

Towards More Stable and Ion-Conductive Organic Electrolytes for Rechargeable Batteries

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Rechargeable batteries are important enablers of sustainable energy use, as they can be employed to store energy generated from renewable but intermittent source. The electrolyte in a battery physically separates and transports ions in between the electrodes to sustain electrochemical reactions. Enhancing the functionality of battery electrolytes, such as (electro)chemical stability and ion conductivity, can improve battery energy density, operation efficiency, and safety. This thesis explores strategies to improve the stability and ion conductivity of organic electrolytes for rechargeable batteries.

Special attention is given to aprotic lithium-oxygen (Li-O₂) batteries, which offer theoretical energy densities that are 2 to 4 times increase over the state-of-the-art Li-ion batteries (LIBs). Currently, the practical development of rechargeable Li-O₂ batteries is hindered by severe electrolyte degradations. Numerous families of organic solvents, polymers, and ionic liquids have been evaluated as electrolyte candidates; none are stable against the oxygen electrode in Li-O₂ batteries. Moreover, the decomposition pathways of many molecules are poorly understood.

To investigate the structure-property relationships governing the stability of organic molecules in the aprotic Li-O₂ electrode environment, we developed a comprehensive stability framework based on four key descriptors: bond dissociation energy, deprotonation free energy (i.e., acidity), nucleophilic substitution free energy, and electrochemical oxidation/reduction potentials. This framework was applied to a library of organic molecules with varied functionalities using density functional theory (DFT) calculations. Additionally, the chemical stability of the molecules was investigated experimentally. The computed and experimental results were in excellent agreement, and have been employed to identify unstable chemical moieties and to provide insight into the design of new electrolyte components that would be more stable in the Li-O₂ cathode environment. Using the guiding principles provided by this stability framework, we developed a number of fluorinated aryl sulfonimide salts as well as sulfamide- and sulfonamide-based solvents, and critically examined their (electro)chemical stability under the aprotic Li-O₂ condition, where interesting structure-stability relationships have been observed. Furthermore, the tradeoff between chemical and electrochemical oxidative stabilities was discussed. In particular, several electrolyte candidates have been found to exhibit promising (electro)chemical stability under testing conditions, highlighting the power of rational molecular design for the development of new organic electrolytes for the next-generation rechargeable batteries.

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