Theory, Modeling, and Design Principles of Redox-mediated Electrochemical Systems

by

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Abstract:

Electrochemical systems offer a pathway toward directly harnessing sustainable electricity to manage intermittency in renewable power production, decarbonize transportation, and unlock new routes for chemical and material production. However, to compete with their thermochemical counterparts, emerging electrochemical processes of interest must achieve lower system costs, higher efficiencies, and longer operating lifetimes. Redox-mediated electrochemical systems are an emerging technology concept aiming to address these challenges. These devices utilize a chemical looping approach in which a soluble mediator species is circulated between an electrochemical reactor, where it is activated, and a chemical reactor, where the activated mediator drives an "off-electrode" chemical redox reaction. This decoupling of the desired chemical transformation from the electrochemical reactor simultaneously alters the underlying design landscape, offering new routes toward cost-effective reactor architectures and conversions. Redox-mediated processes have been demonstrated to improve the energy density of redox flow batteries, catalyze impractical or inefficient electrochemical transformations, increase selectivity and efficiency of separations and recycling, and facilitate spatial and temporal flexibility in chemical manufacturing. However, the complex interplay between the reactors and multiple active species obfuscates the underlying behavior of these systems, hindering efforts to understand, improve, and scale them.

In this thesis, I develop a continuum model framework capable of capturing and rationalizing the thermodynamics, reaction kinetics, and transport phenomena that govern the performance dynamics of redox-mediated systems for energy storage and conversion. Leveraging (electro)chemical engineering principles and drawing upon mixed potential theory (originally developed to describe metallic corrosion), the derived models qualitatively track datasets extracted from experimental redox-mediated systems. Such findings suggest the framework can provide new insights and avenues to probe system design and operation. I begin by relating physical and operational parameters to system-level performance trends in redox-mediated flow batteries, revealing performance regimes and a dimensionless "collapsed relationship" for solid utilization and tradeoffs in system energy and power. Guided by the assumptions and consequences of the underlying theory, I then pursue a suite of modeling and empirical analyses to uncover the implications of different system designs and operational protocols. Specifically, I investigate how "delocalized" charge transfer in conductive composites, cycling protocol, active material degradation, non-ideal thermodynamics, and intraparticle transport are anticipated to alter the underlying dynamics and system performance of redox-mediated flow batteries. Building off these developments for redox-mediated flow batteries, I shift to analyze emerging redox-mediated systems relevant to industrial chemical transformation, exploring continuously mediated solid transformations and mediated gas-evolving reactions as case studies. Ultimately, the goal of this thesis is to advance theory, analysis tools, and design principles that guide the study, development, and enhancement of emerging redox-mediated systems for sustainable energy conversion and storage.

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