Breakout Session I – Research needs for non-aqueous chemistries

Key Material Parameters

- Long-term durability (both calendar and cycle life) is necessary for viability and to deliver a 20 year service life
- Non-aqueous RFB chemistries are competing with aqueous for viability so need to deliver on the specific advantage of higher voltage couples
- Higher voltage of some non-aqueous systems makes them competitive at low current densities but fall short under higher rate conditions. Need to show increased rate capability in non-aqueous systems to push current limits.

New Material Concepts

- Solvated electrons: Solvated electrons can act as an ideal anion and occur when free electrons reside in a "cage" of solution species. Literature by Bard has shown you can make solvated electrons via electrochemical methods. Potentially employ an aminopolymer to create an artificial cavity to trap electrons in solution.
    - Solvated electrons would likely be very difficult to stabilize
- "Self-healing" materials: To enable longer service life for systems that inevitably experience degradation there is need for materials that can "self heal" in one form or another, similar to how VRFBs can be rebalanced to restore performance. Options discussed include materials that passively recover when not being cycled, materials that signal when they have degraded though fluorescence or another noticeable change, materials that can be recovered through a specified cycling protocol or the addition of a specific additive or pumping over a catalyst bed.

Key Areas of Further Investigation

- Characterization of materials degradation pathways and products. This can allow for mitigation strategies to reduce degradation as well as inform the "self-healing" materials concepts on the specific products or reactions that need to be reversed. Can also disambiguate reversible degradation processes from irreversible losses.
    - Example here is the presence of linked bipyridyl ligands that occur during degradation and the cleavage of those links via an oxidation process to recover the ligands
- Identification of alternative application space where the reduction in stack size offered by the higher voltage non-aqueous RFB systems can provide more advantages than cost reduction. For example, transportation energy storage applications where reducing system mass and volume are important parameters.

Establishment of Standards for Analysis (this will be covered in more detail in break out session III)

- Selection and use of key performance terms for effective comparison and understanding of the actual performance of different chemistries. Test parameters can often be toyed with to artificially inflate certain system characteristics. Establishment of standard definitions for things like depth of discharge, electrochemical yield, round-trip efficiency, coulombic efficiency, etc. as well as which are most relevant when analyzing new materials. Disambiguates presented performance data and allows for valid comparisons across systems.
- Understanding and reporting of limitations to certain measurement techniques. For example cyclic voltammetry is appropriate for identifying the approximate redox potential of a species and the approximate reversibility, but this does not translate to the system level where actual performance can be effected (and often degraded) by longer time scales, the presence of other system components, and greater concentrations of materials in the electrolyte. In addition measurements like the absolute species solubility does not translate to practical solubility due to competition with the supporting salt in the electrolyte solution.

Breakout Session I – Research needs for non-aqueous Solvents/Electrolytes/Membranes

Membranes

Targets:

Conductance: (ASR) ≤ 3Ω.cm^2

Cross-over: Coulombic efficiency ≥ 95% for symmetric systems and ≥ 99.99% for asymmetric system.

Cost: ≤ \$10/m^2

Solvent cross-over: ≤ 10^{-14} cm/s

Conductivity: A 10mS/cm target and help guide research

Research Directions:

Porous separates are the most advanced membranes available to date. While Celgard type membranes are commonly used in research they are not practical for anything other than symmetric systems. Research in size exclusion membranes like Daramic could benefit non-aqueous flow batteries. Research in ion-exchange membranes for non-aqueous systems is in its infancy. Issues including conductivity and cross-over mechanisms need to be better understood. Ionic membranes need to be tailored to specific redox systems to improve conductivity and decrease crossover.

Crossover requirements need to be determined based on application. Some useful guidelines are 80% capacity retention after 2000 cycles or approximately 0.0005% decay per day. System solutions of preloading the catholyte or anolyte with the other species (in case of non-reactive systems) can help ease crossover requirement. Solvent crossover is also important and needs to be addressed in acetonitrile and other solvents. Minimizing solvent uptake while improving ion conductivity could be a focus area of membrane research .

Cost ranges for today's membranes range from ≤ $\$10/m^2$ for Daramic separators to \$300 for PFSA type membranes. Membrane cost can be a significant fraction of the system costs and need to be optimized. Encourage the commercialization of alternate ionic membrane technologies to provide more options to the community.

The Vanadium acetylacetonate system with an acetonitrile solvent and ionic liquid supporting (TEA, TBA, PF4, BF6, F) electrolytes can be used as a baseline to demonstrate promising concepts and develop basic design principles that can then be applicable more widely. Benchmarking of the conductivity and cross-over of currently available porous separators, and ionic membranes would be beneficial.

Solvents

Targets:

Targets for Viscosity, Toxicity, Cost, and Volatility need to be developed. Viscosity and Cost targets for acetonitrile are sufficient. Toxicity and volatility needs to be determined so as to avoid double containment.

Potential window: ≥ 5V

Redox solubility: ≥ 1M

Research Directions:

While acetonitrile is the default solvent for research groups, other solvents need to be explored before commercialization. Ionic liquids, glymes and DMF are alternates but have their own challenges in terms of viscosity, conductivity and stability. Stability needs to be considered in the presence of the electrolyte and redox active species. The solubility of redox species is also critical and the potential window needs to be high to accommodate most redox reactions.

Electrolytes

Targets:

Conductivity: ≥ 10 mS/cm

Cost: ≤ $5/kg

Solubility: ≥ 1M in solvent

Research Directions: Electrolytes need to be compatible with the redox active species and research should try to minimize their effect on the solubility of the redox species. Electrolytes need to be redox innocent and have a donor number similar to acetonitrile (14.1 kCal/mol). Low cost electrolytes and membranes need to be developed in conjunction since the IR losses in the electrolyte and membrane will determine the performance of non-aqueous systems. Improving the electrolyte conductivity while retaining compatibility with the membrane will be crucial in the commercialization of non-aqueous flow battery systems.