



## Chemistry Colloquium

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

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Host: Stefan Freunberger

**Title:** Singlet oxygen formation in Ni-rich cathodes for Li-ion batteries  
**Abstract:** 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 O<sub>2</sub> loss from the (012) surface of delithiated LiNiO<sub>2</sub>, 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 LiNiO<sub>2</sub>. 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 O<sub>2</sub> surface loss route observed here consists of 2 surface O•- radicals combining to form a peroxide ion, which is oxidised to O<sub>2</sub>, leaving behind 2 O vacancies and 2 O<sub>2</sub><sup>-</sup> ions: effectively 4 O•- radicals disproportionate to O<sub>2</sub> and 2 O<sub>2</sub><sup>-</sup> ions. The reaction liberates ca. 3 eV per O<sub>2</sub> molecule. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion, with spin conservation dictating the preferential release of 1O<sub>2</sub>, the strongly exergonic reaction providing the free energy required for the formation of 1O<sub>2</sub> in its excited state.

**Thursday, June 13, 2024 03:30pm - 04:30pm**

Moonstone / Ground floor / Seminar Room F



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