SAND2018-10588C

Relating Membrane Materials Properties to Crossover Mechanisms in Flow Batteries

DOE OE Energy Storage Peer Review

26 Sep 2018

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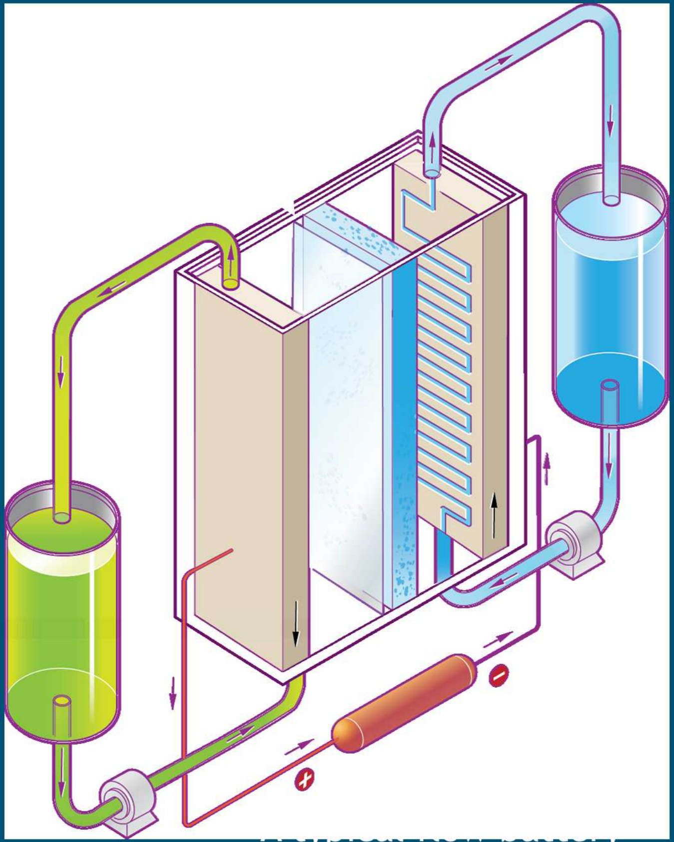
Redox Flow Batteries for Grid Scale Energy Storage

- Redox flow batteries offer an easily scalable solution for grid scale energy storage.
- In previous years we have consistently found the membrane to be the weak link in performance. Why?
- Understand membrane limitations to drive a 2× decrease in capacity fade vs. state of the art.



A typical flow battery

Can we predict flow battery ***membrane*** performance from fundamental materials properties?

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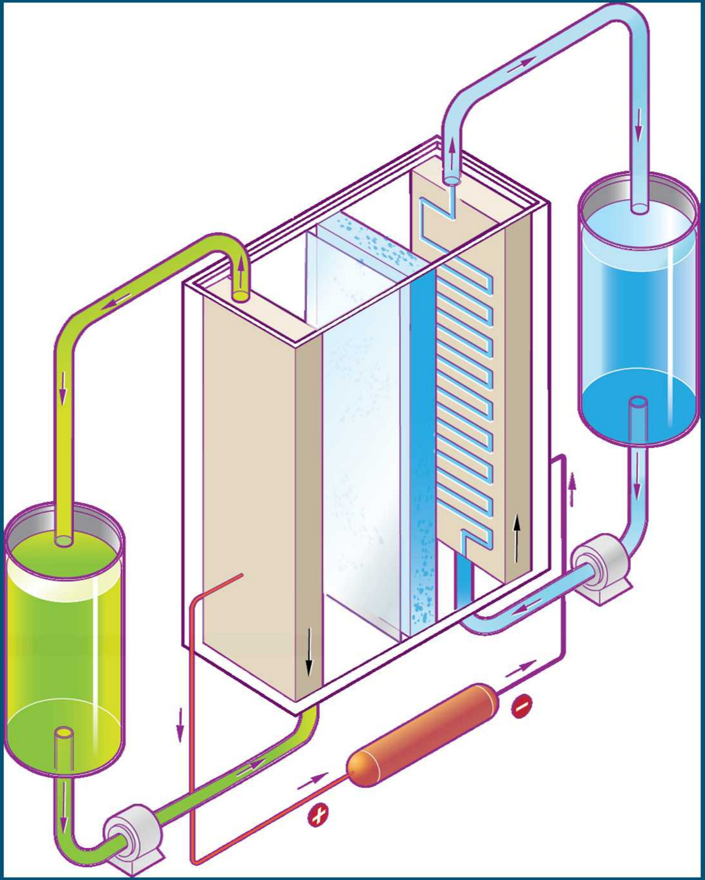
A Model Aqueous Soluble Organic Redox Flow Battery

- Use widely available methyl viologen-TEMPO redox couple chemistry[1] to compare performance of five commercial anion-exchange membranes:
  - Neosepta AFX, AHA
  - Selemion AMV, ASV, DSV

- Redox reactions on charging
  - Catholyte: TEMPO → $\text{TEMPO}^+ + e^-$
  - Anolyte: $\text{MV}^{2+} + e^- \rightarrow \text{MV}^+$

- Electrolyte
  - 1.5 M NaCl + 0.5 M MV or TEMPO
  - blanketed under argon

- 100 cycles at ±50 mA cm^{-2}



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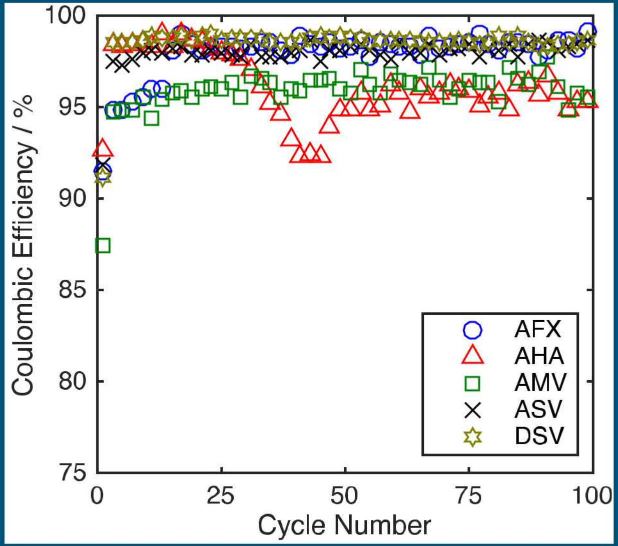
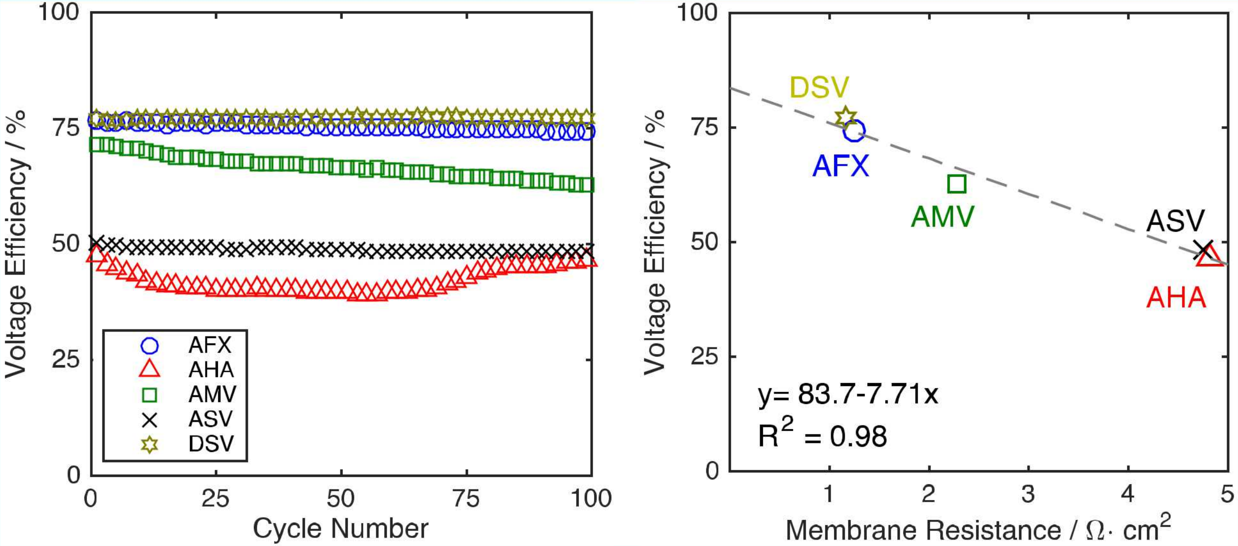
[1] T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, *Adv. Mater.* **2016**, *6*, 1501449.

Influence of Membrane on RFB Efficiencies



All membranes display >95% Coulombic efficiency.

Voltage efficiencies ranged 50-75%, inversely proportional to membrane resistance.



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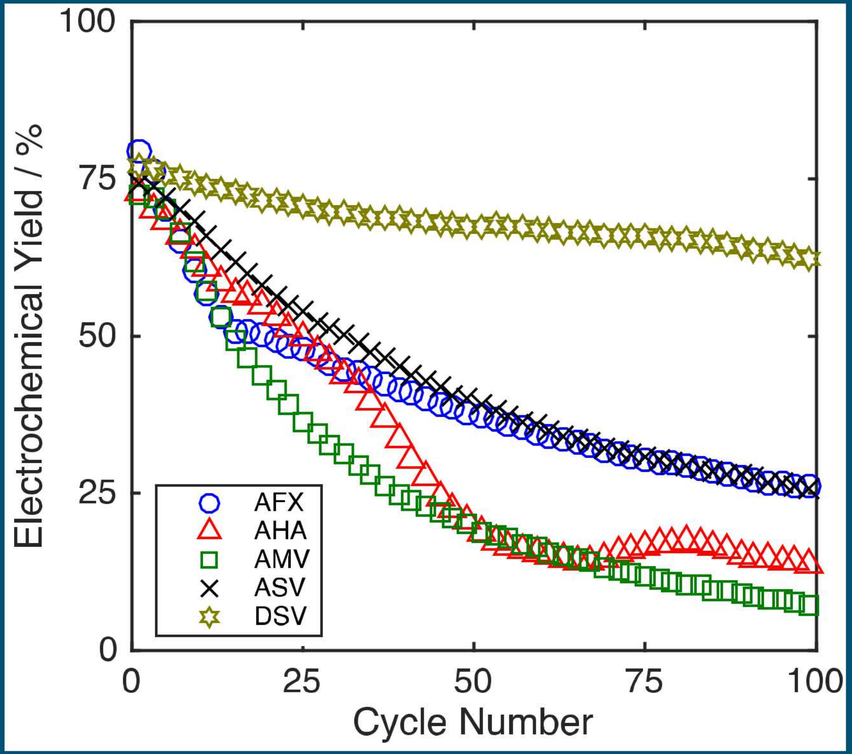
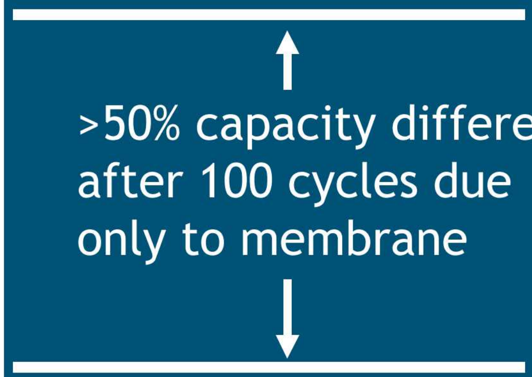
Membranes Display Wide Variation in Capacity Fade





>50% capacity difference after 100 cycles due only to membrane

- No physical membrane deterioration observed in SEM.
- No chemical changes observed in IR.

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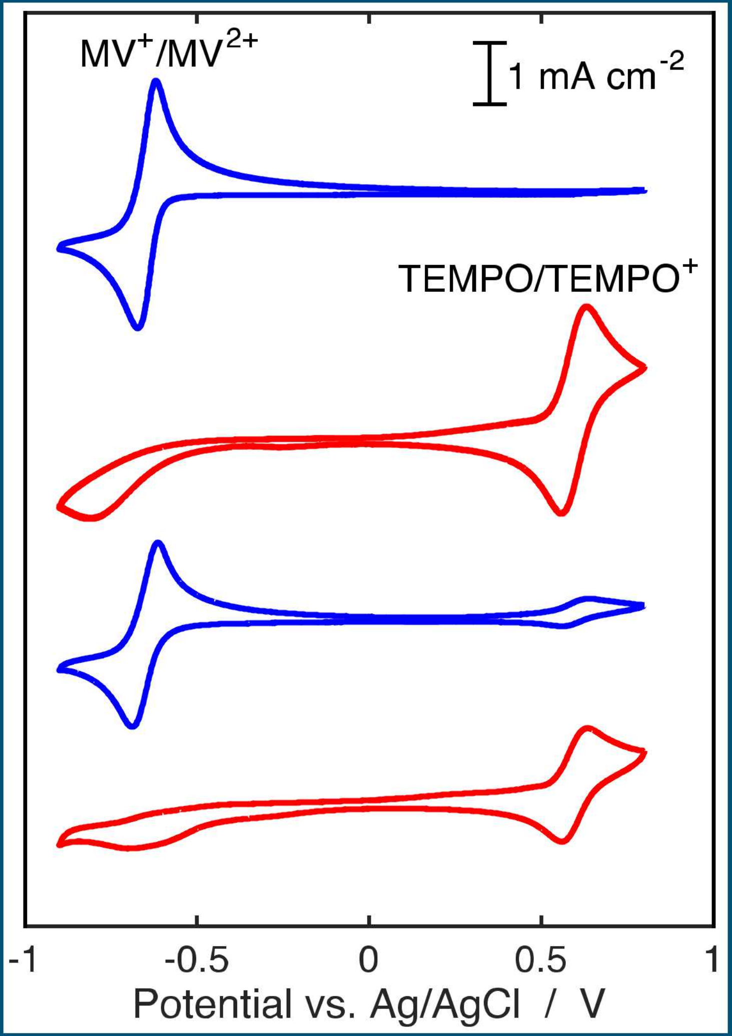
Differences in Capacity Fade Are Due to Crossover

Cyclic Voltammetry of diluted RFB electrolytes



Anolyte (MV) before

Catholyte (TEMPO) before

Anolyte after: TEMPO crossed over

Catholyte after: MV crossed over

Electrolyte from DSV membrane diluted 50x with 1.5 M NaCl
100 mV/s, 25 °C
glassy carbon working electrode

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Crossover Mechanisms

- Diffusion of Ions

Continuously occurs

- Migration
- Electroosmotic Drag

Only occurs when flow battery operates

- Pressure Driven Flow
- Diffusion of Solvent (Osmosis)

Minor contribution to crossover for this system

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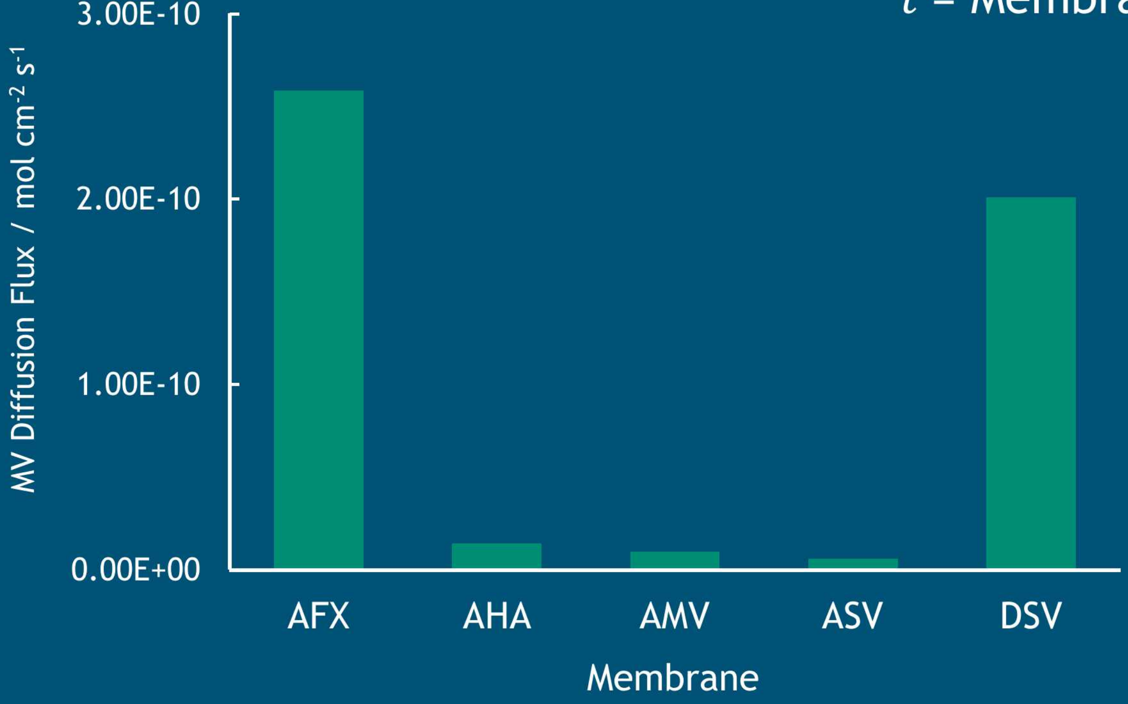
Crossover Mechanism: Diffusion of Ions

Crossover flux due to diffusion[1]:

$$n = \frac{D\Delta c}{t}$$

n = flux
D = diffusion coefficient
Δc = concentration difference
t = Membrane thickness



Counterintuitively, membranes with the ***highest diffusion flux*** had the ***lowest capacity fades***. Something else is dominating capacity fade.

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[1] Darling et al, *J. Electrochem. Soc*. 163, A509-A5040 (2016).

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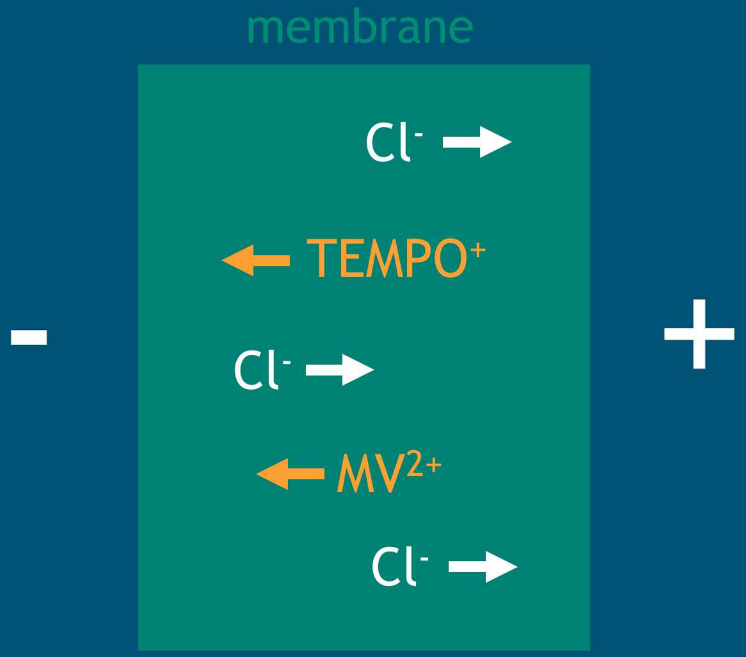
Crossover Mechanism: Migration

- Electric field in membrane drives movement of ions
- Membrane materials properties that are important:
  - resistivity
  - diffusion coefficient
  - concentration



membrane

Cl^- →

← $TEMPO^+$

\-

\+

Cl^- →

← MV^{2+}

Cl^- →

Membranes with ***lower resistances*** generally exhibited ***lower capacity fades***.

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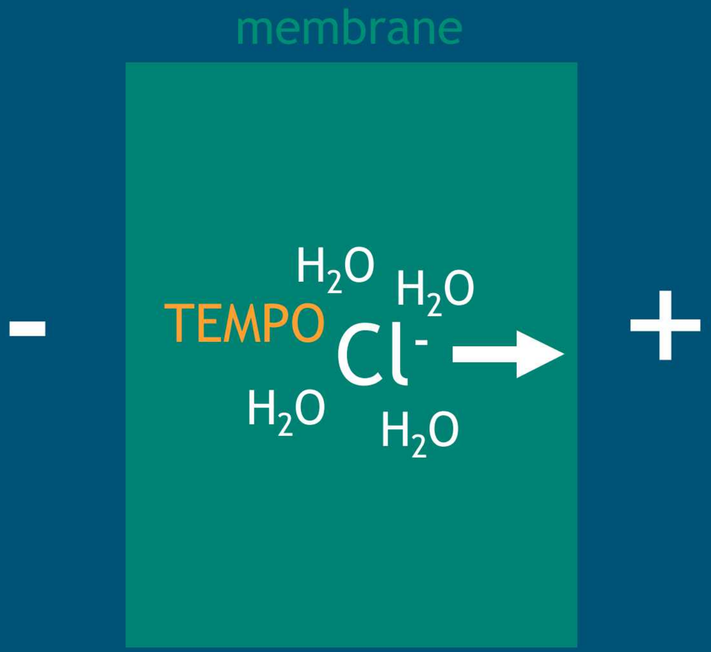
Crossover Mechanism: Electroosmotic Drag

- Movement of Cl^- by migration is accompanied by H_2O which in turn drags TEMPO or MV.

- Membrane materials properties that are important:
  - Electroosmotic drag coefficient
  - TEMPO and MV concentration *in membrane*
  - Membrane water content



Membranes with the ***highest water contents*** generally had ***lower capacity fades***.

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Dominant Crossover Mechanism Varies

Measurement of more than 10 materials constants for each membrane allows identification of primary crossover mechanism.

Membrane	Primary Crossover Mechanism	Capacity Loss
AFX	diffusion + migration	53.6%
AHA	electroosmotic drag	59.6%
AMV	electroosmotic drag	65.1%
ASV	electroosmotic drag	48.9%
DSV	diffusion	14.8%

Different membrane types exhibit different crossover failure mechanisms, even for the same flow battery chemistry!

Moving Forward

We can predict relative flow battery performance of different membranes based on their fundamental materials properties.

Optimizing a membrane specifically for one crossover mechanism may inadvertently increase another mechanism, rendering the membrane an overall worse performer.

Design custom membranes with Cy Fujimoto (Sandia)
- Vary materials properties: water content, ion exchange capacity, etc.
- Systematically minimize crossover, ***using a known chemistry***

Integrated materials analysis
- *In-situ* monitoring of electrolyte masses
- *In-situ* IR monitoring of membrane degradation

Analysis of membranes for nonaqueous flow batteries

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Acknowledgements

Sandia National Labs

Dr. Chad Staiger

Dr. Cy Fujimoto

Dr. Imre Gyuk
DOE Energy Storage Program

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Questions?

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