



Three Oxidation States for Renewable Energy Storage

Abouti Mounir and Dr. Nora Planas-Roure ❖ Chemistry Department ❖ University of Wisconsin-Eau Claire
❖ Eau Claire, Wisconsin 54702



Abstract

In today's economy, energy based on fossil fuels is destined to end. There is a strong possibility that we will eventually run out of fossil fuels, but with the emergence of renewable energy a promising alternative is presented. One of the main obstacles preventing the implementation of renewable energy is the lack of low cost and efficient energy storage technologies [1]. Redox flow batteries (RFBs) are fully rechargeable electrochemical energy storage devices that convert and store electrical energy into chemical energy and release it in a controlled fashion, when required. RFBs have low operation costs and high storage efficiency. However they often suffer from low voltage (~1.2V) and cross contamination.

In this research project, we aim to overcome the limited voltages by designing new first row transition metal complexes as electrolytes (chemical species responsible for energy storage). We have synthesized a family of polypyridyl ligands, which, after metalation, will yield a series of metal complexes. The resulting species can be characterized by spectroelectrochemical techniques. The electrochemical properties of the complexes will be tested by cyclic voltammetry to determine the maximum voltage attainable. With this study we aim to gain insight towards a rational design of future electrolytes with improved properties.

Background Information

In a RFB during the electrical energy is stored in two soluble redox couples separated by a membrane and contained in external electrolyte tanks. The fluids containing electro-active materials (electrolytes) are pumped from the storage tanks to flow through electrodes where chemical energy is converted to electrical energy (discharge) or vice versa (charge). Current large-scale RFB technologies provide high conductivity, easy purification and low cost [2]. The issue is that the battery voltages are typically limited (~1.2 V) and the devices suffer from cross-contamination across the membrane. The idea in this project is to overcome the main known limitations that hinder the large-scale implementation of RFB by employing First Row transition Metal Complexes as electrolytes.

With the use of non-aqueous electrolytes the attainable cell voltage will be increased[3]. We will increase cell voltage by designing a single redox species with three possible oxidation states as the electrolyte system, so that the discharged species is the same on each side of the cell (A = C in Figure 1), the problem of cross-contamination is eliminated.

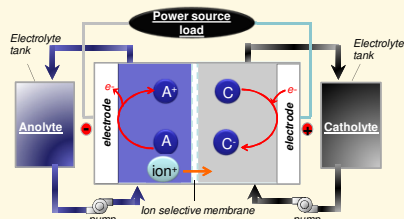


Figure 1. Illustration of a typical individual RFB system. In the discharge mode, an anolyte solution reacts with the anolyte electrode to generate electrons that flow through the external circuit. The charge-carrying species (Ion⁻) are then transported through an ion selective membrane to the catholyte solution that, in turn, reacts with the electrode recruiting electrons and closing the electrochemical cycle.

The prototype species explored for this task is tris(2,2-bipyridine)ruthenium (II) [Ru(bpy)₃]²⁺ which offers a possible cell potential of 2 V[4], or its iron analog, [Fe(bpy)₃]²⁺, which is significantly cheaper[5]. Despite of being more earth abundant and environmentally benign than their second and third row congeners, M(II) polypyridyl complexes (M=first row transition metal) have been explored to a lesser extent in the RFB field. This is due to the undesirable tendency of these metals to yield complexes which are highly labile. Ligand lability can be drastically reduced by employing multidentate ligands. However, some first row transition metals also suffer from having only two accessible oxidation states.

Objective

❖ In this work we will synthesize a new ligand family designed to make higher redox states accessible by the use of Anionic Binding Sites.

Hypothesis

❖ The introduction of the N-H moieties through the incorporation of pyrrole units within the ligand scaffold, will permit the alteration of the electrochemical properties of the metal complex species. The new ligands, through the deprotonation upon coordination will lower the redox potential of the higher oxidized species.

Results

❖ The polypyridyl ligand L_{N2AO} has been successfully synthesized following the synthetic procedure reported below[6]

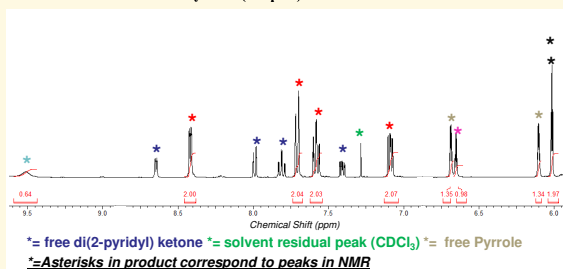
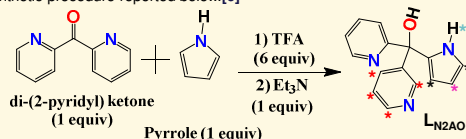
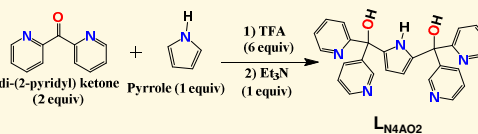
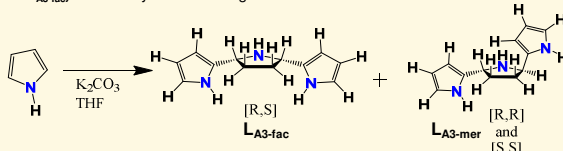


Figure 2. ¹H-NMR spectrum in CDCl₃ of the synthesis reaction crude.

❖ Current efforts are focused on the optimization of the synthesis protocol of another polypyridyl ligand (L_{N4AO2}) and the subsequent purification.



❖ A new family of polypyridyl ligands containing multiple pyrrole groups (L_{A3-mer} & L_{A3-fac}) is currently under investigation.



❖ Upon deprotonation, each pyrrole unit in ligands L_{N2AO}, L_{N4AO2}, L_{A3-fac}, and L_{A3-mer} should provide a negative nitrogen donor atom to coordinate to a metal center forming a coordination complex.

❖ Preliminary Molecular Mechanics structure optimization of the potential octahedral coordination complexes with general formula [Fe(L_{A3})Cl₃] predict that the ligand's isomer [R,S] could act as a tridentate meridional ligand whereas the [R,S] and [R,S] enantiomers would adopt a facial coordination mode.

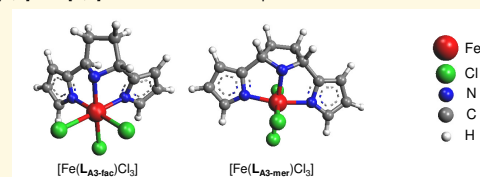


Figure 3. Ball and stick representation of the optimized structures for [Fe(L_{A3-fac})Cl₃] and [Fe(L_{A3-mer})Cl₃] using the molecular mechanic force field UFF.

❖ Once coordinated to a central metal ion, the presence of eight potential donor atoms (five N-based and two O-based) provides the possibility to obtain different linkage isomers. According to Hard-Soft Acid-Base Theory the N-donor atoms are expected to be preferred in lower oxidation states whereas O⁻-donor atoms should be preferred by higher oxidation states.

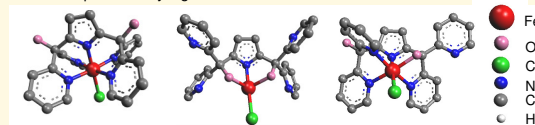


Figure 3. Ball and stick representation of the optimized structures for three representative linkage isomers for [Fe(L_{A3AO2})Cl] using the molecular mechanic force field UFF. Hydrogen atoms have been omitted for clarity.

Methods

❖ The ligand synthesis has been carried out under an Argon atmosphere using Schleck techniques and the products have been characterized through 1D and 2D ¹H NMR on a Bruker 400 MHz instrument.

❖ Coordination complex geometries have been optimized by means of Molecular Mechanics calculations employing UFF force field as implemented in Argus Lab software[7].

Future Work

❖ Optimize the synthetic and purification procedures for this new family of Polypyridyl ligands.

❖ Metallate the new ligands and separate and characterize the resulting coordination complex isomers through spectroscopic, electrochemical and quantum chemical calculations.

❖ Assess the influence of the different coordination environments induced by the various isomers on the redox properties and complex stability in view of their potential application as single electrolyte component in RFB's.

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Acknowledgments

❖ Special thanks to UWEC Office of Research and Sponsored Programs (ORSP) & UWEC Learning & Technology Services

❖ Special thanks to Dr. David Lewis for insightful discussions