Evaluating Aqueous Flow Battery Electrolytes: A Coordinated Approach

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PERSPECTIVE

Evaluating Aqueous Flow Battery Electrolytes: A Coordinated Approach

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Here, we outline some basic pitfalls in the electrochemical investigation of aqueous metal complexes and advocate for the use of bulk electrolysis in redox flow cells for electrolyte analysis. We demonstrate methods of operation and performance of a lab scale redox flow battery (RFB), which is assembled from unmodified, commercially-available material and cycled with a vanadium electrolyte in order to provide a comparative baseline of expected performance. Common misconceptions about the thermodynamic window for water splitting are addressed and further express the need to develop next generation aqueous redox flow battery electrolytes. Although non-aqueous electrolytes are a popular approach, they suffer from distinct challenges that limit energy and power density in comparison with aqueous electrolytes. Expanding the scope of aqueous electrolytes to include metal-chelate complexes allows electrolytes to be as tailorable as organic species, while maintaining robust metal-based redox processes. A flow battery assembly and operation guide is provided to help facilitate the use of flow battery testing in the evaulation of next generation electrolytes.

1. Introduction

In May of 1986, Prof. Skyllas-Kazacos published a brief communication reporting a “New All-Vanadium Redox Flow Cell”,[1] which formed the basis for vanadium redox flow battery (VRFB) technology that is now being implemented to store gigawatt-hours of electrical energy around the world.[2–4] One year before this monumental report, her group reported a detailed electrochemical study of the aqueous $V^{3+/2+}$ redox couple using cyclic voltammetry (CV), noting that when using a finely polished glassy carbon electrode, “no peaks corresponding to the reduction of V(III) could be observed.”[5] A quasi-reversible current response was observed only after increasing the concentration of VCl_3 to 110 mM, increasing the sulphuric acid/sulphate concentration to 1.5 M, and “polishing” the electrode with 1200 grit sandpaper. This result highlights a key motivation for this perspective: *experimental electrochemical techniques need to go beyond basic cyclic voltammetry experiments to determine the chemical behaviour of a redox process.*

Here, we describe the need for renewed investigations into the redox properties of aqueous metal coordination complexes and highlight the importance of bulk electrolysis studies in small but scalable flow cell platforms. These flow cell platforms are composed of positive and negative liquid electrolytes which are continuously flowed across electrodes where redox reactions occur, and which utilize a membrane or separator between the positive and negative electrode to maintain charge balance. Interest in RFBs is partially driven by their all liquid nature, which intrinsically results in the decoupling of the scaling of energy and power, and therefore creates economic advantages for large scale energy storage systems. For our colleagues new or unfamiliar with these devices, we have provided a thorough experimental and operational procedure in the supporting information section detailing how to implement a high-performance flow battery cell in the evaluation of new flow battery chemistries. Finally, we briefly describe some opportunities for molecular coordination chemistry to address basic research on the inhibition of water splitting, oxidation state tuning, and multi-electron proton-coupled electron transfer (PCET) processes. Routine implementation of flow cells for electrochemical analysis can provide clearer insight into the bulk properties of reduced or oxidized species than CV or other half-cell studies, as well as enable determination of the efficiency of their synthesis on practical mmol scale.

2. Need for Aqueous Chemistries

Over the past thirty years, the performance and efficiency of electrochemical systems have been improved in part by the development of advanced membrane technologies. The implementation of proton-exchange membranes (PEMs) based on perfluorosulfonic acid (PFSA) functional groups resulted in large performance gains in both fuel cells and water electrolysis systems.[6,7] The high efficiency of PEM-based systems is a result of their high proton conductivity, which is critical for many PCET reactions employed in renewable energy applications.[8]

Flow batteries represent an important opportunity for molecular inorganic chemistry to contribute to critical aspects of our energy storage infrastructure. A considerable portion of the current basic research in this area continues to focus on non-aqueous systems,[9] which are often incompatible with high performance and efficient PEM-based electrochemical systems. Although aqueous electrochemistry laid the foundation for modern electrochemical studies, the study of aqueous coordination complexes has received less attention in recent decades, perhaps due to the rise in organometallic catalysis that prefer non-aqueous solvents. While acknowledging the benefit of continued research into non-aqueous coordination complexes, with the approaching demand for large-scale energy storage, we suggest that now is an opportune time for the inorganic chemistry community to revisit aqueous coordination complexes for new flow battery electrolytes.

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2.1 Challenges of Non-aqueous Flow Batteries

Non-aqueous redox flow batteries have been investigated for over 30 years due to their promise of improving the energy storage density of flow batteries through achieving higher voltages over aqueous systems.[9] One of the first reported systems exploited the redox properties of $Ru(bpy)_3{}^{1+/2+/3+}$ and demonstrated a 2.6 V cell potential, though the power output and efficiency were low.[10] Since this report, other non-aqueous systems have been reported using metals supported by acetylacetonate[11–15] and bipyridine,[16–18] among others.[19–21] Although these non-aqueous electrolytes often show promise for improving the storage density of aqueous systems through higher cell potential or multielectron redox processes, none can yet achieve the storage density, power performance, and efficiency of aqueous systems such as the all-vanadium RFB.[4,22]

There are several reasons for the shortcomings of non-aqueous flow batteries described in the literature. First, cell resistances are typically at least an order of magnitude higher in non-aqueous systems, meaning that when considering power output (V^2/R), the increased cell potential is cannibalized by resistive losses that lead to low discharge voltages and low efficiency.[23,24] Second, due to lower solvent dielectric constants, non-aqueous flow batteries often struggle to achieve high concentrations of electro-active species, and they have been suggested to run up against fundamental physical limitations in concentration, viscosity, ion conductivity, and diffusivity.[25] Finally, most non-aqueous solvents are not stable at the high potentials that have been promised.[9,26] It has been suggested that as molecules become more reducing, they often exhibit increased basicity, which can lead to “natural limitations to the energy density that is realistically achieved” for solvents such as acetonitrile due to chemically irreversible proton transfer reactions.[27] These challenges, most of which are based on fundamental physical properties, suggest that non-aqueous flow battery electrolytes do not provide an efficient platform for solution-phase electrochemical processes.

One argument often used in favor of non-aqueous electrolytes is that water is limited by the water splitting potential (1.23 V),[9] which restricts the energy storage capacity due to parasitic hydrogen and oxygen evolution reactions. This analysis, however, confuses the thermodynamic stability window of water with its reactivity, a fundamentally kinetic phenomenon. From a thermodynamic perspective, water is among the most stable solvents, with the 1.23 V window being defined by the ΔG_f of water (−237 kJ/mol)[28] through the equation $\Delta G = -nFE$. On the other hand, most organic solvents are thermodynamically *unstable* with respect to their elemental compositions. For example, the ΔG_f of acetonitrile is +86.5 kJ/mol,[29] implying a *negative* thermodynamic stability window.

Obviously, in practical terms, many redox processes can be carried out in acetonitrile because it is often kinetically inert towards electrochemical reactivity, but this distinction between the theoretical thermodynamic window and the working kinetic window is critical because unlike thermodynamics, the kinetics of a reaction can often be controlled and inhibited by the absence of reactive species or catalysts. For instance, using a highly inert fluorinated diamond electrode, a 5-Volt window was demonstrated for water, which is limited only by 1-electron redox processes that generate atomic hydrogen and hydroxyl radicals.[30]

In summary, non-aqueous flow batteries fall short of matching water in thermodynamic stability, high dielectric constant, and low cell resistance. Additionally, the higher voltage (>2.5 V) promised by non-aqueous flow battery chemistry is rarely proven stable for extended periods of time.[26] On this basis, we suggest that water provides the best electrolyte medium for high-efficiency flow batteries.

2.2 Opening the aqueous window with coordination chemistry

Despite the 1.23 V thermodynamic window of water, efforts to exploit the kinetics of water splitting in order to expand that effective redox window beyond 1.23 V are often employed, including the previously mentioned 5 V window on a fluorinated diamond electrode. A ubiquitous example of this overpotential exploit is the lead-acid battery, which operates in an aqueous acid electrolyte, yet has a 2.0 V nominal cell voltage and is utilized in most automobiles in the world. However, these attempts to increase the water splitting overpotential often are based on minimizing heterogeneous water splitting kinetics between water and the electrodes, such as utilizing carbon based electrodes in aqueous RFBs, and not on minimizing homogeneous water splitting kinetics between water and highly reducing or highly oxidizing species in solution.

By considering the kinetic processes that lead to water splitting, our group sought to improve the energy storage capacity of aqueous flow batteries by limiting the coordination of water to a transition metal ion. Recently, we demonstrated this ability through the use of ligands that inhibit the coordination of water to a highly reducing Cr^{2+} ion.[31] Due to the strong binding of the chelating ligand, 1,3-propanediaminetetraacetate (PDTA), which has an equilibrium binding constant, pK_a of 11.1 to Cr^{2+},[32] the complex is remarkably inert towards reaction with water, despite exceeding the thermodynamic potential for the hydrogen evolution reaction (HER) by over −600 mV at pH 8. We suggest that by preventing water from coordinating to Cr^{2+}, catalytic pathways for HER are avoided, leading to a large kinetic barrier to proton reduction. Comparison of the equilibrium cell potential of our flow battery chemistry based on $K_2CrPDTA$ and Br_2 (2.13 V) with that of a zinc-bromine hybrid flow battery (1.8 V) suggests that the reducing ability of $K_2CrPDTA$ exceeds metallic zinc by over 300 mV, and places it among the most reducing homogeneous species ever synthesized in aqueous solution without evolving hydrogen.

3. Full Cell Reaction Experiments

3.1 Need for full cell validation of half-reactions

We anticipate abundant opportunities to exploit the electrochemical properties of molecular coordination compounds for their use in energy storage and conversion processes. At the same time, coordination chemists are rarely familiar with the type of experimental techniques and electrochemical cell platforms required to accurately determine electrolyte performance in a working flow battery system.

Electrochemical analysis of a coordination complex typically begins with an investigation of the redox half-reaction using cyclic voltammetry. This technique uses a reference electrode, effectively isolating the redox reaction occurring at the working electrode from the counter electrode. Although this is essential for electrochemical analysis, this is not a bulk conversion process and typically operates on picomolar quantities of anolyte. Just as Skyllas-Kazacos observed a minimal electrochemical response from the $V^{3+/2+}$ redox couple using standard cyclic voltammetry conditions, this technique often proves inadequate as the sole tool for investigating the redox properties of small molecules. This is especially true for aqueous systems where higher solvent reorganization energies can reduce the electron transfer rate constant, and thus the observed current response, of redox processes.[33]

3.2 Advantages of the zero-gap cell architecture

A modern “zero-gap” PEM fuel cell design minimizes the separation between anode and cathode by incorporating an ion-selective membrane between the electrodes.[34] More than being an “applied” system, these cells enable bulk electrolysis of redox-active materials on the mmol scale using 10 mL of electrolyte. We contend that the efficient bulk study of redox active materials is every bit as important as measuring an isolated yield from a vial-scale reaction for a chemical reaction.

Bulk electrolysis using a flow battery can reveal key challenges with instability, solubility, and reactivity that are often obscured by simple CV experiments. For an ion or molecule to be a viable active species for energy storage, all oxidation states that would be present within the battery during operation need to be studied. However, because CVs are often performed at low concentrations, over a short timeframe, and with the bulk of the active species never being converted from the initial oxidation state, it can be very difficult to determine the long-term behaviour of any of the other oxidation states of the active species. As an example, for the common flow battery electrolyte $Fe(CN)_6$, the sodium salt solubility of the Fe^{3+} form is 1.20 M, while the Fe^{2+} form is less than half of that at 0.56 M.[35] If one only studied the Fe^{3+} form, one might overestimate the maximum energy density to be that of the Fe^{3+} form, but if tested in a flow battery at high concentration, solids would precipitate during operation. Similarly, many anthraquinone-based flow battery electrolytes have reversible CVs, but over time will slowly decompose or react with the solvent when in a particular oxidation state, which may not be able to be seen without long-term study of all oxidation states via bulk electrolysis.[36] Therefore, simply determining electrochemical reversibility via CV for a single oxidation state does not provide accurate information on the viability of that active species for usage within a battery system.[9]

A flow cell test also provides valuable knowledge about system level performance that one would not be able to determine if running in a static cell, such as an H-cell. Static cells suffer from large solution resistances, possibly unknown electrode surface area, and a diffusion limited maximum current unless the solutions are stirred. With the “zero-gap” structure minimizing cell contact resistance and the fluid flow minimizing mass transport limitations, accurate voltage and energy efficiency performance for a cell can be collected. The flow cell also allows for higher current densities to be achieved, which enables more charge/discharge cycles to be completed in an in an allotted amount of time, which can provide insight into any cycle-based decomposition mechanisms. The high current densities can also provide information on any membrane-based current limitations due to a maximum ion transport rate, which would not be evident at lower current densities of static cells.

3.3 Vanadium Flow Battery Example

Although PEM fuel cell and flow batteries were once custom made, they are now readily commercially available and easily assembled and used. To help disseminate this experimental tool to the chemistry community, we describe in the supporting information detailed assembly and operation procedures for a VRFB using commercially available materials. Using 10 mL of electrolyte (1.5 M $V^{3+/4+}$), we observed a peak power output of 675 mW cm^{-2} and round-trip energy efficiencies approaching 90% per cycle. The VRFB example provides an off-the-shelf test platform that is common among flow battery researchers exploring other flow battery chemistries including various redox-active organics,[37–39] inorganics,[34] and coordination complexes.[31,33,40] We hope that the detailed procedures enable more researchers to use these systems for novel flow battery chemistries and other electrochemical research.

4. Opportunities for Coordination Complexes

4.1 Challenges with Vanadium Flow Batteries

Increased deployment of VRFBs is limited primarily by the cost of vanadium in the electrolyte.[41,42] In addition, VRFB electrolytes are typically operated around 1.6 M because the VO_2^+ ion is unstable at high concentrations with respect to precipitation as V_2O_5.[43] The precipitation rate of VO_2^+ increases at higher temperatures while VO^{2+} precipitates at low temperatures, effectively limiting the operating temperature range of a VRFB from about 10 to 40 °C.[44] This limitation was addressed by the use of a mixed acid H_2SO_4/HCl electrolyte, which improved the solubility to 2.5 M and operating temperature range to −5 to 50 °C,[45] however the HCl makes the electrolyte significantly more corrosive to the cell and associated battery materials. Another challenge with vanadium is that the strongly oxidizing VO_2^+ can corrode carbon electrodes and requires the use of more expensive PFSA rather than hydrocarbon-based membranes for long-term stability.[46]

The challenges with VRFBs drive the need for further research and the development of new flow battery electrolytes. Recently, organics molecules based on anthraquinone,[37,47,48] phenazine,[38,49] and others[50,51] have shown promise as scalable alternatives to vanadium that can undergo 2-electron redox processes to further improve the energy density of the electrolyte. An ongoing challenge with organic systems, however, is addressing their long-term stability.[36] Other recent flow battery electrolytes include polymer based [52–54] and ionic liquid based systems.[55–57] However, these systems present their own challenges. Polymer electrolytes struggle with low energy density, less than 20 Ah/L, and ionic liquid systems, while able to achieve high energy density, suffer from issues with active species mass transport and membrane conductivity.[58]

Transition metal coordination complexes provide a compelling research direction because they can exploit the stability of metal-based redox processes and the tunability of organic ligands. We identify four areas of basic research that can be addressed using transition metal coordination complexes: inhibition of water splitting catalysis, inhibition of hydrolysis, control of reactive transition metal oxidation states, and multi-electron proton-coupled redox processes.

4.2 Inhibition of water splitting

Most commercially viable aqueous battery technologies, ranging from the VRFB to the lead acid battery, operate at voltages beyond the thermodynamic potential for water splitting without dramatic efficiency losses.[59] Just as there is a need to understand the mechanistic basis for catalytic water splitting reactions, we suggest that the design and basic understanding of materials that can inhibit this reaction is equally warranted. As previously mentioned, we theorize that our CrPDTA electrolyte can achieve high current efficiencies by inhibiting H_2O coordination from the highly reducing Cr^{2+} metal centre, thus avoiding catalytic HER losses.

Research into the inhibition of water splitting should explore metals across the periodic table, including main group and lanthanides, to improve our understanding of water splitting. In addition, extending this approach to water splitting catalysts and materials such as platinum group metals could shed light on catalyst deactivation and reactivation pathways in water electrolysis and fuel cell systems.

4.3 Inhibition of hydrolysis

In addition to prohibiting HER pathways, many physical properties of metal ions, including solubility and pH range stability, can be influenced by inhibiting water coordination or altering water-metal interactions. Being able to tune these properties can provide valuable benefits for applications such as flow battery electrolytes. In fact, the earlier mentioned increased VO_2^+ solubility in a mixed acid H_2SO_4/HCl electrolyte is believed to be the result of a Cl^- ligand exchanging with a coordinated H_2O, which reduces the acidity of the remaining coordinated H_2O molecules and therefore disrupts the hydroxo-speciesbased hydrolysis precipitation mechanism that forms V_2O_5.[60]

Our previously mentioned CrPDTA electrolyte provides an example of increasing the pH stability range of a metal ion using a chelating ligand, as hexaaquachromium(III) will form insoluble $Cr(OH)_3$ well below the CrPDTA operating pH of 9. Recently, we provided additional support for our hypothesis that inhibiting water coordination is key for supporting aqueous coordination complex flow batteries. In contrast with the KCrPDTA system, iron complexes with hexadentate ligands like ethylenediaminetetraacetate (EDTA) and PDTA often coordinate an additional water or hydroxide ion to form a heptacoordinate complex with a pseudo-pentagonal bipyramidal geometry. This bound water or hydroxide can, at above neutral pHs, lead to the formation of dimers (FeEDTA) through a bridged water or cause the decomposition of the complex and formation of insoluble species (FePDTA).[61,62] The use of diethylenetriaminepentaacetate (DTPA) enforces the preferred pentagonal bipyramidal geometry of iron at a pH of 9 and enabled stable cycling of an electrolyte using the $K_2FeDTPA/K_3FeDTPA$ redox couple at 1.35 M. [33]

These mentioned processes, as well as others, such as disproportionation, that are facilitated through a coordinated water and result in undesired products, would be an area of research that coordination complexes may be able to address.

4.4 Control of oxidation state potential

New ligand development is essential for aqueous coordination complex flow battery development. In particular, the tailoring of ligands with high binding constants could potentially stabilize unusual metal ion oxidation states in aqueous solution. For example, coordination complexes of Ti^{2+} are typically strongly reducing and extremely reactive, even in non-aqueous solvents.[63] On the other hand, under strongly acidic aqueous conditions, Ti^{2+} ions have been spectroscopically characterized and the standard $Ti^{3+/2+}$ redox couple has been measured.[64–66] The example of Ti^{2+} demonstrates that transition metal oxidation states considered highly reactive by the inorganic and organometallic communities should not be automatically ruled out from being stable in aqueous solution.

Ligand development for aqueous coordination complexes can also focus on shifting common metal redox potentials. For example, the standard $Fe^{3+/2+}$ potential of 0.77 V can be increased to 1.1 V in the case of $Fe(bpy)_3^{3+/2+}$ or shifted as low as −1.2 V in the presence of triethanolamine in alkaline conditions.[67,68] Continued expansion of the $Fe^{3+/2+}$ couple and those of other earth-abundant metals could lead to the development of new approaches for cost-effective energy storage and electrochemical conversion processes.

4.5 Multi-electron PCET

The investigation of molecules capable of undergoing multielectron redox processes is a compelling approach for increasing the energy density of flow battery systems. To undergo multi-electron transfer processes, small molecules typically require a change in their chemical structure to alleviate the coulombic repulsion of accepting more than one electron at the same potential. In aqueous solution, the transfer of protons or changes in hydrogen bonding provide a convenient way to facilitate rapid multi-electron transfer processes, such as the 2-electron 2-proton reduction of quinone to hydroquinone.[69]

Transition metal complexes can also participate in multielectron PCET processes, particularly through the interconversion of aquo, hydroxide, and oxo ligands. For example, the dichromate ion, $Cr_2O_7^{2-}$, can undergo a 14-proton, 6-electron reduction to Cr^{3+} at 1.33 V. Although the $Cr^{6+/3+}$ couple is electrochemically irreversible, further interrogation of the oxidation of Cr^{3+},[70] perhaps with the aid of coordinated ligands, could provide new strategies for the use of multi-electron PCET processes in energy conversion and storage.

5. Conclusions

In this perspective we have identified critical needs in aqueous flow battery research that the inorganic and coordination chemistry communities are well-suited to address. To facilitate research in this area, we have provided a detailed procedure for the evaluation of flow battery chemistries using a versatile and high-performance flow cell platform. We hope that the use of the PEM flow cell platform will enable inorganic chemistry researchers to routinely evaluate the performance of novel coordination complexes on an efficient and scalable test platform.

Conflicts of interest

There are no conflicts to declare.

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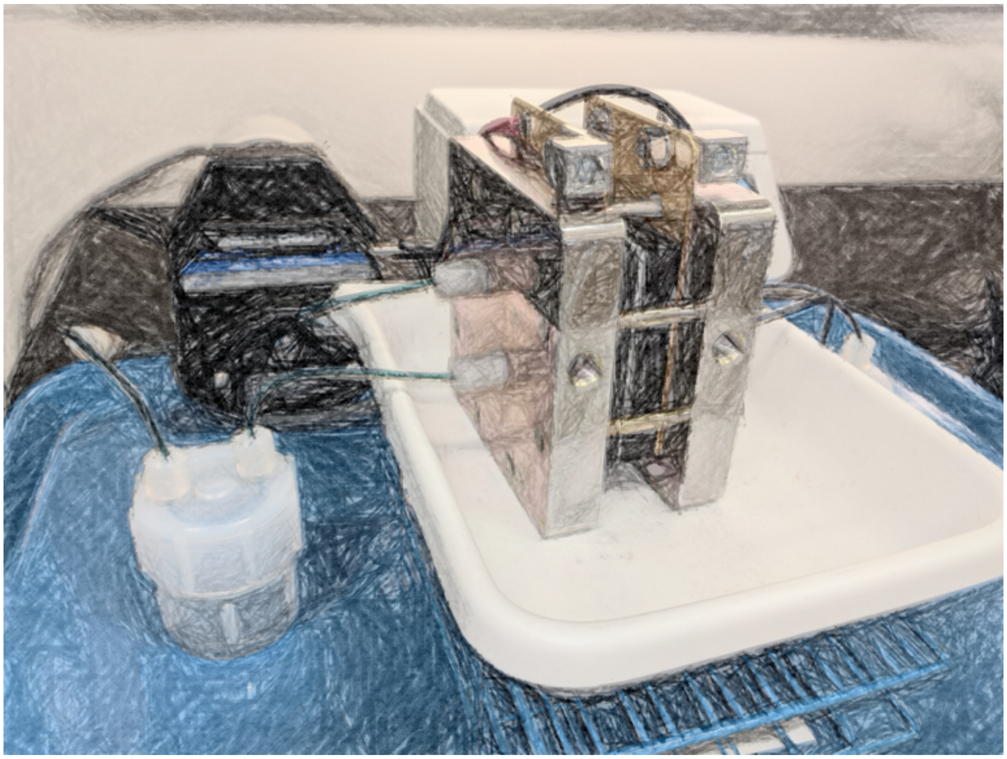58 D. S. Silvester and R. G. Compton, *Zeitschrift für Physikalische Chemie*, 2006, **220**, 1247–1274.
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