

Oxygen Hole Formation Controls Stability in LiNiO₂ Cathodes: DFT Studies of Oxygen Loss and Singlet Oxygen Formation in Li-Ion Batteries

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. We find that the origin of the instability lies in the pronounced oxidation of O during delithiation, i.e., O plays a central role in Ni O redox in LiNiO₂. For LiNiO₂, NiO₂, and the prototype rock salt NiO, 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). 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.