

# Towards Stabilizing Positive Electrodes in Li-ion and Li-O<sub>2</sub> Batteries

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Understanding chemical / electrochemical reactions at the electrode – electrolyte interface (EEI, or often referred to as solid electrolyte interface, SEI) is essential to enhance stability and cycle life of Li-ion batteries. However, there is still limited understanding on the mechanism of formation, composition and effect of the EEI layer on charge-discharge performance<sup>[1]</sup>. Although an EEI model on the negative electrode side (Lithium metal, graphite) has been relatively well accepted in the past few decades, the mechanism of formation and understanding of EEI layers for positive electrodes is presently much less clear. Particularly, positive electrode active materials such as layered transition metal oxide (LiCoO<sub>2</sub>, LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub>, etc.) in different states-of-charge show different degrees of reactivity with carbonate based electrolyte, which are commonly used in Li-ion battery systems<sup>[2]-[4]</sup>. In addition, rechargeable Li-O<sub>2</sub> batteries have recently attracted enormous attention due to their high theoretical energy density. However, to realize reversible and stable operation of Li-O<sub>2</sub> batteries, many serious problems, such as electrolyte decomposition by O<sub>2</sub><sup>-</sup> radical, have to be solved.

Conventional electrolytes used for Li-ion and Li-O<sub>2</sub> battery research (with typical concentrations of ~1 mol/L) have a large proportion of free solvent molecules. These days, however, highly concentrated electrolytes have attracted much attention owing to their unique properties<sup>[5]</sup>. In solutions containing Li salts, due to electrostatic and induction interactions between Li<sup>+</sup> ions and the solvent, Li<sup>+</sup> is solvated by solvent molecules and forms a solvated [Li(solvent)<sub>n</sub>]<sup>+</sup> cation. With increasing concentration of Li salt, the amount of free solvent that does not participate in the solvation of Li<sup>+</sup> is decreased. In the extreme case, all of the solvent molecules are involved in the solvation, and free solvent is not present in solution. Electrolyte solutions with extremely high salt concentrations (≥ 3 mol/L) have been recently termed “solvent-in-salt” and/or “superconcentrated” electrolytes. It has already been reported that by changing lithium salt concentration, the proportion of solvent bound with Li compared with free solvent can influence the redox potentials of Li/Li<sup>+</sup> and O<sub>2</sub>/O<sub>2</sub><sup>-</sup><sup>[6], [7]</sup> as well as the reactivity of solvent molecules with O<sub>2</sub><sup>-</sup> radical species<sup>[8]</sup>. In this work, we report and review electrochemical investigations into Li-ion cathode materials (LiMO<sub>2</sub>) with composite and thin-film electrodes as well as oxygen cathodes to study the mechanism of SEI formation and the influence of the electrode-electrolyte interface and electrolyte concentration.

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