Exploration of catalytically-driven redox processes for electrochemical energy storage and conversion

by

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Abstract

Long-duration (e.g., days to months timescales) energy storage (LDES) technologies are necessary for broad deployment of renewable power generators. Electrochemical LDES requires inexpensive redox couples, of which several candidates necessitate an electrocatalyst to ensure sufficient reaction rates, efficiency, and/or selectivity to be economically feasible. Because electrocatalysts can also exhibit a broad range of negative behaviors (e.g., fouling, dissolution), it is important to quantify their durational performance. In this thesis I explore several catalyzed electrochemical systems intended for energy and/or hydrogen storage with a focus on durational performance. In **Chapters 1** and **2**, I respectively address the isopropanol/acetone and formate/bicarbonate redox couples, which are both promising for hydrogen storage in a relatively dense liquid medium. Primarily, I study the factors which influence 3-electrode experiments (often used to benchmark catalyst efficacy) of IPA oxidation on Pt and formate oxidation on Pd. My measurements highlight a persistent catalyst performance decay challenging interpretation of typically-employed cyclic voltammetry techniques and suggesting poor durational performance. A pulsed-potential catalyst remediation method is then shown to enable on-average higher reaction rates. Further, simple thermodynamic modeling for the formate/bicarbonate system hints at unique design considerations (sealed reservoirs, pressure management) for rechargeable reactor designs. In **Chapter 4**, I focus on the polysulfide ferri-/ferro-cyanide flow battery. First, using a diagnostic flow cell configuration, I explore the roles of elevated temperature and electrode material choices to increase device efficiency through elevating polysulfide reaction kinetics. Then, I discuss challenges with durational flow battery performance and design including those related to electrode stability and crossover. In **Chapter 5**, I use a model non-aqueous electrolyte system (employing a room-temperature-stable redox couple) to demonstrate the utility of accessible methods for interrogating performance gains (ohmics, kinetics, mass transport) and active species decay in elevated-temperature redox flow cells. Finally, in **Chapter 6**, I explore the exploitation of self-heating to elevate reactor performance through low dimension modeling. The extent of performance improvements is related to operating conditions (e.g., flow, current densities), system design (material choices, scale), and empirical/theoretical temperature-performance relationships, yielding simple models to assess tradeoffs and basic system design considerations. Investigations in this largely experimental thesis capture considerations for durational performance across redox chemistries, electrodes, and operating conditions (e.g., temperature, pressure) principally through the lens of electrochemical techniques.

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