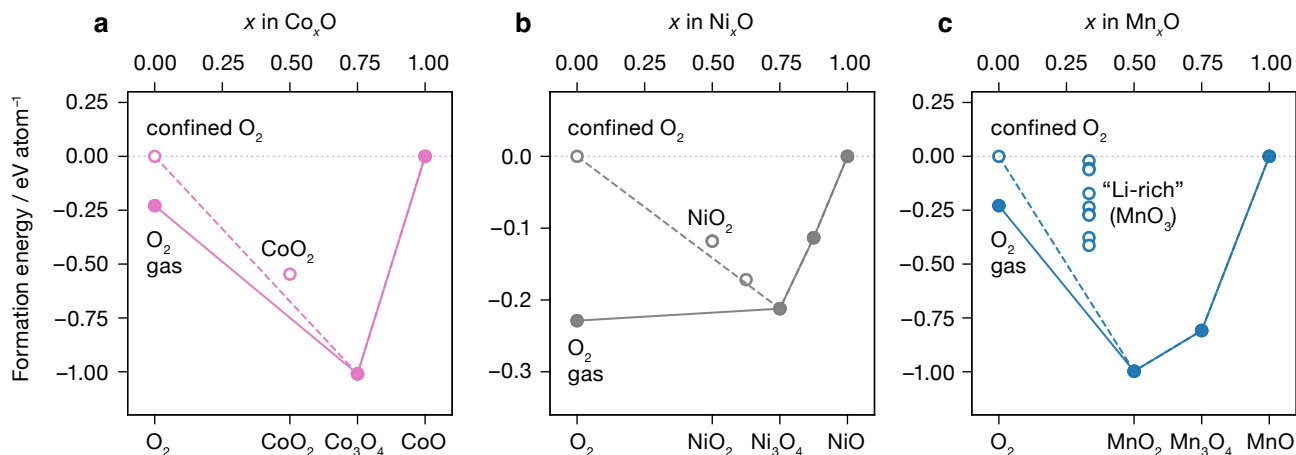
FIG. 1. Formation energy versus composition plots showing the thermodynamic stability of delithiated LiMO$_2$ cathode materials. The x-axis represents the composition of the structures along the O$_2$–MO$_2$–MO tie-line, while the y-axis represents their formation energy. Tie-lines are constructed for M = (a) Co, (b) Ni, (c) Mn with the O$_2$ end-member calculated either as gas-phase O$_2$ (solid lines) or O$_2$ confined within the bulk (dashed lines). Filled markers denote ground-state structures, while empty markers represent metastable structures.

and O$_2$ confined in the cathode bulk. For comparison, we include equivalent data for the O$_2$–MnO$_2$–MnO system. Our calculated formation energies are presented in Fig. 1 as convex hull plots: points above each convex hull correspond to phases that are unstable with respect to decomposition into competing phases with the same average composition; this condition corresponds to a negative free energy change for reaction (1), while points on the convex hull are thermodynamically stable.

The free energy of bulk-confined O$_2$ is higher than that of gas-phase O$_2$ by ~ 0.23 eV/atom due to its high density (~ 1.7 g cm^{-3}) [7]. Despite this, our results predict that layered CoO$_2$ and NiO$_2$ are both unstable with respect to decomposition into their respective metal-rich MO$_x$ phases ($x < 2$) and molecular O$_2$, even if the O$_2$ is then confined in the bulk (Fig. 1(a,b)). In contrast, MnO$_2$ is thermodynamically stable (Fig. 1(c)). As a point of comparison, we also show points for delithiated Li-rich Mn-oxides, MnO$_x$ ($x > 2$), which are predicted to be unstable with respect to forming gas-phase or confined O$_2$, in agreement with previous studies [7, 14].

Our analysis indicates that formation of bulk-trapped O$_2$ is thermodynamically favourable in Li-stoichiometric layered LiCoO$_2$ and LiNiO$_2$ on charging, just as in Li-rich Li$_{1+x}$M$_{1-x}$O$_2$ cathode materials. This result explains experimental reports of the RIXS signature of molecular O$_2$ in LiNiO$_2$-based stoichiometric cathodes, [4, 10, 11] and observed void formation [4, 6, 10]. These phenomena are linked: voids correspond to regions containing only O$_2$ and are formed by TM migration [7], driven by phase separation of delithiated MO$_2$ into O$_2$ and MO$_x$ ($x < 2$).

Recent DFT calculations have shown that in charged LiNiO$_2$, O$_2$ formation is energetically favourable at twin

boundaries [15]. Our results extend this understanding, indicating that the formation of bulk O$_2$ is thermodynamically favoured even in the perfect crystal. However, the formation of O$_2$ within the bulk of stoichiometric cathode materials depends not only on the thermodynamics but also on the kinetics of this process. O–O dimerisation requires localisation of holes on specific O^{2-} ions, and this is likely facilitated by point and extended defects that break crystalline symmetry. Any consequent O^{2-} formation will further disrupt the local crystal structure, enabling subsequent hole trapping and associated O^{2-} formation and, potentially, void growth.

Our results suggest that the long-term cycling stability in LiMO$_2$-based cathode materials depends on kinetic stabilisation not only of their surfaces but also within their bulk. As such, one potential strategy to enhance stability is to minimise defects that may act as nucleation sites for bulk O$_2$ formation.

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[1] H. Zhang, H. Liu, L. F. J. Piper, M. S. Whittingham, and G. Zhou, Oxygen loss in layered oxide cathodes for Li-ion batteries: Mechanisms, effects, and mitigation, Chem. Rev. **122**, 5641 (2022).
[2] R. A. House, J.-J. Marie, M. A. Pérez-Osorio, G. J. Rees, E. Boivin, and P. G. Bruce, The role of O$_2$ in O-redox cathodes for Li-ion batteries, Nat. Energy **6**, 781 (2021).
[3] A. Grenier, G. E. Kamm, Y. Li, H. Chung, Y. S. Meng, and K. W. Chapman, Nanostructure transformation as a signature of oxygen redox in Li-rich 3d and 4d cathodes, J. Am. Chem. Soc. **143**, 5763 (2021).

[4] A. Mikheenkova, S. Mukherjee, M. Hirsbrunner, P. Törnblom, C.-W. Tai, C. U. Segre, Y. Ding, W. Zhang, T. C. Asmara, Y. Wei, T. Schmitt, H. Rensmo, L. Duda, and M. Hahlin, The role of oxygen in automotive grade lithium-ion battery cathodes: an atomistic survey of ageing, J. Mater. Chem. A **12**, 2465 (2024).

[5] E. Zhao, K. Wu, Z. Zhang, Z. Fu, H. Jiang, Y. Ke, W. Yin, K. Ikeda, T. Otomo, F. Wang, and J. Zhao, Quantifying the anomalous local and nanostructure evolutions induced by lattice oxygen redox in lithium-rich cathodes, Small Methods **6**, 2200740 (2022).

[6] R. Lin, S.-M. Bak, Y. Shin, R. Zhang, C. Wang, K. Kisslinger, M. Ge, X. Huang, Z. Shadike, A. Pattammattel, H. Yan, Y. Chu, J. Wu, W. Yang, M. S. Whittingham, H. L. Xin, and X.-Q. Yang, Hierarchical nickel valence gradient stabilizes high-nickel content layered cathode materials, Nat. Commun. **12**, 2350 (2021).

[7] K. McColl, S. W. Coles, P. Zarabadi-Poor, B. J. Morgan, and M. S. Islam, Phase segregation and nanoconfined fluid O_2 in a lithium-rich oxide cathode, Nat. Mater. **23**, 826 (2024).

[8] R. A. House, H. Y. Playford, R. I. Smith, J. Holter, I. Griffiths, K.-J. Zhou, and P. G. Bruce, Detection of trapped molecular O_2 in a charged Li-rich cathode by neutron PDF, Energy Environ. Sci. **15**, 376 (2022).

[9] D.-H. Seo, J. Lee, A. Urban, R. Malik, S. Kang, and G. Ceder, The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials, Nat. Chem. **8**, 692 (2016).

[10] M. Juelsholt, J. Chen, M. A. Pérez-Osorio, G. J. Rees, S. De Sousa Coutinho, H. E. Maynard-Casely, J. Liu, M. Everett, S. Agrestini, M. Garcia-Fernandez, K.-J. Zhou, R. A. House, and P. G. Bruce, Does trapped O_2 form in the bulk of $LiNiO_2$ during charging?, Energy Environ. Sci. **17**, 2530 (2024).

[11] A. S. Menon, B. J. Johnston, S. G. Booth, L. Zhang, K. Kress, B. E. Murdock, G. Paez Fajardo, N. N. Anthonisamy, N. Tapia-Ruiz, S. Agrestini, M. Garcia-Fernandez, K. Zhou, P. K. Thakur, T. L. Lee, A. J. Nedoma, S. A. Cussen, and L. F. J. Piper, Oxygen-redox activity in non-lithium-excess tungsten-doped $LiNiO_2$ cathode, PRX Energy **2**, 013005 (2023).

[12] M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, and A. Van der Ven, Narrowing the gap between theoretical and practical capacities in Li-ion layered oxide cathode materials, Adv. Energy Mater. **7**, 1602888 (2017).

[13] R. A. House, J.-J. Marie, M. A. Pérez-Osorio, G. J. Rees, E. Boivin, and P. G. Bruce, The role of O_2 in O-redox cathodes for Li-ion batteries, Nature Energy **6**, 781 (2021).

[14] J. Vinckeviciute, D. A. Kitchaev, and A. Van der Ven, A two-step oxidation mechanism controlled by Mn migration explains the first-cycle activation behavior of Li_2MnO_3-based Li-excess materials, Chem. Mater. **33**, 1625 (2021).

[15] A. G. Squires, L. Ganeshkumar, C. N. Savory, S. R. Kavanagh, and D. O. Scanlon, Oxygen dimerization as a defect-driven process in bulk $LiNiO_2$, ACS Energy Lett. **9**, 4180 (2024).