Acid Based Blend Membranes for Redox Flow Batteries

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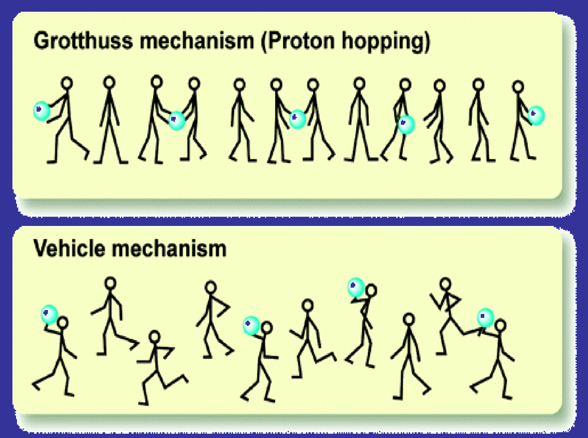
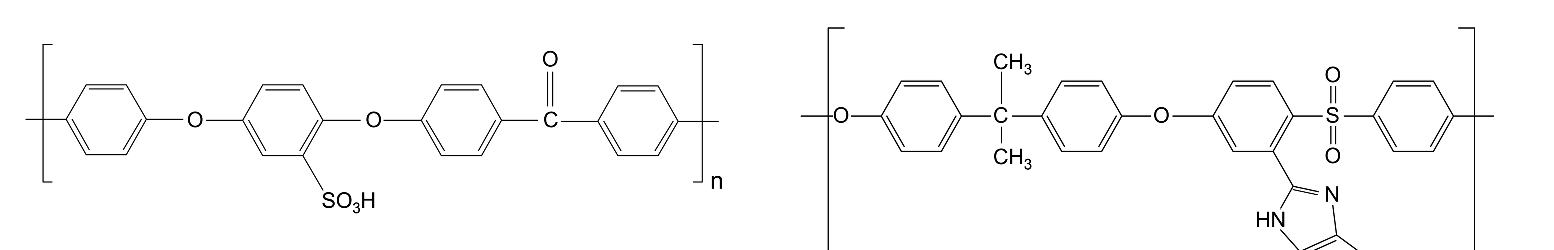
Introduction

- Redox flow batteries (RFBs) have been considered a promising technology to store electrical energy from intermittent renewable sources such as solar and wind power. The advantages of RFBs include modularity, transportability and flexible operation, making them well suited for transmission and distribution deferral applications. **Despite the advantages, RFBs with reduced cost and improved performance (*i.e.*, efficiency and durability) need to be developed to achieve broad market penetration.**
- **Drawbacks of Nafion® widely used as an ion exchange membranes in RFBs to separate the two soluble redox couples include its price and high permeability for reactive species, *i.e.*, vanadium ions.** The membrane separating the electroactive species should allow rapid proton transport but suppress the transport of the reactive species between anode and cathode compartments while suppressing permeation of reactive species.
- **Development of a low-cost, highly selective proton-conducting membrane has the potential to contribute to producing cost effective, high performance RFBs** for grid energy storage to off-set membrane cost as a significant contributor to system cost,.

Objective/Approach

- The objective of this Phase I SBIR project was to develop a low-cost, robust, and highly selective proton-conducting composite membrane for RFBs for stationary electrical energy storage with a low cost (target cost << $100/m^2), high proton conductivity (≥ 0.08 S/cm), and low permeability for reactive species.
- Utilizing a membrane produced from a blend of an acid polymer and a base polymer offers great promise to directly access the Grotthuss proton conduction route to permit high proton mobility while suppressing the mobility of larger, more highly charged species (*i.e.*, vanadium species).
- By evaluating compositions with different combinations of acidic and basic components and different ratios of components identify the most effective combination.
- Optimize the composition of composite membranes to maximize proton conductivity and minimize water uptake, dimensional change, and permeability of reactive species; correlate the relationship of composition-property-performance

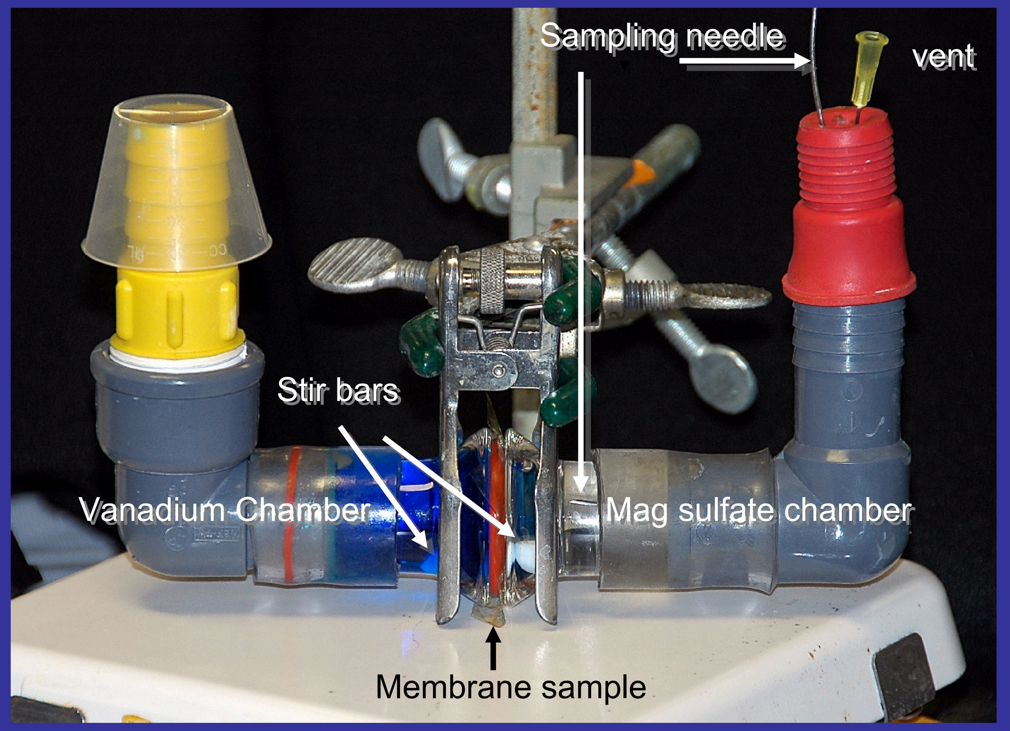


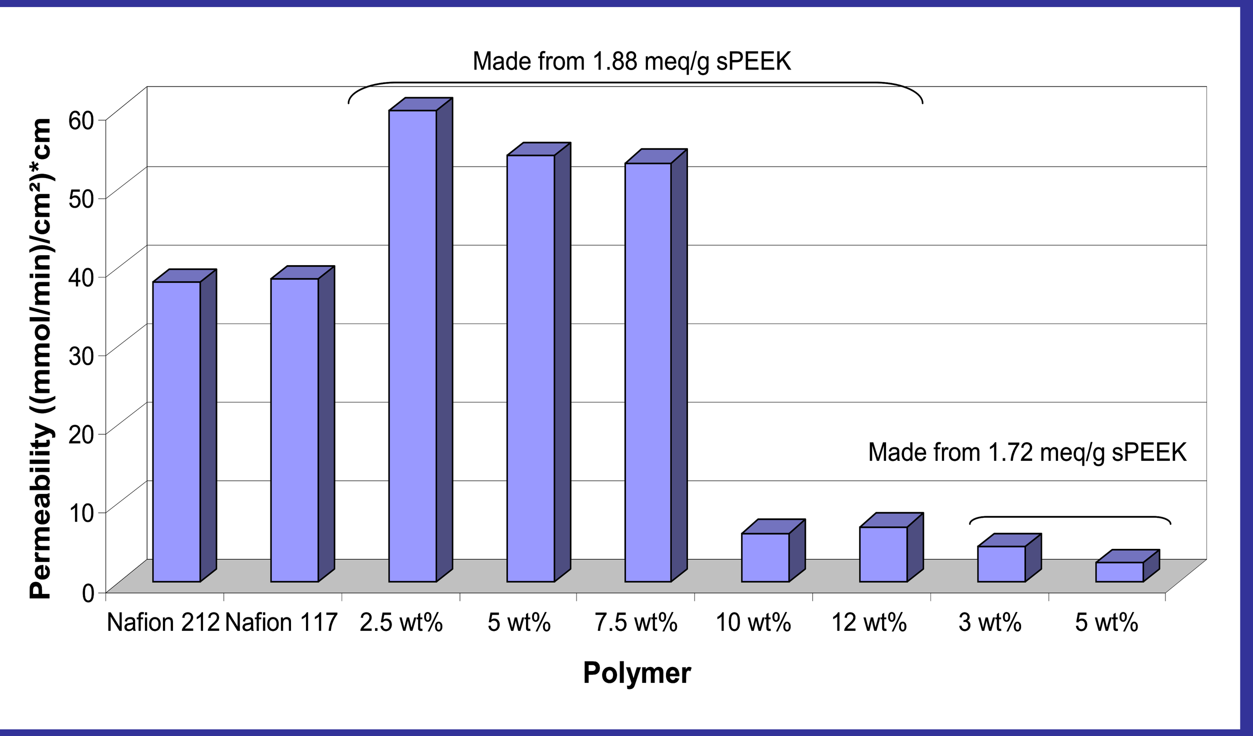


Sulfonated Polyetheretherketone (SPEEK)

Benzimidazole Derivatized Polysulfone (PSf-BIm)

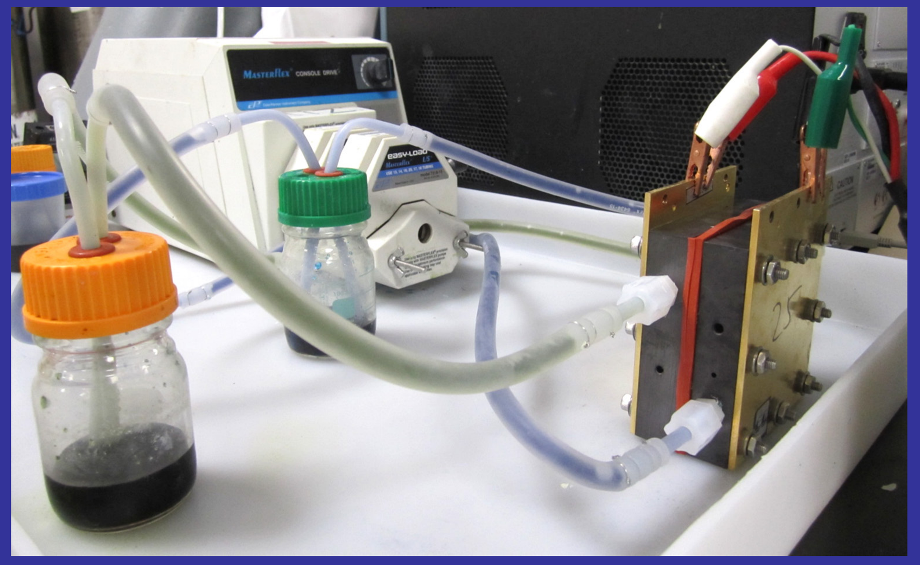
VO^{2+} Ion Permeability Test

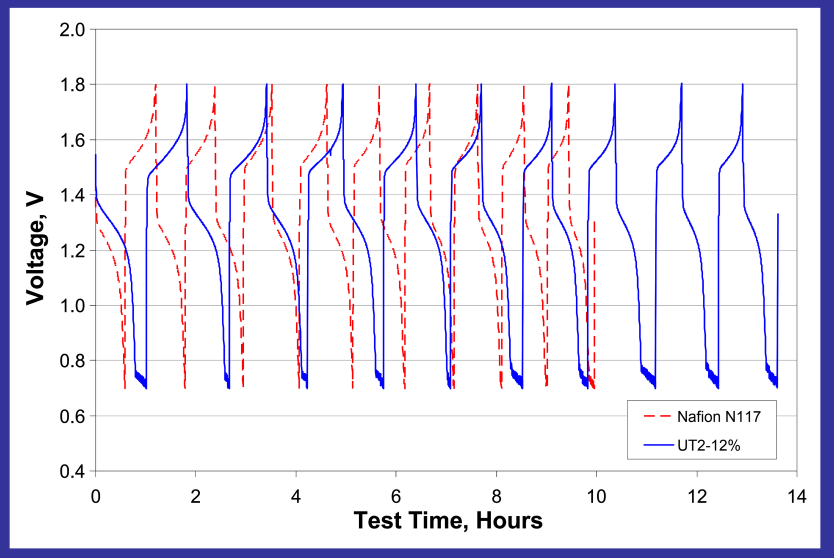




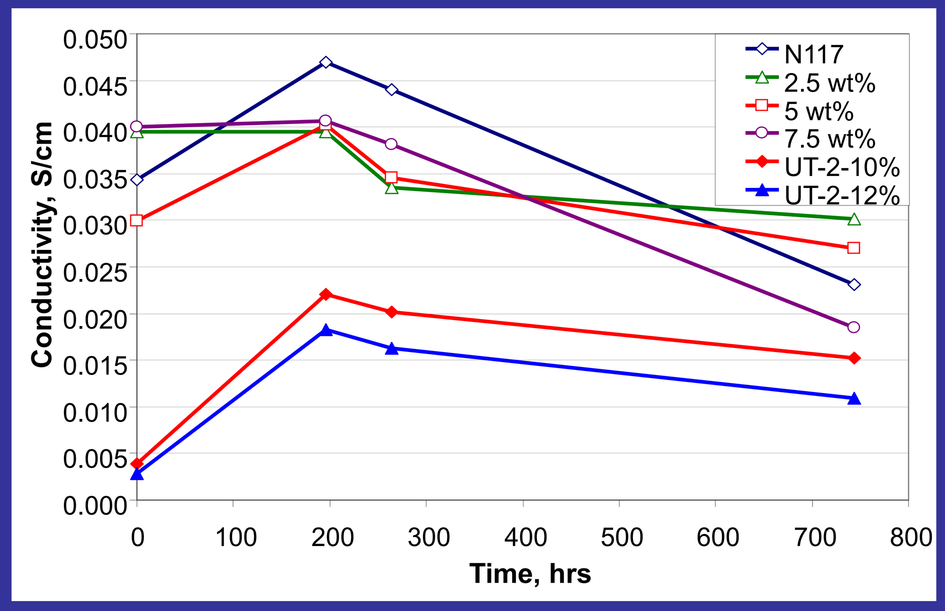
- The composite membranes can have substantially lower vanadium permeability than Nafion membranes.
- Membrane permeability varies with both composition (here weight fraction PSf-BIm in SPEEK) and base polymer functional group concentration, with the difference between 1.72 meq/g and 1.88 meq/g being significant for SPEEK.
- (Note, in this figure the bar for 2.5 wt% PSf-BIm in 1.88 meq/g SPEEK has been truncated to less than half of its actual height in an effort to make the other values more easily seen and compared.)
- All values here are normalized for thickness and reported as permeabilities rather than as permeation.

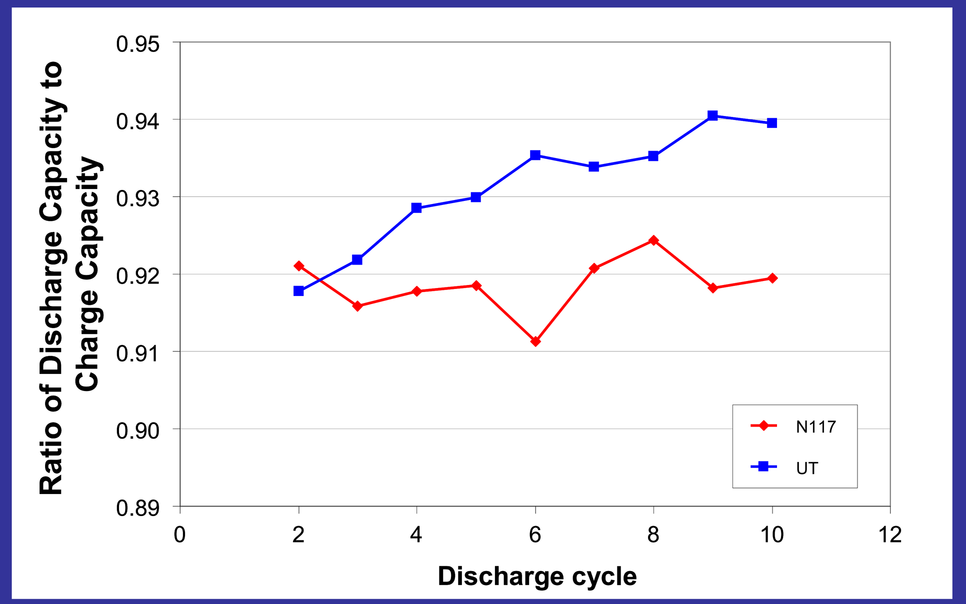
Flow Battery Test Cell



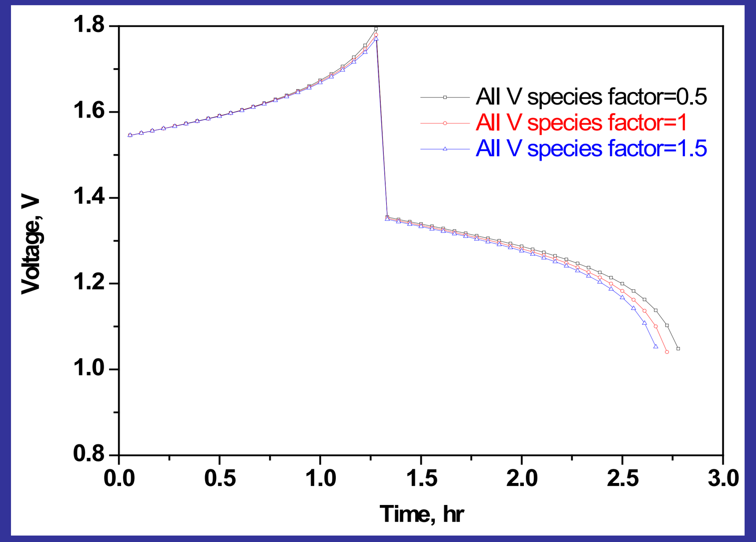


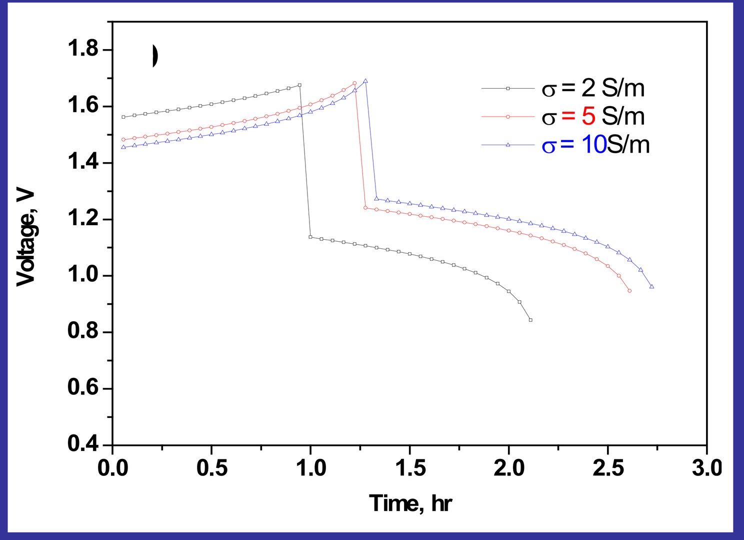
- Testing used an automatic control system (Arbin).
- Pumps are synchronized to keep flows matched.
- Blend membranes produce a higher capacity than Nafion under the same conditions.





- Less loss of conductivity when exposed to V^{+5}.
- Blend membranes produce higher round trip efficiency.





- Membrane conductivity has been demonstrated to have a greater impact on cell performance than permeability.

Technology Advantages

- **Low cost**. The composite membranes are based on industrial polymers (polysulfone or poly(ether ether ketone).
- **Tunable proton conductivity and physical properties**. The polymers can be sulfonated and base functionalities added to the desired degree and polymer ratios varied to tune proton conductivity.
- **High proton conductivity and Ultralow permeability of reactive species**. The composite membrane consists of components that conduct protons primarily by the Grotthuss mechanism, which does not require water and leading to low reactive species permeability.
- **Improved performance of RFBs**. The composite membrane can improve columbic/voltage/energy efficiencies and durability of RFBs.

Conclusions

Lynntech, in conjunction with the University of Texas and the University of Texas at Arlington, developed a new series of low-cost polymer blend membranes with high proton conductivity and ultralow vanadium ion permeability. The proton conductivity and physical properties of these membranes are tunable by adjusting the ratio of acid and base components. Membrane conductivity was found to be more critical to performance than permeability.

Because it is based on polymers already in large scale production, this composite membrane has the potential to rapidly move to mass production.