## 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 batteriesAbstract: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.

**Thursday, June 13, 2024 03:30pm - 04:30pm**
Moonstone / Ground floor / Seminar Room F

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