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## Organic Radicals for Symmetric Redox Flow Batteries

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## Summary

Redox flow batteries (RFBs) are considered one of the pivotal technologies for addressing the intermittency problem in renewable energy sources, due to their modular design that allows for the decoupling of power and energy and high cost-effectiveness in long-duration storage. Despite their promise, various techno-economic challenges have hindered the widespread commercialization of traditional metal-based RFBs. Alternatively, redox-active organic molecules have gained increased attention in the last decade as cheap and sustainable charge-storage material for organic RFBs. Conventional organic RFBs rely on two different active materials in the posolyte and negolyte to facilitate the positive and negative electrode half-reactions, respectively, though often suffer from irreversible capacity loss due to cross-contamination of electrolytes. To address these complications, there has been a surge in the development of symmetric RFBs constructed with identical electrolyte composition on both sides of the battery containing one single parent molecule which possesses bipolar electrochemistry.

In this thesis we present several new developments in the field of (symmetric) organic RFBs, which are the following: (1) development of Blatter radicals as novel bipolar redox-active organic molecules for both aqueous and non-aqueous symmetric RFBs. (2) Study of decomposition pathways of electrolytes containing Kuhn's verdazyl and Blatter radicals as active material that occur during battery charge/discharge cycling. Gaining a better understanding of the degradation mechanism at play is essential for the design of more stable battery material. (3) Method development of *in situ* NMR spectroscopy for studying battery performance during cycling. A detailed outline of the research results achieved in the projects is as follows:

In **chapter 2**, the (electro)chemical properties and battery performance of electrolytes employing the Kuhn-type verdazyl radical as bipolar active material are studied. Charge/discharge cycling experiments in an H-cell battery showed a gradual decay in capacity. Both the cycling data and post-cycling analysis of the spent electrolytes suggest that, rather than the charged states, degradation of the parent verdazyl radical is responsible for the loss of capacity. DFT calculations and kinetic experiments provide insights in the decomposition mechanism, which is shown to occur via bimolecular disproportionation leading to the formation of diamagnetic leuco-verdazyl and 1,2,4-triazole. Our data suggest that sterically blocking the CH<sub>2</sub> group in the heterocyclic core of the verdazyl radical, or replacement of the hydrogens of said group by substituents that are not easily abstracted, could potentially increase the battery lifetime.

In **chapter 3**, 1,2,4-benzotriazin-4-yl radicals (commonly known as Blatter radicals) are reported as a highly promising class of bipolar materials for symmetric RFBs. The bipolar electrochemistry of Blatter radicals in organic solvents is explored on the cyclic voltammetry timescale (seconds to minutes) and the timescale required for battery applications (weeks and more). Moreover, addition

of water (up to 33 vol%) does not affect the electrochemical reversibility, though the reduction potentials shift to more positive values leading to a decrease in cell potential. The redox potentials of derivatives with an electron-withdrawing C(3)-substituent are least affected by the presence of water, which is ascribed to their lower basicity. Electrolyte solutions employing C(3)-CF<sub>3</sub> substituted Blatter radicals as active material display exceptionally high capacity retention (~94%) after continuous cycling in a H-cell battery setup. A pumped cell test with a representative radical at 0.1 M concentration exhibited an overall capacity retention of 98% after 100 cycles (32 hours) and demonstrated that polarity inversion in a symmetric RFB may be used to rebalance the cell.

In **chapter 4**, the design, synthesis, and electrochemical characterization is reported of several water-soluble Blatter radicals bearing either one or two sulfonate groups. At neutral pH, the cyclic voltammograms display the reversible bipolar electrochemistry of the Blatter radicals with theoretical cell potentials between 0.6 - 0.7 V. At low pH, the reduction processes of the radicals shift anodically resulting in a dramatic decrease in theoretical cell voltage. Whereas, at high pH, the oxidation process becomes completely irreversible indicating that OH<sup>-</sup> has a detrimental influence on the stability of the oxidized state. All things considered, our data suggest that the sulfonated Blatter radicals have great potential to be employed as bipolar material at neutral pH in symmetric aqueous RFBs.

In **chapter 5**, a Blatter radical bearing a “distant” fluorine-containing moiety (-OCF<sub>3</sub>) is prepared to aid in the detection of the redox-active material by NMR spectroscopy. Both the changes in the chemical shift of the OCF<sub>3</sub> resonance on <sup>19</sup>F NMR and the changes in solvent bulk magnetization on <sup>1</sup>H NMR can be used as a (direct) indicator of the state-of-charge (SOC) of a battery when implementing *in situ* NMR spectroscopy during cycling. This provides the opportunity to correlate electrochemical data (e.g. capacity fade) to molecular decomposition. Battery cycling of a symmetric H-cell employing the Blatter radical as active material displays a sudden decay in capacity after prolonged charge/discharge cycling. Post-cycling analysis of the spent electrolytes indicate that the capacity decay is accompanied with decomposition of the supporting electrolyte and etching of the borosilicate glass of the H-cell. Initial decomposition studies demonstrate that the presence of the oxidized species and water play a significant role in the electrolyte degradation.