Materials and Architectures for Convection-Based Electrochemical Energy Storage

by

Trent A. Weiss

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Abstract:

Electrochemical energy storage can support the transition to a sustainable energy economy by bridging the mismatch between renewable energy production and end-use requirements. However, displacing incumbent, carbon-intensive energy technologies requires storage systems that satisfy application-specific constraints in cost, performance, and safety. These metrics arise from coupled thermodynamic, kinetic, transport, and resistive processes that depend on both material properties and device architecture. Consequently, material-level advances only translate to improved device or system performance when the relevant architecture can access the expected benefits.

This dissertation examines materials and architectures for two convection-based electrochemical energy storage technology classes: convection-enhanced lithium-ion batteries and redox flow batteries. I begin with lithium-ion systems, where I investigate through-plane electrolyte convection as a strategy for improving species and heat transport. I construct prototype electrodes and cells using fabrication approaches closely aligned with conventional lithium-ion manufacturing, establishing platforms that reveal hydraulic access, mechanical integrity, and flow distribution as primary constraints on convection-enhanced operation. To address some of these limitations, I subsequently examine nonsolvent induced phase separation as a route to thicker, structurally controlled lithium-ion electrodes with greater mechanical rigidity. Using a polyacrylonitrile-lithium nickel manganese cobalt oxide electrode system, I connect composition and processing conditions to morphology, conductivity, and electrochemical behavior, showing how process-induced chemical interactions can be diagnosed and mitigated through modification of the materials set and fabrication route. I then transition to redox flow batteries, studying a model series of redox-active TEMPO oligomers to assess how oligomerization alters transport, electrochemical behavior, and flow-cell performance. This work shows that solution-phase electroanalytical properties of the oligomers translates directly to device-level operation, while also revealing that molecular size alone does not govern macromolecular transport. I next identify the mechanism responsible for suppressed electrochemical activity in concentrated TEMPO-based electrolytes near their solubility limits. Voltammetry and phenomenological simulations show that local accumulation of the oxidized species can drive transient interfacial phase formation, thereby limiting accessible redox activity during operation. Finally, I quantify the repeatability of a redox flow cell architecture, documenting its configuration and operation and measuring variability across repeated builds and multiple users, distinguishing platform-induced variability from material and operational effects. Collectively, these studies demonstrate that electrochemical energy storage technologies must be advanced across multiple scales, with material design, electrode processing, cell architecture, and system-level constraints considered together to identify practical pathways for improvement.

Thesis Supervisor: Fikile R. Brushett
Title: Ralph Landau Professor of Chemical Engineering Practice and Director of the Practice School