

## **Breakout Session II – Research needs for non-aqueous flow battery performance and durability**

### **Commonly Observed Challenges in Achieving Durability**

There are a wide range of components that make up NA RFBs and compatibility between the different components and over a wide electrochemical range can affect longevity, e.g. different species in contact in mixed electrolyte systems, mechanical components of flow cells (researchers widely employ Teflon-lined systems), salts, membranes, and solvents. From an electrochemical point of view, appropriate cycling conditions for select chemistries need to be identified to minimize or avoid side reactions and degradation. IR losses can force polarization of materials beyond their stability ranges, and this can be exacerbated in high rate test conditions. There is a need for enhanced understanding of materials compatibility and electrochemical stability of materials.

Environmental contamination introduces another range of variables that can artificially degrade components. Many new compounds show variations in first cycle performance compared to subsequent cycles. Could this be related to materials irreversibility or a result of reactions with other cell components or contaminants? This is highlighted in work on V-acac, where an effort to rigorously remove moisture contamination from all components resulted in dramatically improved cycle life relative to what was conventionally observed. Much laboratory work is conducted in inert atmosphere gloveboxes to avoid such issues related to moisture or oxygen contamination. Does this environmental restriction present barriers for scale-up and commercialization? General consensus is that such limits can be controlled by engineering efforts.

### **Commonly Observed Challenges in Achieving High Performance**

There are many related and overlapping issues in achieving high performance and durability, in no small part because durability is a metric for high performance. Cell viscosity and conductivity are two of the key performance challenges identified that limit high performance of NA RFB cells. High IR losses from viscous or low-conductivity systems can prevent electrochemical access of active species and lead to premature cell failure. Is higher temperature operation a viable approach to reduce viscosity and improve conductivity or will the increased kinetics of degradation cause overall performance to suffer? Membrane selection is also a common source of inefficiencies that is not standardized across NA RFB chemistries. Much work relies on PFSA ion-exchange membranes or microporous size-exclusion membranes that are not designed for NA RFB systems and may require additional pretreatment or conditioning to ensure they do not artificially show test chemistries to be ineffectual.

### **Modelling Needs**

There are split opinions on the need for modelling of NA RFB systems in their current state. Proponents say such modelling efforts can help to optimize test chemistries and avoid issues of

premature cell death related to high viscosity or IR losses by recommending viable operating conditions (temperatures, rates, voltage cut-offs). This is still a complex model space with no established standard complexes so modelling efforts will have to be carried out in parallel to achieve impactful results. For example, modelling work of species solubility by LANL should serve to inform models on species potential and reversibility, thereby maintaining material relevance in this multi-faceted performance space. Opponents question value of models in such a varied and developing technology space, will the models offer any predictive capability or will they just validate things that are observed in experiments. Proponents counter that validation offers information on the mechanisms of operation within experimental cells.

## **Barriers to Scale-up and Commercialization**

Fielded technology will not be cycled in the same controlled, idealized methods employed in laboratory studies. To achieve commercial viability NA RFBs need to have an improved understanding of the impacts of abuse conditions on the cycling or efficiency of the system. This non-ideal space needs to be explored by testing the impacts of water inclusion, acid inclusion, over-discharge, over-charge, etc. on the longevity and efficiency of NA RFB chemistries.

There are significant engineering challenges related to prototyping scale-up of NA RFB chemistries. A few identified issues are as follows: solvent evaporation leading to pressure build-up or sealing issues, ability to isolate from contaminants for service life, cross-over contamination, degradation of materials over the cycle life, precipitation of electrolyte species during operation. To justify the engineering effort to make large-scale prototypes viable, the stability of high performing electrolyte components over wide voltage ranges need to be demonstrated for a relevant time frame. The currently established baseline NA RFB chemistries for proving new components are ferrocene and viologen, which yields too low of a cell voltage to justify scale-up efforts. Alternative baselines with higher voltages should be pursued to justify the investment in this scale-up prototyping (e.g. dialkoxybenzene, benzothiodiazole, N-methylphthalimide).

General opinion is that NA RFB technology is not ready to “bridge the gap” and move from laboratory scale testing to larger scale prototyping. Some consider the only short term option for scale-up is to offer incremental improvements over existing aqueous flow battery systems. General consensus is that materials work needs to demonstrate a viable and persistent chemistry before commercialization effort can continue in earnest.

## **Targets**

Non aqueous Redox flow battery (NARFB) system targets should be same as Aqueous RFB (ARFB) systems already defined by DOE. Targets should be defined for Capital cost, round trip efficiency, Levelized cost of Storage and Durability. NARFB power electronics should be compatible with existing power electronics for ARFBs. Cost and performance targets should be defined for the power electronics including DC/DC and AC/DC. Costs for NARFBs should include installation costs, purity of reactants required, maintenance costs and materials costs

(materials with specific compatibility with non-aqueous solvents). CapEx and OpEx tradeoffs should be considered at fixed electricity cost (say 2.5 cents/kWh). Durability of electrolyte should be considered in determining makeup vs recycling and replenishing. Minimum requirements for redox couples need to be established before scaling up systems. An OCV of 3V or greater is suggested. Moreover, the stability of these systems needs to be established using bulk electrolysis experiments and not just cyclic voltammograms (CV). Carbon felt electrodes are recommended instead of Glassy carbon electrodes for all CV experiments. It is recommended that a standard 3-electrode cell be made available for the cycling experiments. A simple H-cell with all relevant details can be made available through the DOE-OE and Sandia Energy Storage Program websites. LANL and SNL will co-ordinate this effort and will seek input from various research groups working in this area including MIT, University of Tennessee, JCESR, UTRC, University of Michigan, and Harvard. All relevant valence states of the redox compounds needs to be stable before flow battery cycling experiments. One standard cell that could be utilized for this testing is the 2.5cm<sup>2</sup> non-aqueous cell developed by JCESR. Alternates would be the various 25cm<sup>2</sup> cells published in the literature with numerous flow field and electrode combinations. The durability of systems needs to be defined both in terms of minimum hours and minimum number of cycles. The Harvard durability protocol defined for aqueous systems can be adapted for non-aqueous systems. Operating temperature effects and the effect of impurities and side reactions need to be considered while evaluating the durability. Finally, flammability and toxicity targets need to be established for non-aqueous solvents.

## **Other Research Areas**

Multi electron redox species can greatly enhance the energy derived from each redox moiety and should to be considered when appropriate. While the Energy and capital costs of such systems could be lower, the power electronics costs could be higher. Suitable applications need to be identified for such multi-electron systems with either double or even triple potentials of oxidation/reduction. Series instead of parallel operation can also have advantages with these systems similar to EnerVaults Engineered Cascade technology with the Iron Chrome system.