Understanding Oxygen Redox Activity in Li-Rich Cathode Materials: An Experimental and Theoretical Core-Level Spectroscopic Study

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Using oxygen redox reactions to obtain higher capacity in Li-ion batteries (LIBs) is an intriguing route. Despite numerous experimental and theoretical attempts to unravel the electronic origin of oxygen redox behavior, whether the oxidation of oxygen occurs via the formation peroxo-like species or depletion of electrons from non-TM-bonding states is still, however, an open question. It is also unclear how the electron-depleted oxygen states manifest themselves in experimental observations. In this study, using the Li-rich Li_5FeO_4 and and Li_2IrO_3 as model systems, we performed *ab-initio* Molecular Dynamics (AIMD) simulations to investigate the structural response of oxygen matrix to delithiation. The oxygen K-edge X-ray absorption near-edge spectra (XANES) were modeled using Bethe-Salpethe Equation (BSE) approach and compared with experiments, from which the oxygen redox mechanism is uncovered. This work demonstrates the effectiveness of combining experimental core-level spectroscopy with first-principles simulations to unambiguously identify the signature of oxygen reactivity, and has profound implications in understanding and exploiting the oxygen capacity in Li-rich LIB systems.