Probing of Reaction Mechanisms, and Development of Polymeric Materials for Lithium-Air Batteries

By

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Abstract

Limiting the use of fossil fuels is vital to stemming climate change. Incorporation of renewable energy technologies into the grid, and the shift to electric vehicles for transportation increases the need for better energy storage media. Lithium-air (O_2) batteries are of great interest because they have high theoretical energy densities. However, conventional Li–O_2 batteries face challenges such as the use of volatile and flammable liquid electrolytes, side reactions between the electrolyte/electrode with oxygen reduction products, and high charging overpotentials that lead to poor cycle life. We address these challenges by developing non-flammable polymeric-based electrolytes and electrodes, and investigate their performance and stability in Li–O_2 batteries.

In this thesis, we synthesized and studied the properties of a nonvolatile and nonflammable siloxane solid polymer electrolyte that can support Li–O_2 discharge, but show it is vulnerable to reaction with the desired Li_2O_2 discharge product. We developed a screening tool that involves mixing commercial Li_2O_2 with various polymers of interest for Li–O_2 batteries, and formulate polymer reactivity rules where the presence of electron-withdrawing groups on the polymer and adjacent hydrogen atoms make the polymer vulnerable to degradation.

Of the polymers studied in contact with Li_2O_2, poly(methyl methacrylate) was found to be stable, and then used as part of a gel polymer electrolyte with an ionic liquid (IL) and lithium salt. The Li/IL molar ratio in the GPE was shown to allow for a switch from a 2 e^- to 1e^- oxygen reduction chemistry, and the formation of ionic liquid-superoxide complexes as the discharge product. Exploiting this understanding of the influence of a bulky ionic liquid cation on the oxygen electrochemistry, we incorporate ammonium salts in a Li–O_2 battery and show it can also support discharge and lead to > 0.5 V reduction in charging overpotential when compared to lithium salts. Finally, we explore an electron conducting polymer electrode poly(3, 4-ethylenedioxythiophene) (PEDOT) as a Li–O_2 electrode and show the polymeric surface allows for oxygen reduction and Li_2O_2 formation. Coupling fundamental understanding with material selection can empower the design of next generation Li–O_2 batteries.

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