

Point Defects in Lithium Layered Oxides for Energy Storage

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The strength of the metal-oxygen (M-O) bond in oxides principally determines the band structure and the stability of oxygen relative to oxygen 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 lithium metal oxides (Li_xMO_2): 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 peroxy species $(\text{O-O})^{2-}$ 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 O_2 gas. In this talk, I will discuss the connection between local defect configurations and the M-O and O-O bonding in Li_xMO_2 , where M spans 3d, 4d and 5d transition metals.