Membrane for Redox Flow Batteries

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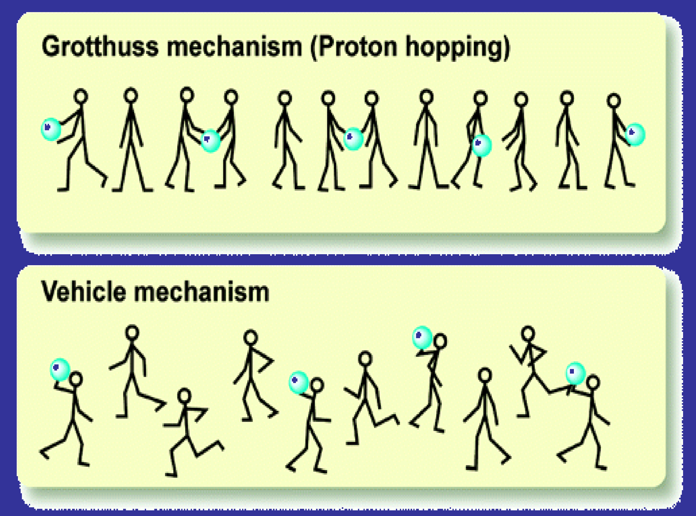
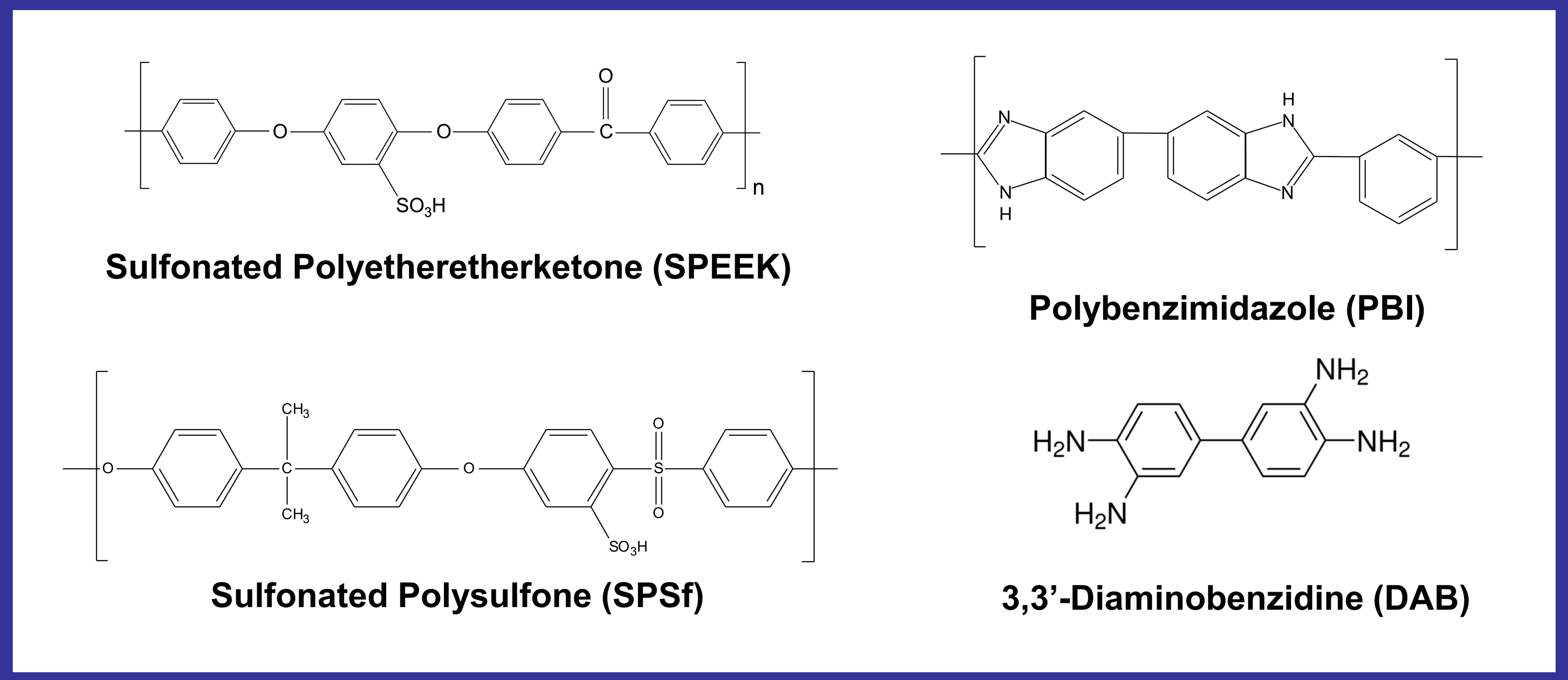
Introduction

- Redox flow batteries (RFBs) are a promising technology to store electrical energy from intermittent renewable sources such as solar and wind power. Although they offer many advantages, **RFBs with reduced cost and improved performance (*i.e.*, efficiency and durability) need to be developed to achieve broad market penetration.**
- Ion exchange membranes in RFBs separate two soluble redox couples should allow rapid proton transport and suppress transport of the reactive species between anode and cathode compartments. Nafion® membranes, while widely used, is expensive and has high permeability for reactive species, *i.e.*, vanadium ions.
- **Development of a low-cost, highly selective proton-conducting membrane has the potential to produce cost effective, high performance RFBs for grid energy storage.**

Objective/Approach

- The objective of this SBIR project is to develop a low-cost, robust, and highly selective proton-conducting composite membrane for RFBs for stationary electrical energy storage with 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 directly accesses the Grotthuss proton conduction (hopping) route** to permit high proton mobility while suppressing the mobility of larger, more highly charged species (*i.e.*, vanadium species).
- We are evaluating compositions with different combinations of acidic and basic components in different ratios to identify the most effective combination for conductivity with low water uptake, dimensional change, and permeability of reactive species.





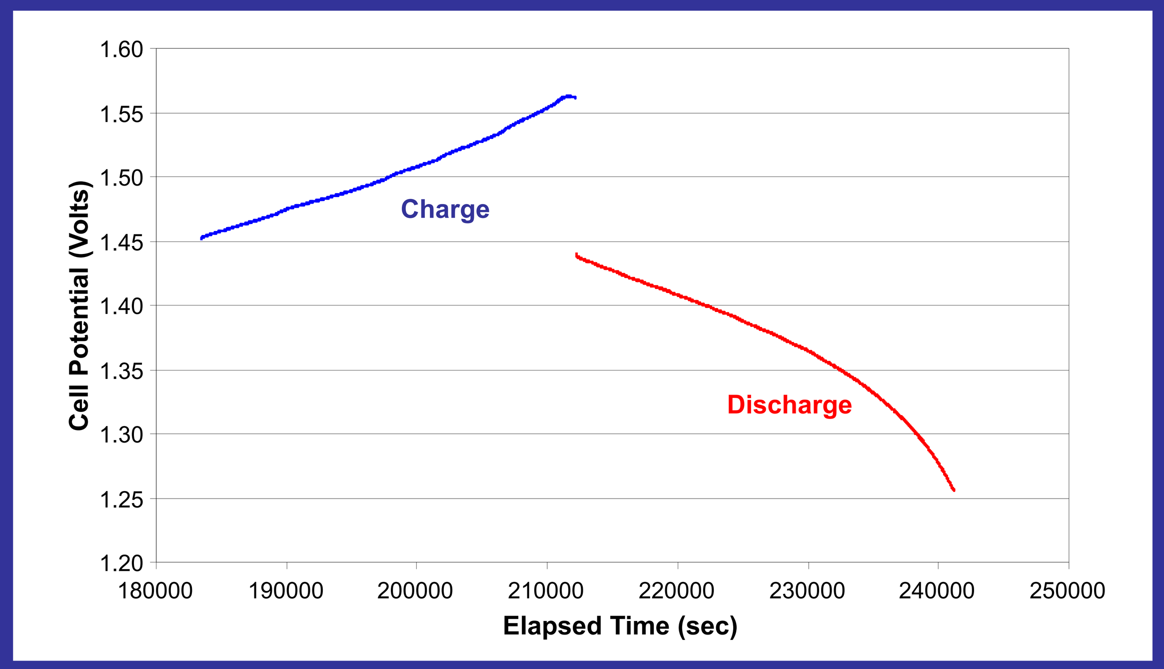
Acid Polymers | Bases

Experimental Methods

- Acid polymers being used are sulfonated versions of commercially available structural polymers already sold in ton quantities. (This ensures a low cost for the membrane material when compared to Nafion.)
- Both basic polymers and basic molecular (*i.e.*, non-polymeric) species are being explored. In acid-base blend membranes the polymer with the opposite functionality rather than water fills the coordination needs of the functional groups.
- Membranes are formed by solvent casting, a process that can be scaled to produce any size membranes desired.
- Casting needs to be carried out promptly after blending, as the interaction of the acid and base functionalities leads to the formation of molecular agglomerates that are less soluble than the individual components.
- **Acid-base membranes have demonstrated excellent resistance to vanadium permeation, with some permeabilities too low to accurately determine.**
- Specific species being tested have changed and will continue to change as the project progresses. Focus is on cost and durability.

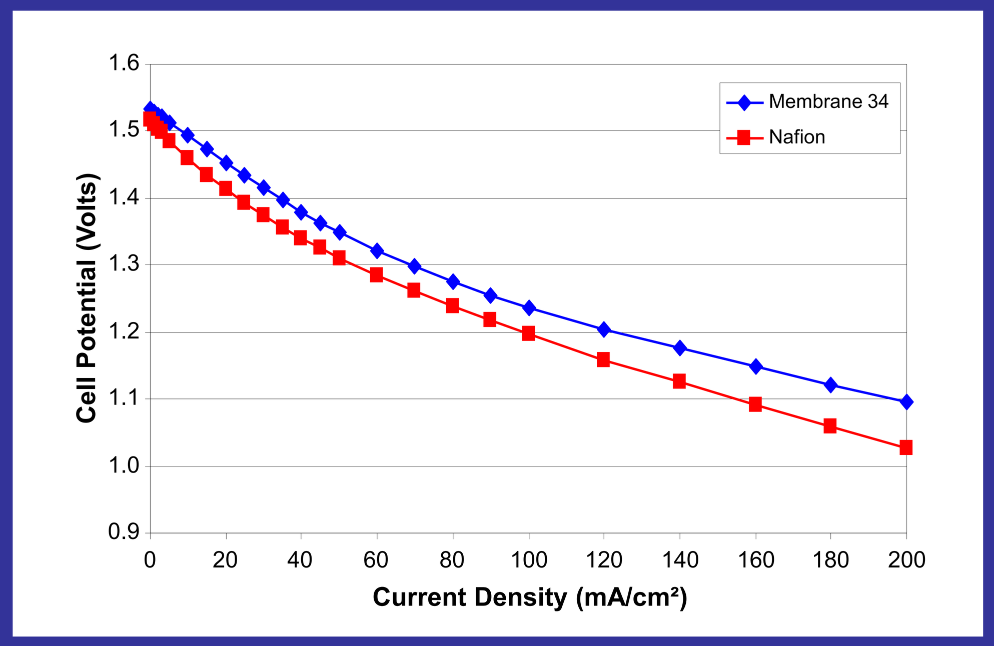
Experimental Results

Cycling Behavior



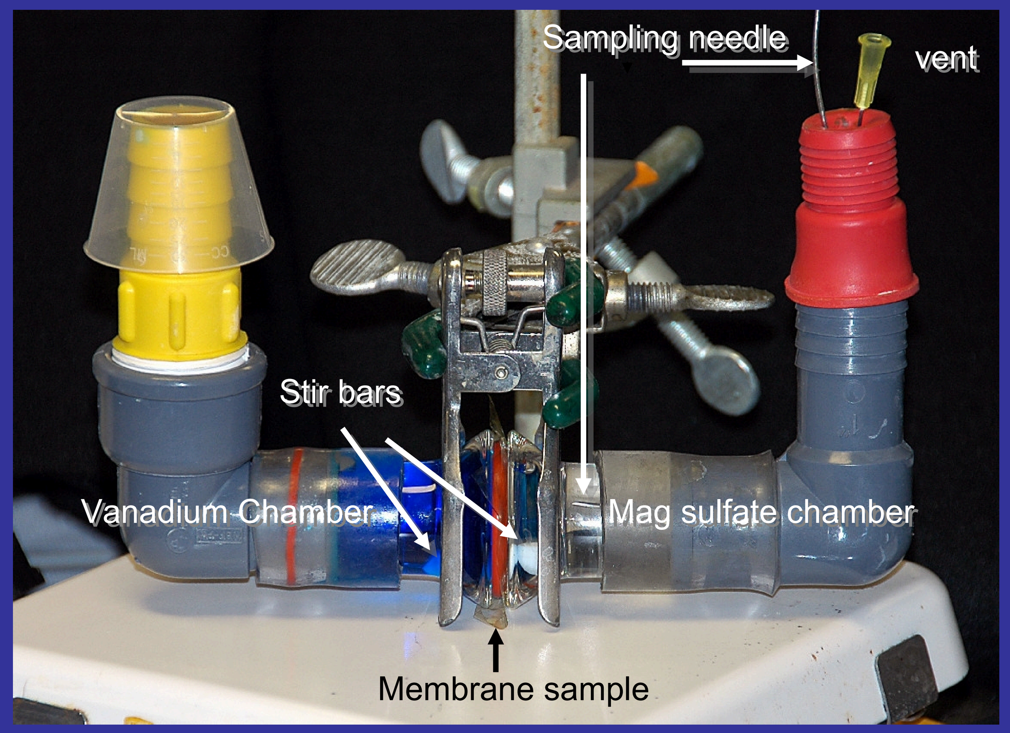
One charge/discharge cycle.
This membrane showed an average roundtrip energy efficiency of ~88%.

Polarization Curves

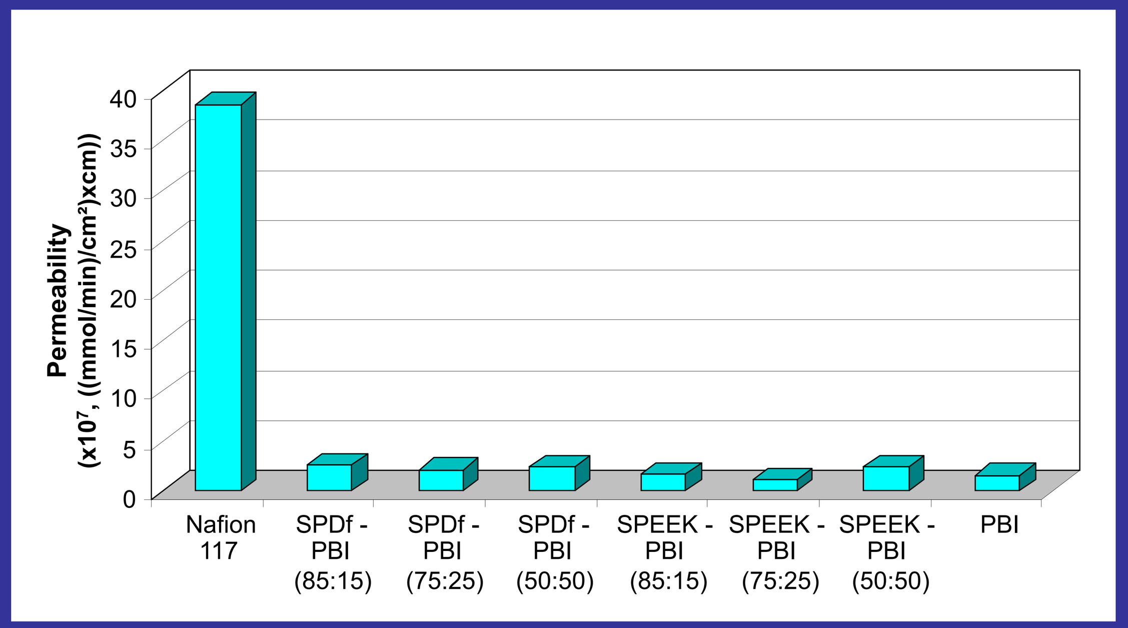


Blend membranes exhibit high conductivity. This membrane, which is more conductive than Nafion, is predominantly SPEEK with a basic additive.

VO^{2+} Ion Permeability



- Left: 1 M $VOSO_4$ + 2 M H_2SO_4
  Right: 1 M $MgSO_4$ + 2 M H_2SO_4
- UV/vis absorbance at 765.5 nm (VO^{2+})
- Record data, initially hourly and at increasing intervals for one to several days.



VO^{+2} permeabilities for blend membranes and for pure PBI (a Grotthuss conductor) are all less than 7% of Nafion. (Note, some of these values represent the maximum permeation possible for a measurement within standard error of zero.)

Advantages of Acid-Base Membranes

- **Low cost**. The composite membranes are based on modification industrial polymers (polysulfone or poly(ether ether ketone) that are already in large scale commercial production.
- **Tunable proton conductivity and physical properties**. The polymers can be sulfonated to the desired degree and polymer to base ratio varied to tune proton conductivity.
- **High proton conductivity and Ultralow permeability of reactive species**. Including components that conduct protons primarily by the Grotthuss mechanism, which does not require water, leads to low reactive species permeability while maintaining high proton conductivity.
- **Improved performance for RFBs**. The composite membrane can improve columbic/voltage/energy efficiencies and durability of RFBs.
- **Current performance is not limited by membrane durability.**