Low Cost and Highly Selective Composite Membrane for Redox Flow Batteries

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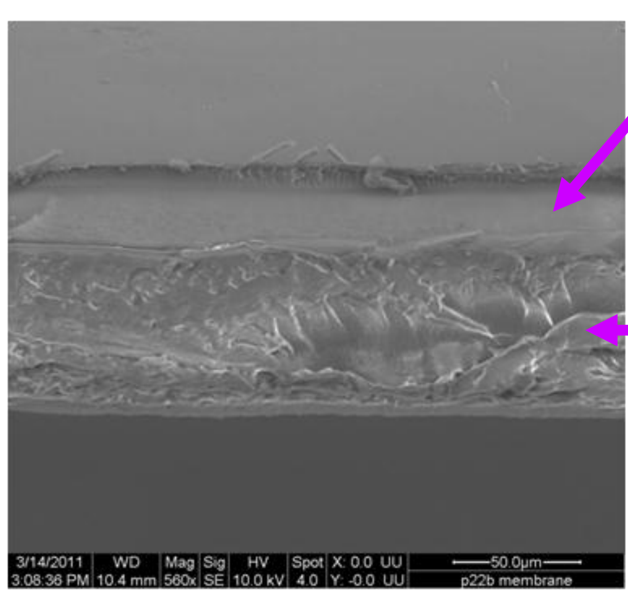
Identification of the Problem and Tech. Approach

Redox flow batteries (RFB) hold great promise for large scale electrochemical energy storage. A critical component of RFB is the membrane which separates anode and cathode compartments. The current state-of-the-art membrane, NAFION is too expensive, lacks selectivity, permitting leakage between anode and cathode electrolyte compartments.

EIC is developing a novel bilayer, interpenetrating network membrane.



SEM image of cross-section of composite membrane

Thin Nafion layer for anode side protection providing oxidative stability.

The bulk part of the membrane consists of a block copolymer comprising ionic and nonionic aromatic blocks that are designed to form an interpenetrating network of ion conducting and inert segments (similar to Nafion). The aromatic polymer is more resistant to leakage of active cationic species. The ionic phase forms conductive channels, inert segments providing mechanical strength. Overall built to be much less costly than pure Nafion while exceeding Nafion in selectivity.

Phase I Program Results

Synthesis of block copolymers

Block copolymer composed by polyetherketone based polymer was synthesized. The hydrophilic block is composed of sulfonated poly(aryl ether Ketone) (SPAEK) polymer and the hydrophobic block is composed of poly(aryl ether Ketone) (PAEK). The block copolymer PAEK-SPAEKP (PSP) is solvent processable and lead to phase separation upon cast into membrane.

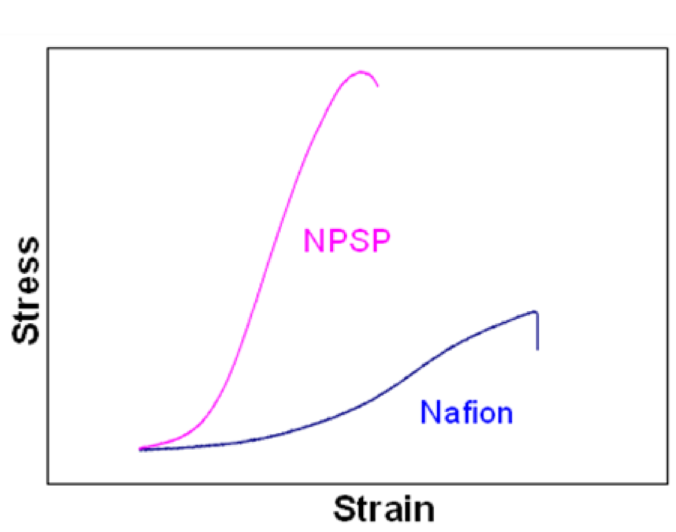
Cast Membranes (NPSP membrane)

1. Block copolymer requires a mix solvents to dissolve and cast, identified solvent system and optimized cast conditions (PSP layer).
2. Use commercial Nafion resin solution to cast top thin layer (N layer).

Membrane Characterization

Scanning Electron Microscopy (SEM). See above

Tensile Testing.

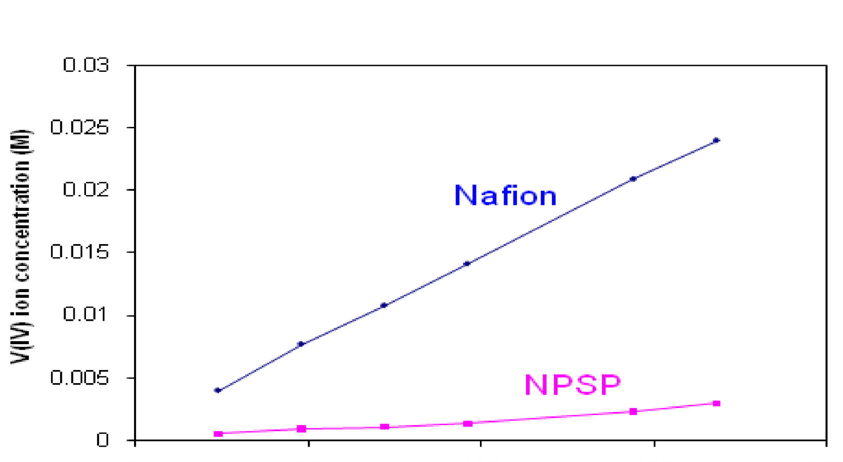


Stress-Strain Diagram

Calculated Mechanical properties of Nafion and NPSP membranes

	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Nafion	20.5	10.4	122
NPSP	205.2	48.6	53

Permeability of Vanadium Ions.



1.5 M $VOSO_4$ in 3 M H_2SO_4 against 1.5 M $MgSO_4$ in 3 M H_2SO_4

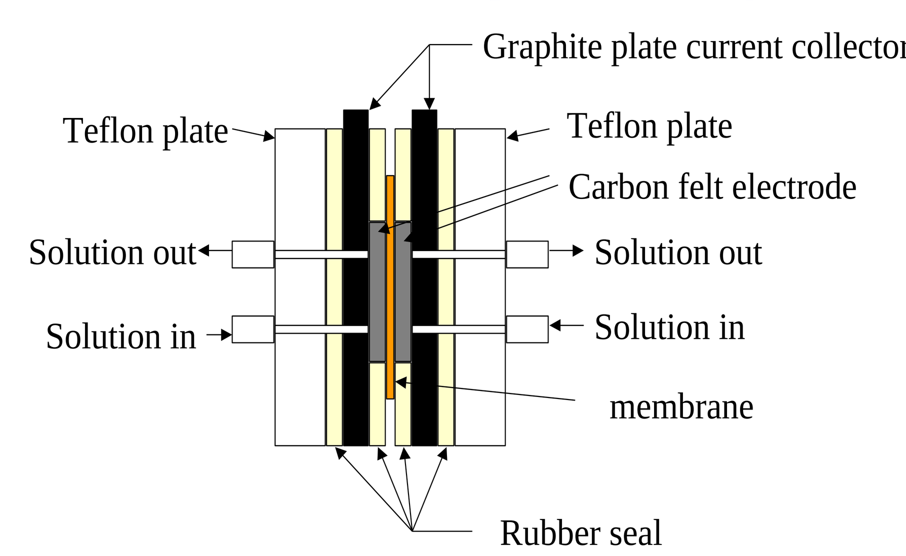
Vanadium (IV) leakage through NPSP and Nafion 117 membranes.

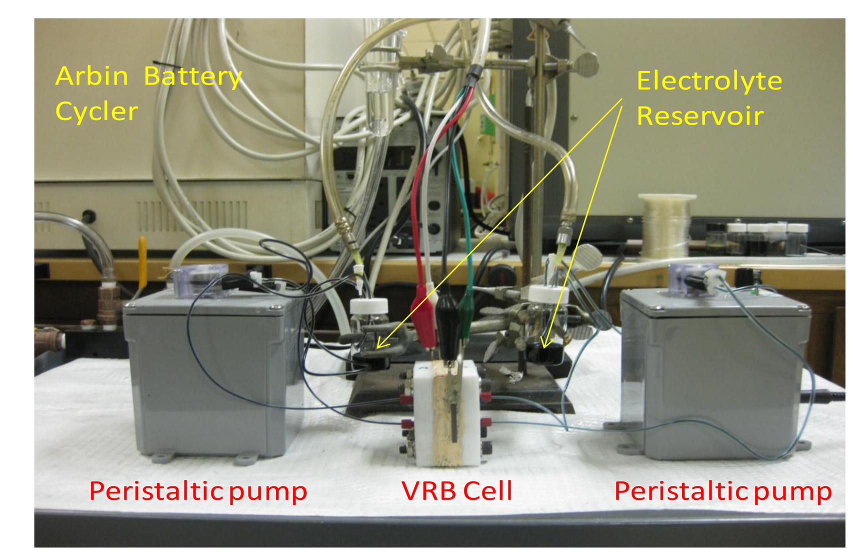
Water Uptake and Swelling, Film Conductivity. ***Ion Exchange Capacity (IEC). Area Resistance in Cell.***

Comparative membrane properties

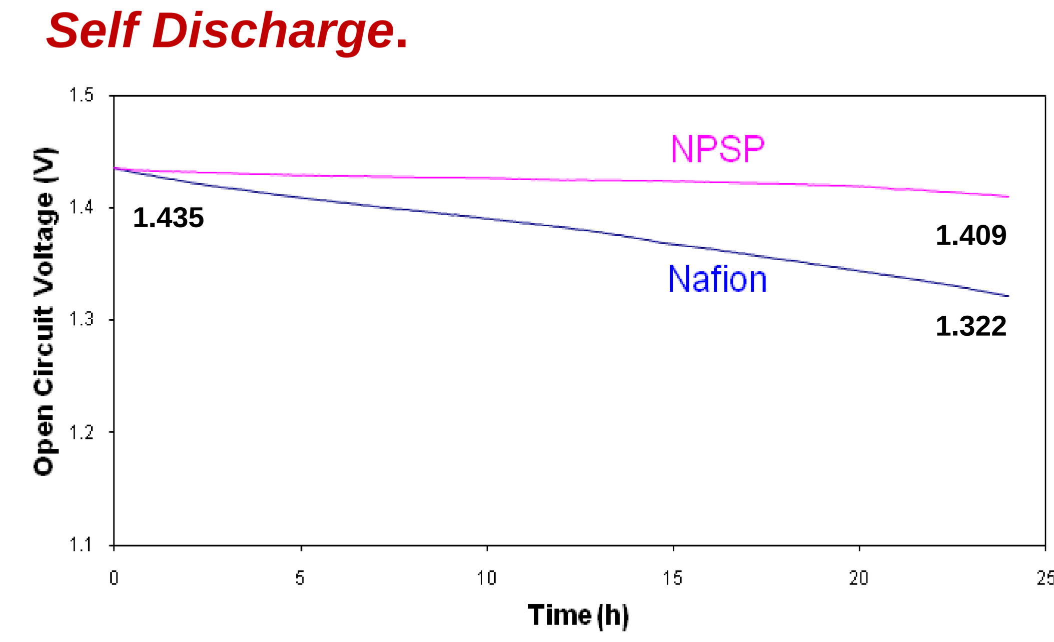
	Nafion	NPSP
Thickness (μm)	178	~90 (Nafion ~25)
Water uptake (%)	14.0	7.8
Length gain (%)	9.2	3.9
IEC (mmol/g)	0.94	0.74
Conductivity (S/cm^{-1}) 2-probe method	3.5×10^{-3}	1.5×10^{-3}
Conductivity (S/cm^{-1}) 4-probe method	3.1×10^{-1}	3.0×10^{-2}
Area resistance(Ω cm^2)	3.8	5.2

VRB Cell Testing on Composite Membrane



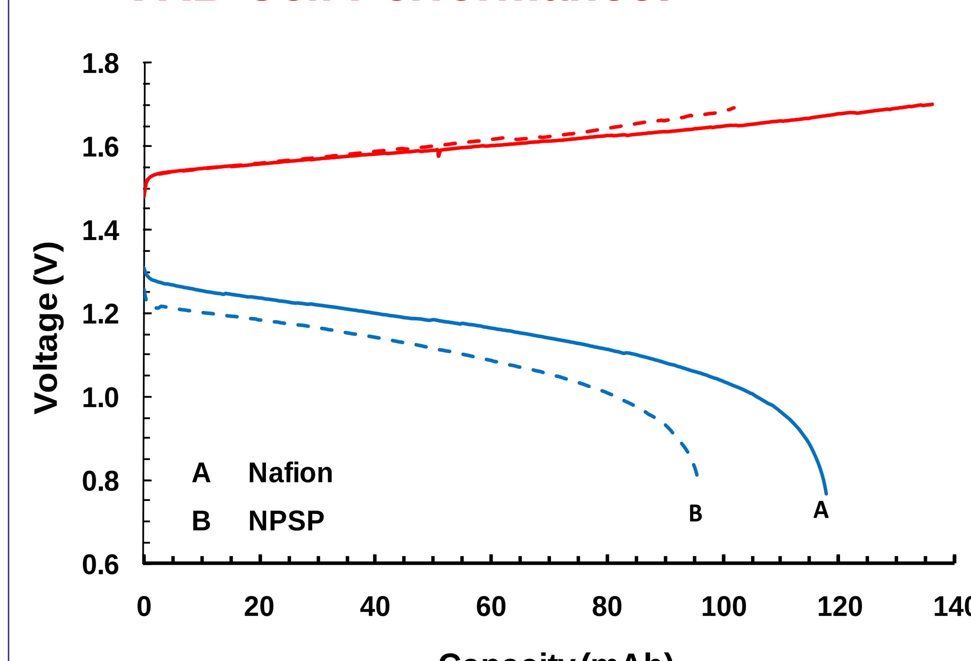


Self Discharge.



VO_2^+/VO^{2+} and V^{3+}/V^{2+} solutions in anode and cathode.
Cell charged to 1.435 V and monitor OCV changes vs. time.

VRB Cell Performance.



	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
Nafion	86.8	74.5	64.7
NPSP	94.8	69.3	65.7

Summary

- A novel soluble amphiphilic PSP copolymer synthesized
- Developed composite NPSP membrane fabrication process
- Better vanadium ions selectivity and mechanical strength demonstrated
- Comparable performance to Nafion demonstrated in unoptimized VRB cell

Future Plans

- To optimize the PSP block copolymer structure to maximize operational figures of merit – change copolymer structure, block length and ratio
- To explore and identify modifications to further reduce membrane costs – investigate other low cost monomers
- To optimize and scale up the membrane casting process – investigate membrane casting condition and performance relations
- To optimize the process of coating the PSP membranes with Nafion – investigate the required thckness of Nafion layer
- To downselect membranes for extended cell testing
- To establish a reliable and reproducible VRB test platform and protocols and conduct extended VRB testing
- To prepare and deliver samples for testing and Phase III development.

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