

MODULATING METAL-OXYGEN BONDING IN LITHIATED METAL OXIDES WITH POINT DEFECTS

William C. Chueh, Department of Materials Science & Engineering, Stanford University
wchueh@stanford.edu

The strength of the metal-oxygen (M-O) bond in oxides principally determines the band structure and the stability of oxygen relative to O₂ gas. Accordingly, such bonding is central to energy storage (for determining the redox potential) and electrocatalysis (for determining adsorbate bonding strength at the electrochemical interface). Traditionally, the M-O bond strength is tuned by changing the metal. We have recently discovered another important knob in Li_xMO₂: metal vacancies and antisite defects. In these materials, which are ubiquitous as positive electrodes in lithium-ion batteries, metal vacancies can form by moving a metal into the Li van der Waals gap. X-ray and neutron scattering measurements confirmed that introducing metal vacancies can substantially contract neighboring M-O bond length, transforming single bonds to double bonds (i.e., terminal metal oxo ligand). In select local configurations, even the peroxo species (O-O)²⁻ can form. These variations of oxygen bonding leads to dramatic variation in the energetics of the bonding and antibonding states as well as the stability of oxygen relative O₂ gas. In this talk, I will discuss the connection between local defect configurations and the M-O and O-O bonding in Li_xMO₂, where M spans 3d, 4d and 5d transition metals.