

Singlet oxygen formation in Ni-rich cathodes for Li-ion batteries



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Ni-rich cathode materials achieve both high voltages and capacities in Li-ion batteries but are prone to structural instabilities and oxygen loss via 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. Using density functional theory calculations and dynamical mean-field theory calculations based on maximally localised Wannier functions, we find that the origin of the material's instability lies in the pronounced oxidation of O during delithiation, *i.e.*, O plays a central role in Ni-O redox in LiNiO₂. Predicted XAS Ni K and O K-edge spectra are in excellent agreement with experimental XAS spectra, confirming the predicted charge states. The calculations also show that a high-voltage O K-edge feature at 531 eV previously assigned to lattice O-redox processes could alternatively arise from O-redox induced water intercalation and O-O dimer formation with lattice O at high states of charge. The O₂ surface loss route observed here consists of 2 surface O^{•-} radicals combining to form a peroxide ion, which is oxidised to O₂, leaving behind 2 O vacancies and 2 O²⁻ ions: effectively 4 O^{•-} radicals disproportionate to O₂ and 2 O²⁻ ions. The reaction liberates *ca.* 3 eV per O₂ molecule. 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 providing the free energy required for the formation of ¹O₂ in its excited state.

1. A. R. Genreith-Schriever, et al. *Joule* **2023**, 7, 1623-1640.
2. A.R. Genreith-Schriever, CS Coates, K Märker, ID Seymour, EN Basse, CP Grey, *Chem. Mater.* **2024**, 6, 4226.
3. A.R. Genreith-Schriever, et al. *Chem. Mater.* **2024**, 36, 2289, eadf874.
4. AR Genreith-Schriever, JP Parras, HJ Heelweg, RA De Souza, *ChemElectroChem*, **2020**, 7, 4694.

Annalena is a postdoctoral researcher in Prof. Clare Grey's group, exploring materials for future batteries. Following her B.Sc. and M.Sc. degrees in Chemistry at RWTH Aachen, Annalena devoted her PhD to oxygen-ion transport in resistively switching devices for data storage, working with Prof. Dr. Roger De Souza. In her first postdoc, she explored the electrical resistance arising at grain boundaries in high-performance oxides.

With a passion for interdisciplinary discourse, Annalena pursued an additional undergraduate degree in Theology at RWTH Aachen and an M.Phil. in Philosophical Theology at Cambridge working on the dialogue between Philosophy/Theology and the natural sciences. Her current research has been awarded the postdoc scholarship of the Leopoldina German National Academy of Sciences.

