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Crossover Mechanisms in Polymer Membranes for Redox Flow Batteries

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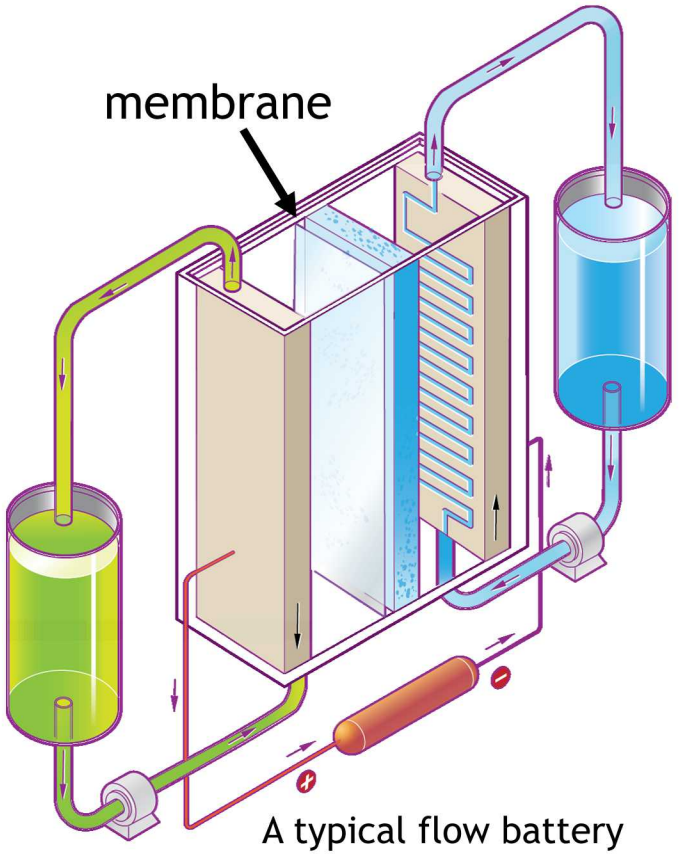
Redox Flow Batteries for Grid Scale Energy Storage

- Redox flow batteries offer an easily scalable solution for grid scale energy storage.
- Many groups have consistently found the membrane to be the weak link in performance. Why?
- Can we predict flow battery ***membrane*** performance from fundamental materials properties?



A typical flow battery

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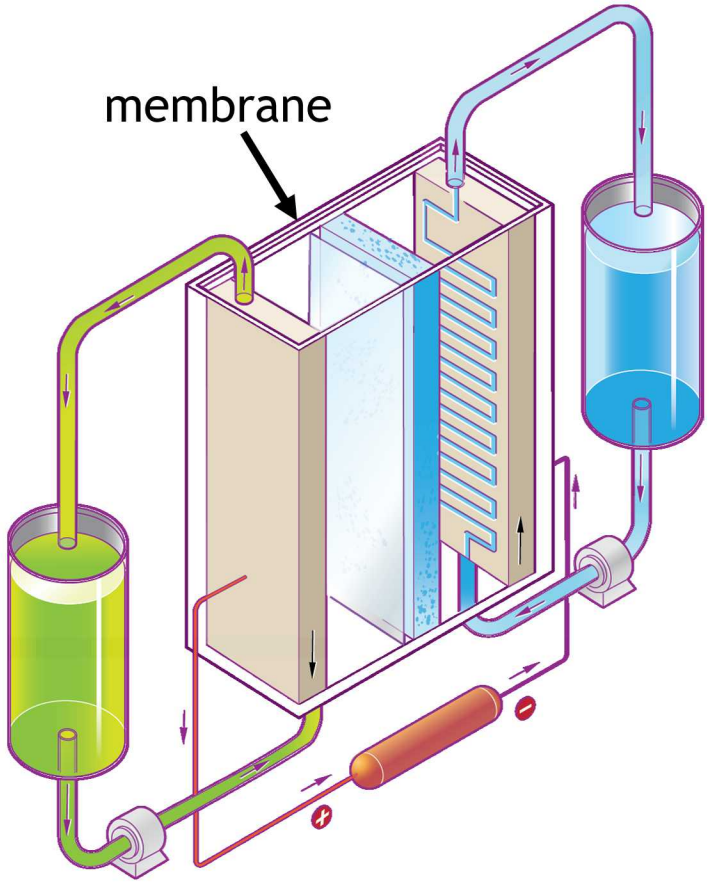
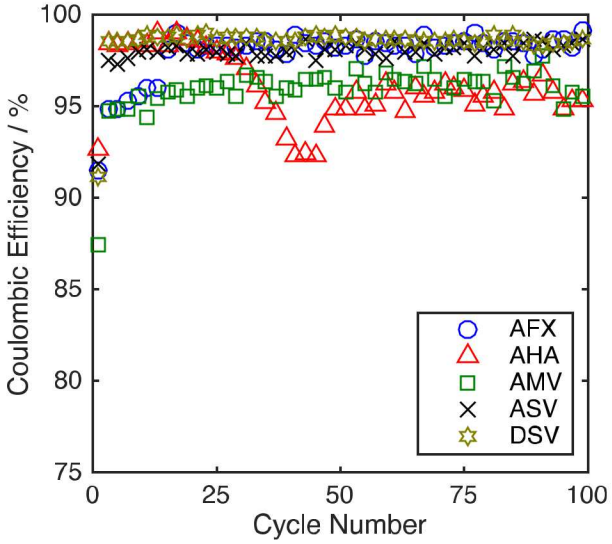
A Model Aqueous Soluble Organic Redox Flow Battery

- 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: $TEMPO \rightarrow TEMPO^{+} + e^{-}$
  - Anolyte: $MV^{2+} + e^{-} \rightarrow MV^{+}$
- Electrolyte
  - 1.5 M NaCl + 0.5 M MV or TEMPO
  - blanketed under argon
- 100 cycles at ±50 mA cm^{-2}



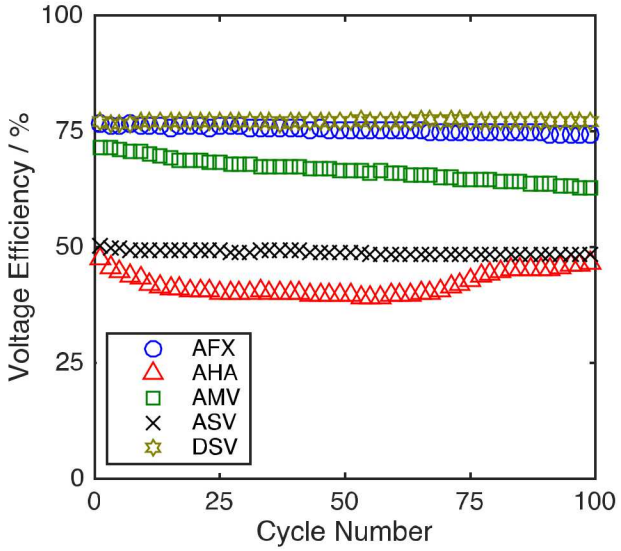
[1]T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, *Adv. Mater.* **2016**, *6*, 1501449.

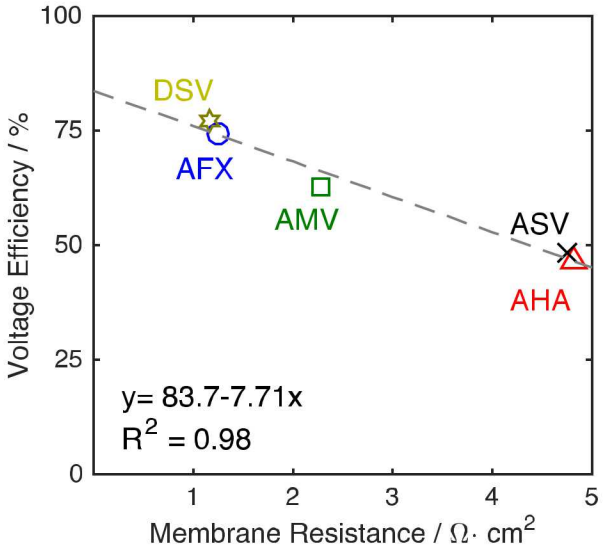
Influence of Membrane on Flow Battery Efficiencies



All membranes display >95% Coulombic efficiency.

Voltage efficiencies ranged 40-75%, inversely proportional to membrane resistance.





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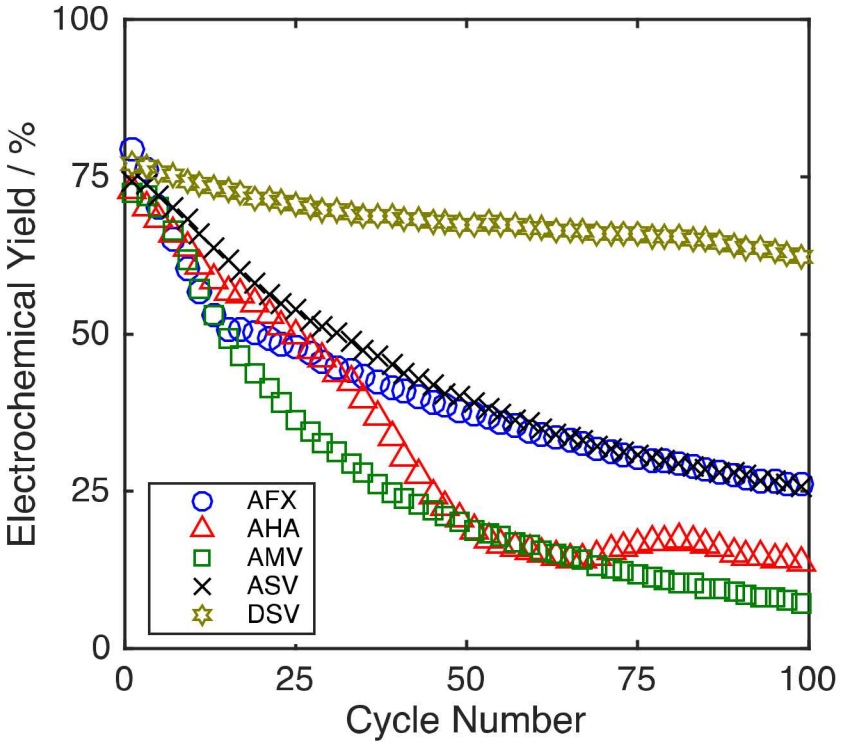
Membranes Display Wide Variation in Capacity Fade



>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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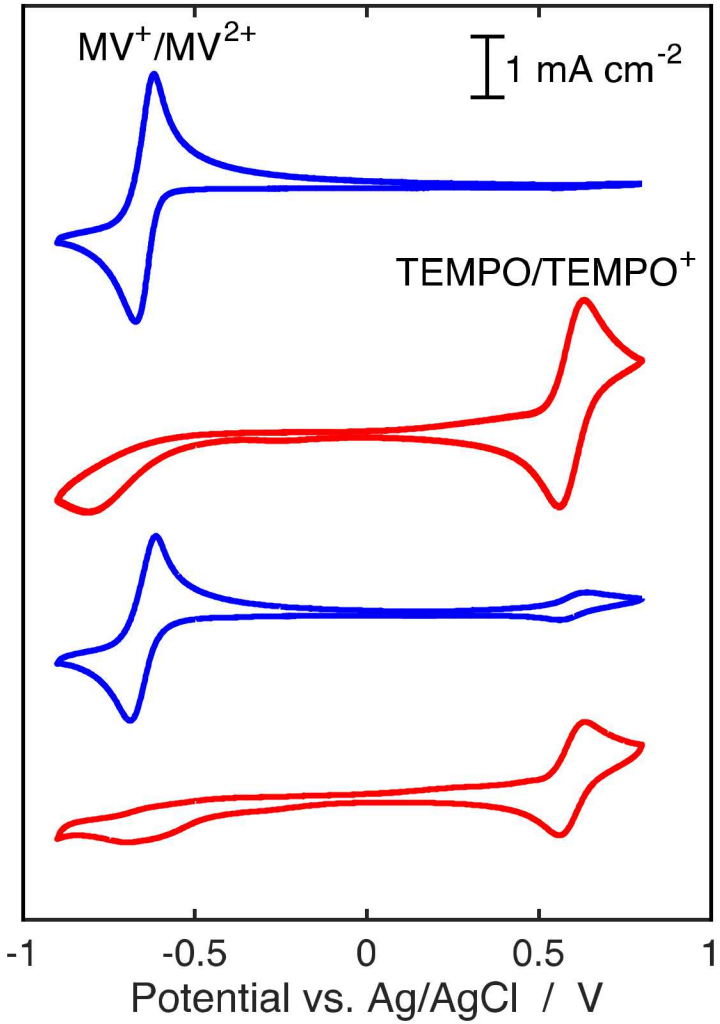
Differences in Capacity Fade Are Due to Crossover

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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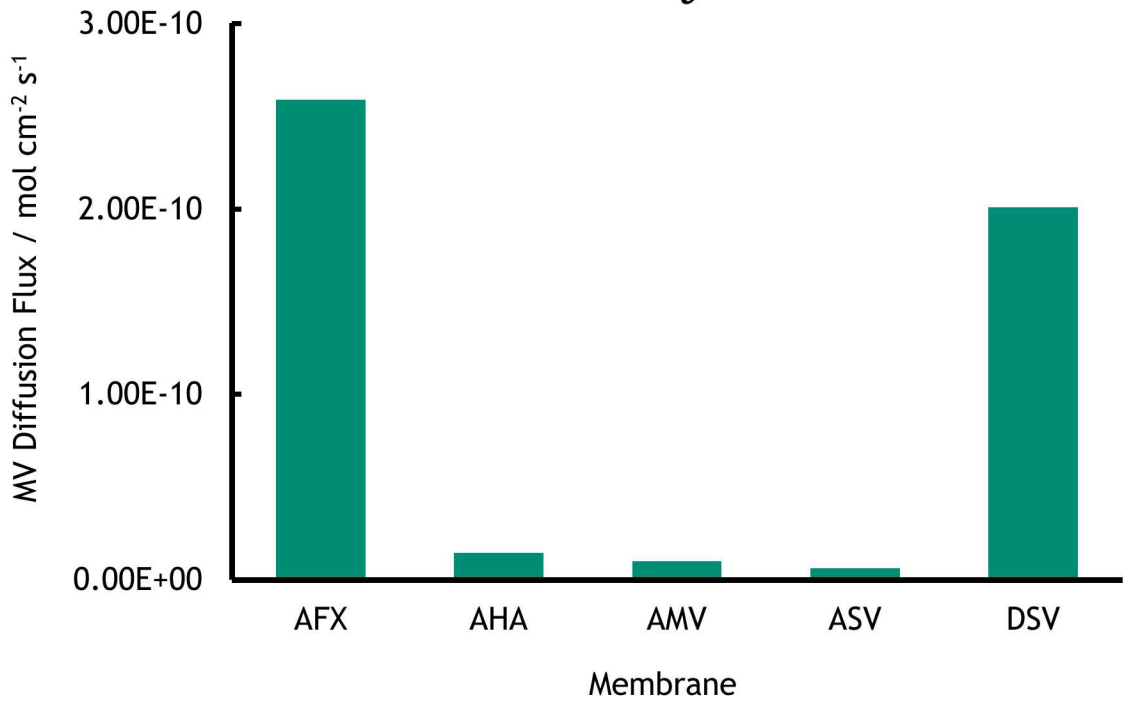
Crossover Mechanism: Diffusion of Ions

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 fluxes*** had the ***lowest capacity fades***. Something else dominates AHA, AMV and ASV's capacity fade.

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

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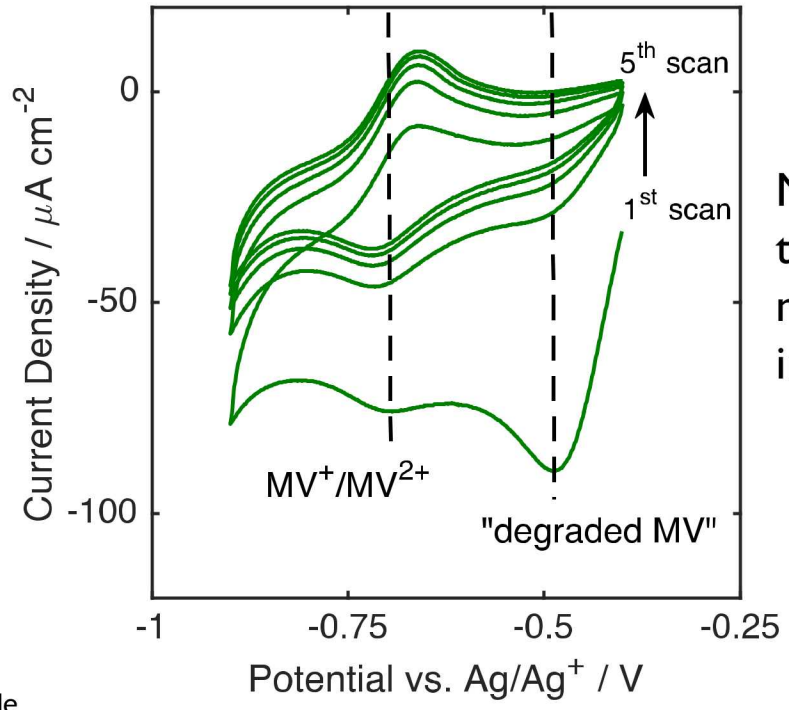
MV Interaction with Membranes During Diffusion Test

- For AHA, AMV, and ASV membranes, some of initial MV^{2+} that diffuses through H-cell is not electrochemically reversible.
- Not seen on AFX and DSV membranes
- Not seen in CVs of RFB electrolyte after cycling

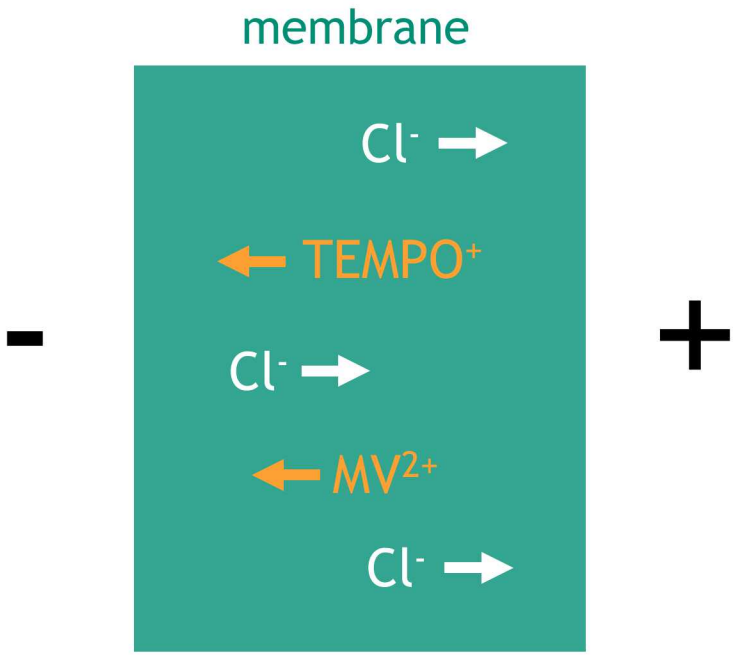


MV that initially diffuses through select membranes has some irreversible component.

glassy carbon working electrode
100 mV/s, 25 °C
Argon-sparged 1.5 M NaCl on diffusion test receiving side

Crossover Mechanism: Migration

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



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

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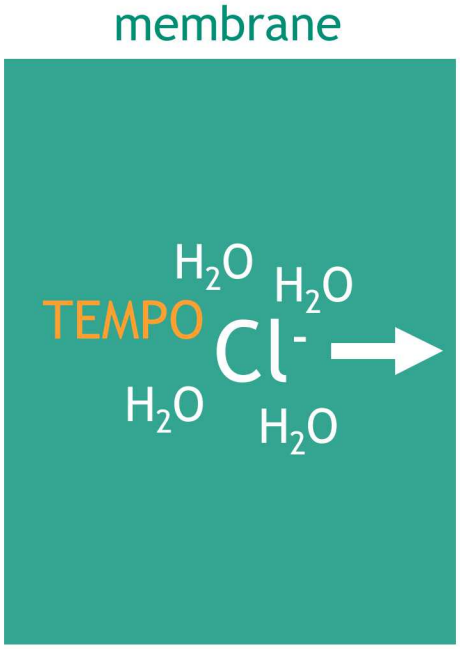
Crossover Mechanism: Electroosmotic Drag

- 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 membranes exhibit different crossover failure mechanisms, even for the same flow battery chemistry!

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Moving Forward

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* monitoring of crossover

Analysis of membranes for nonaqueous flow batteries

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Questions?

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