

# Evaluation of Redox Active Organic Molecules for Use in Nonaqueous Flow Batteries

by

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## Technical Summary:

Technical advances in grid energy storage are of critical importance to facilitate the integration of intermittent renewable sources and to improve the efficiency, reliability, and resiliency of existing fossil fuel infrastructure. Redox flow batteries (RFBs) are an electrochemical technology well suited for stationary energy storage applications due to independently addressable power and energy components, simplified system manufacturing, and long operating lifetimes. While state-of-the-art RFBs, which are based on redox active transition metal salts (*e.g.*, VOSO<sub>4</sub>) dissolved in acidic, aqueous electrolytes, have found success in niche applications, further cost reductions are needed for widespread adoption. This has motivated exploration of alternative redox chemistries including organic redox couples dissolved in nonaqueous electrolytes. Nonaqueous electrolytes offer the dual advantages of wider electrochemical stability windows and compatibility with a broader palette of candidate charge-storage materials. In addition, redox active organic molecules can be modified through targeted functionalization to impart preferred properties (*e.g.*, solubility, redox potential) and consist of earth abundant elements, which may enable scalable, low cost synthesis routes. If realized together, this approach offers a pathway to reduced system costs through increased energy density.

This thesis focuses on organic molecules intended for use as positive electrolyte materials in nonaqueous RFBs and builds upon existing knowledge of redox shuttle additives developed for overcharge protection in lithium-ion batteries. Though there is some overlap in desired properties for both applications (*e.g.*, extreme redox potential), transitioning from an additive to an active material presents new challenges related to solubility, stability, and atom economy. The two primary redox active cores examined in this work are substituted dialkoxybenzenes and phenothiazines. Both molecules served as learning platforms and were systematically functionalized, with one or more substituent groups, to elucidate structure-function relationships with particular emphasis on increasing solubility, gravimetric capacity, and redox potential. Initial efforts focused on the modification of 2,5-di-*tert*-butyl-1,4-bis(2-methoxyethoxy)benzene, a successful overcharge protection material, through subtractive engineering to identify stable minimal structures with increased charge storage capacity. Following these efforts, the impact of halidization was examined leading to a 300 – 400 mV increase in redox potential, but concomitant and severe reductions in cycling stability that trend with halide size. Due to limitations in the stability of the substituted dialkoxybenzenes, subsequent efforts were undertaken using *N*-ethylphenothiazine, another successful overcharge protection material which is more robust. Through an iterative approach of targeted functionalization, (1) the solubility was increased by greater than a factor of five and (2) the second electron transfer was stabilized on the phenothiazine

core resulting in redox active electrolytes with a volumetric charge storage capacity approaching the range envisioned for economically viable flow batteries.

While the moderate stability of the substituted dialkoxybenzenes appears to limit their applicability as active materials, they have utility as model compounds suitable for supporting the development and standardization of testing protocols for RFBs. As organic materials are emergent for flow battery applications, standardized testing protocols and benchmarking techniques have yet to be established, frustrating quantitative comparisons between new materials reported in the literature. To this end, new electrochemical methods are introduced for efficiently evaluating and reporting the stability of new redox active materials at dilute conditions, using bulk electrolysis cycling, and at concentrated conditions, using time-dependent microelectrode voltammetry, and are validated using substituted dialkoxybenzenes.

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