SAND2018-10589C

Ions on the Loose: Quantifying Crossover in Aqueous Soluble Organic Redox Flow Batteries

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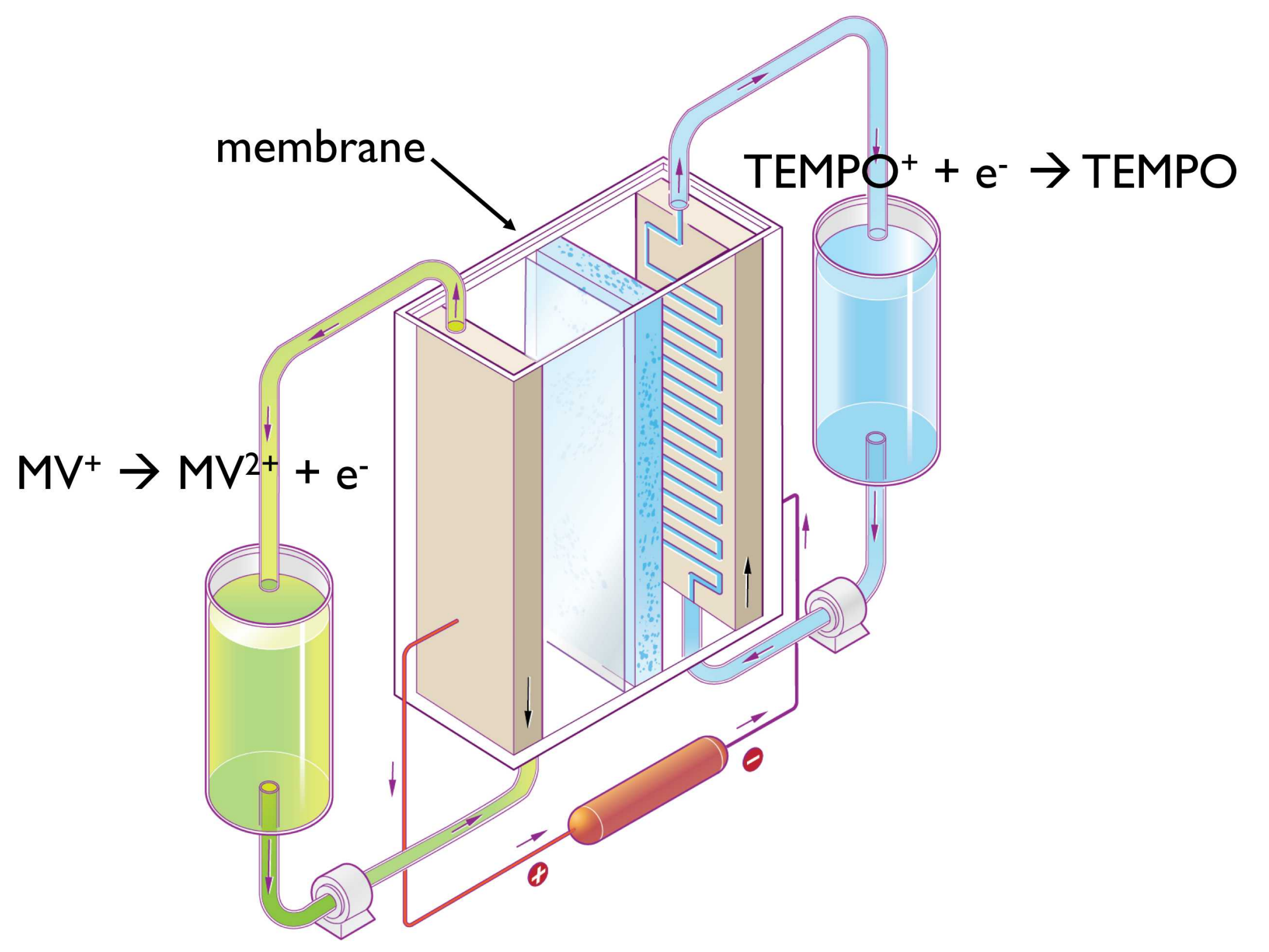
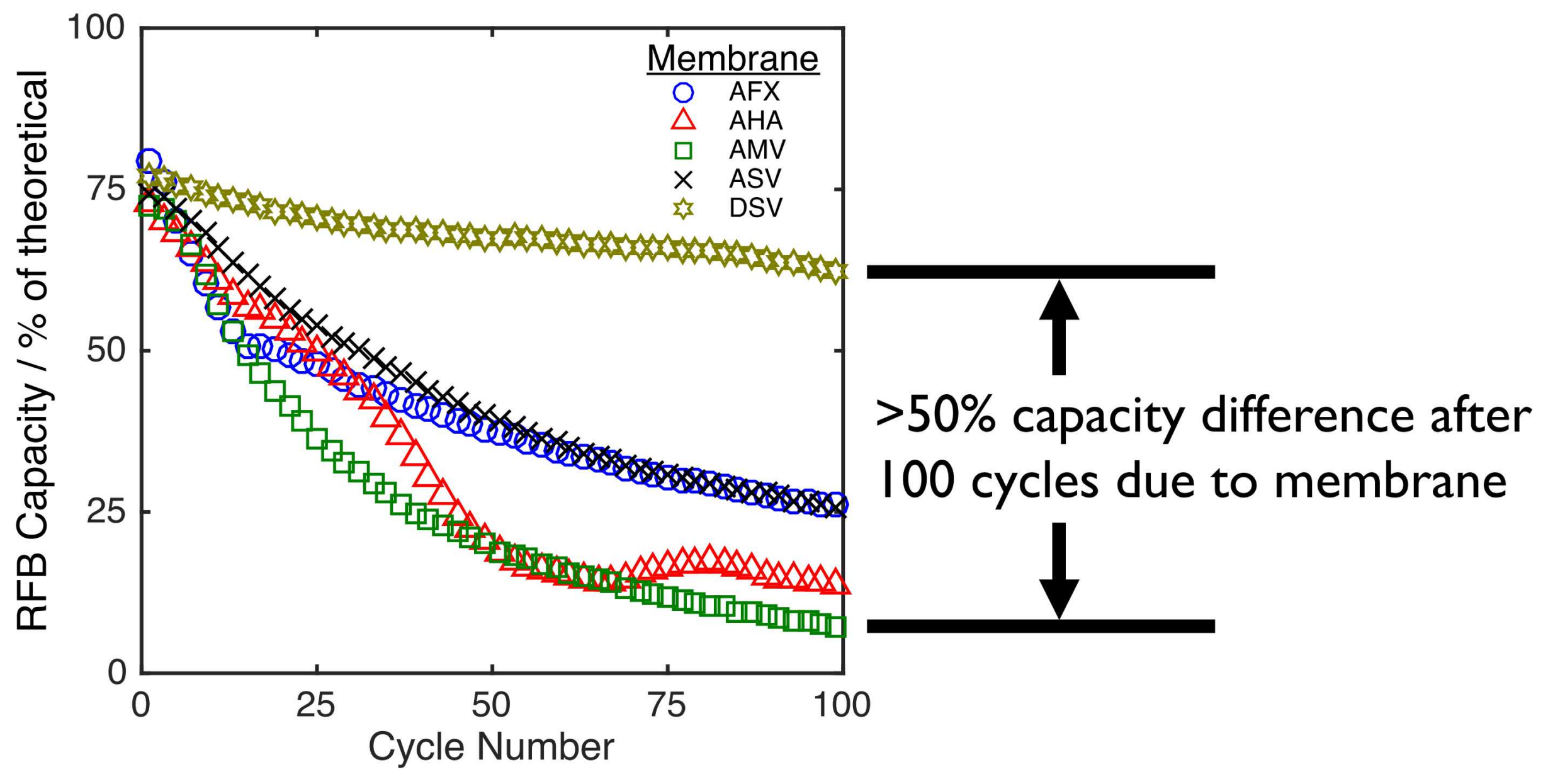
Redox flow batteries (RFBs) offer a readily scalable solution to grid scale energy storage. Throughout our and others' previous works, the membrane that divides the anolyte and catholyte has been consistently noted as a limiting factor in RFB performance. We selected five commercially-available anion-selective membranes and compared their performance in a well-studied aqueous soluble organic system[1] leveraging a methyl viologen (MV)-based anolyte and TEMPO-based catholyte. RFBs with different membranes displayed significant variation in capacity loss due to crossover of the electroactive species from anode to cathode, and vice versa. The underlying crossover mechanism varied from membrane to membrane, and can be predicted from the membrane's fundamental materials properties, enabling superior design of next generation membranes for RFBs.

A typical flow battery

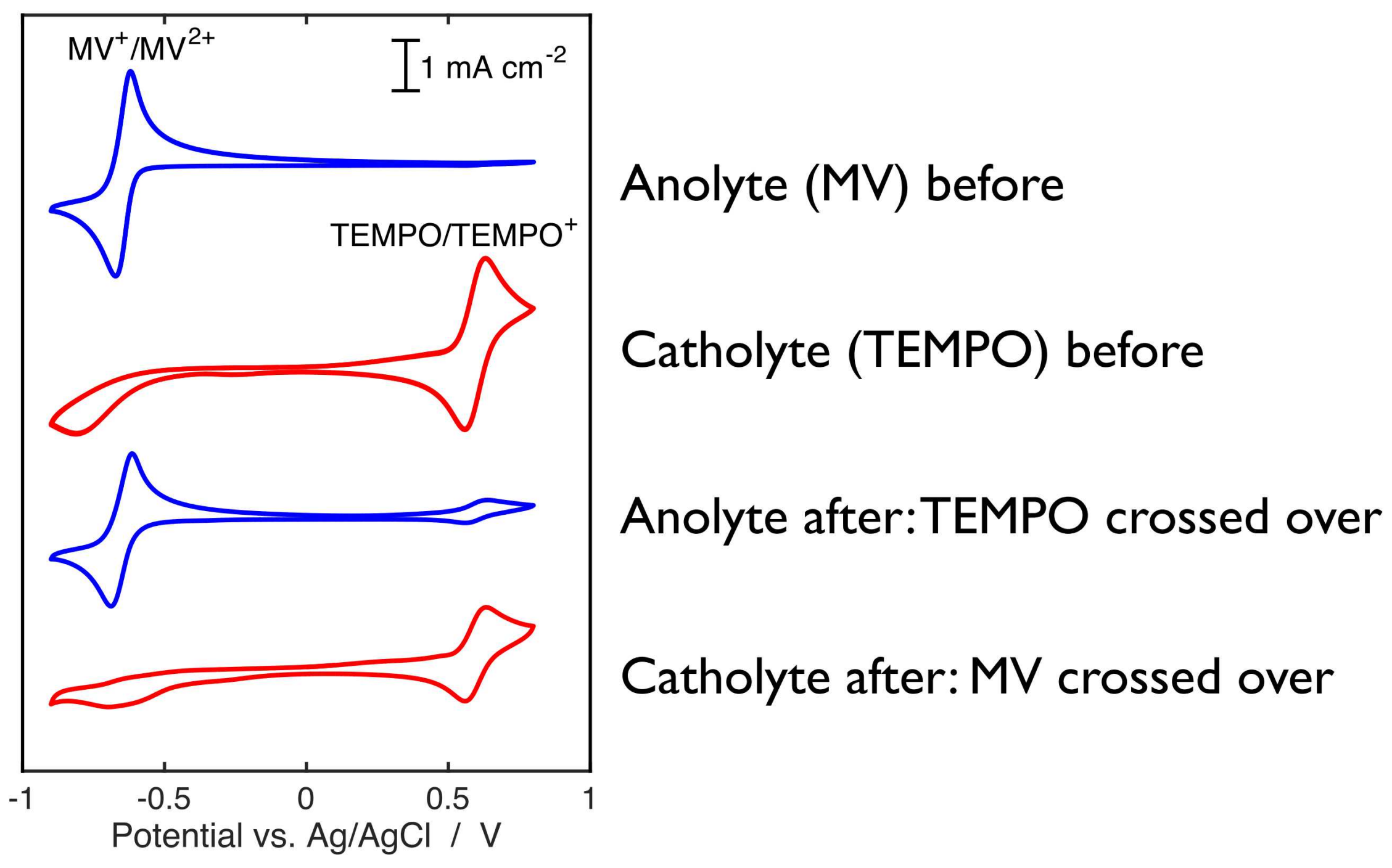


Capacity loss varies significantly with membrane.



±50 mA cm^{-2}, 25 °C
0.5 M MV or TEMPO in 1.5 M NaCl

Cyclic Voltammetry of diluted RFB electrolytes reveals crossover of MV and TEMPO.



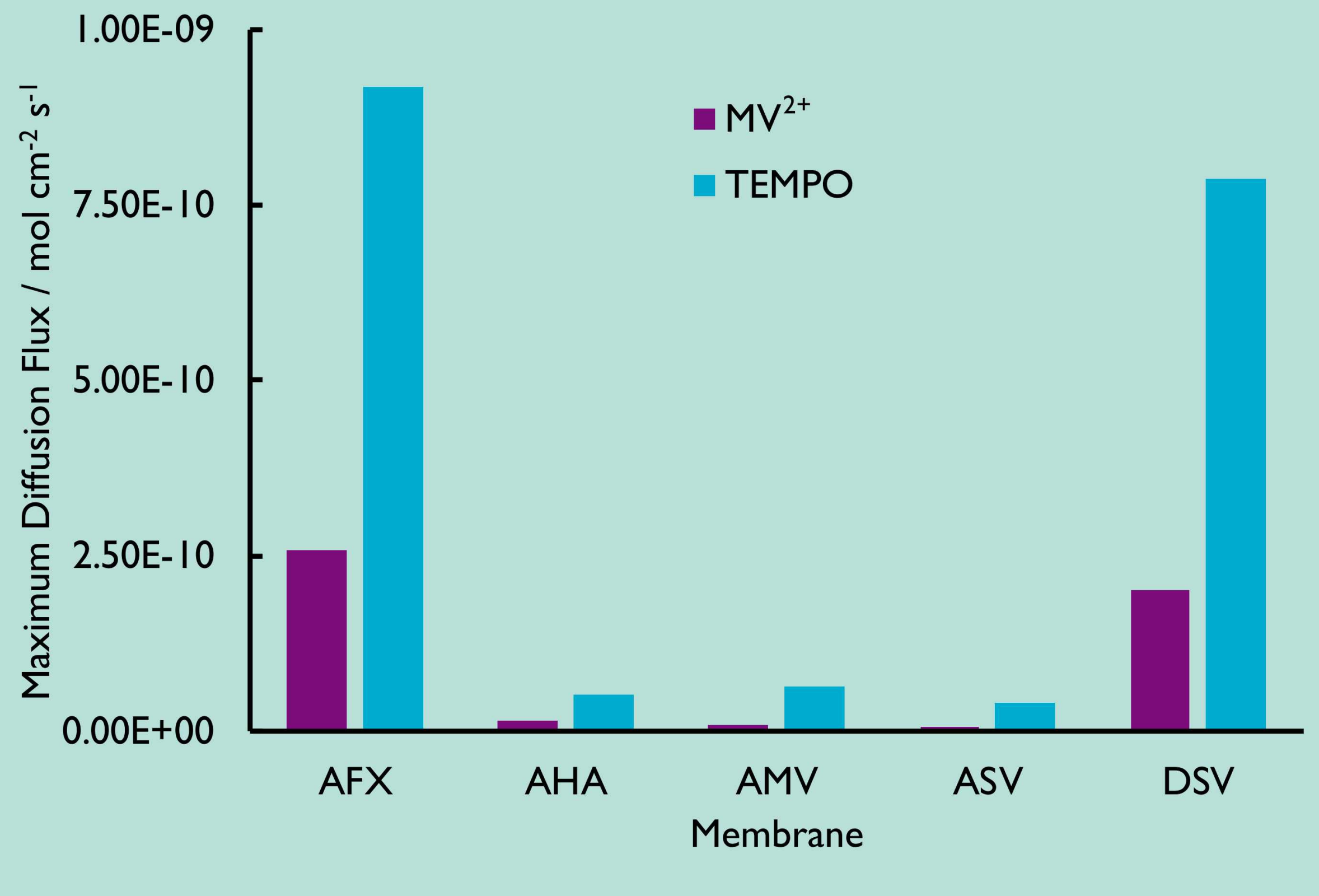
Crossover can occur by several mechanisms, three of which are explained below.

Diffusion of Ions

Crossover flux due to diffusion of methyl viologen (MV):

$$n_{diff,MV} = \frac{D_{MV}\Delta c_{MV}}{t}$$

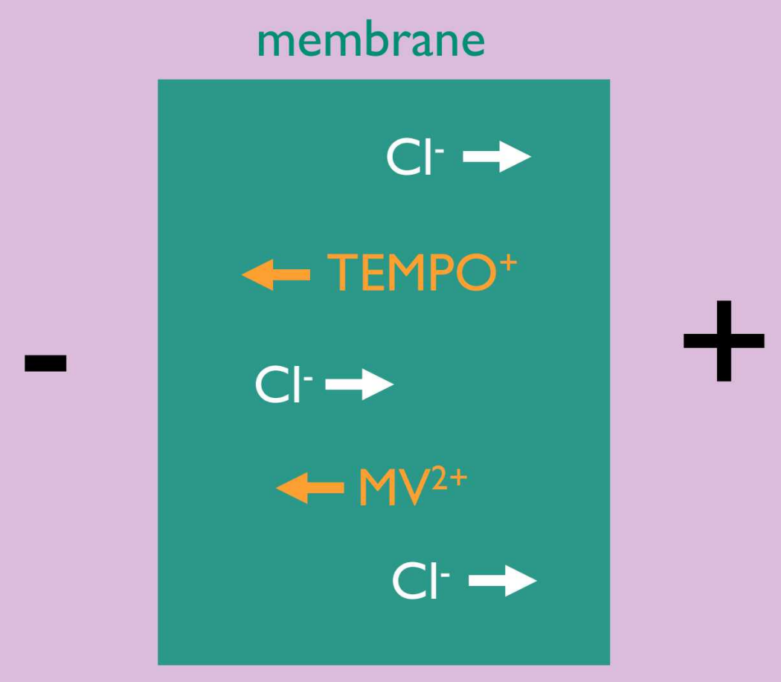
$N_{dff,MV}$ = MV diffusion flux
D_{MV} = diffusion coefficient
Δc_{MV} = concentration difference
t = membrane thickness



Counterintuitively, membranes with the ***highest diffusion fluxes*** (AFX, DSV) had the ***lowest capacity loss.*** Diffusion is not always the dominant crossover mechanism!

Migration

$MV^{+/2+}$ and $TEMPO^+$ in the membrane move under the electric field present during battery operation.



Crossover flux due to migration of methyl viologen (MV):

$$n_{mig,MV} = \underbrace{\frac{z_{MV}F}{RT}}_{\text{constants}} * \underbrace{\mathrm{i}}_{\text{applied current}} * D_{MV}c_{MV}\rho \leftarrow \text{Membrane properties}$$

Membrane properties
D_{MV} = diffusion coefficient
c_{MV} = MV concentration
ρ = resistivity

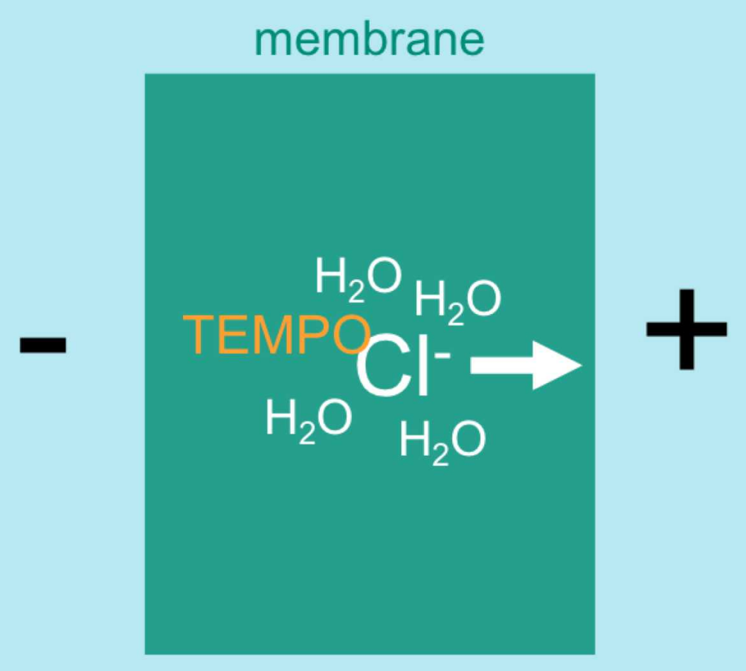
Membrane	Resistivity / ohm*cm
AFX	90.5
AHA	253
AMV	218
ASV	433
DSV	125

1.5M NaCl
25 °C

Membranes with ***lower resistivities*** generally exhibited ***lower capacity losses.***

Electroosmotic Drag

Movement of Cl^- and associated waters during battery operation drags along $MV^{+/2+}$ and $TEMPO^{0/+}$ dissolved in the membrane.



Crossover flux due to electroosmotic drag of methyl viologen (MV):

$$n_{drag,MV} = \underbrace{\frac{1}{F}}_{\text{constants}} * \underbrace{i}_{\text{applied current}} * \frac{c_{MV}\xi}{c_w} \leftarrow \text{Membrane properties}$$

Membrane properties
c_{MV} = MV concentration in membrane
c_w = water concentration in membrane
ξ = electroosmotic drag coefficient

Membrane	Water Content / M
AFX	13.0
AHA	4.70
AMV	9.89
ASV	7.28
DSV	13.2

Membranes with the ***higher water concentrations*** generally had ***lower capacity losses.***

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 fail by different crossover mechanisms, even for the same flow battery chemistry!

[1] T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, *Adv. Mater.* **2016**, *6*, 1501449.
[2] Darling et al, *J. Electrochem. Soc.* **2016**, 163, A509-A5040.

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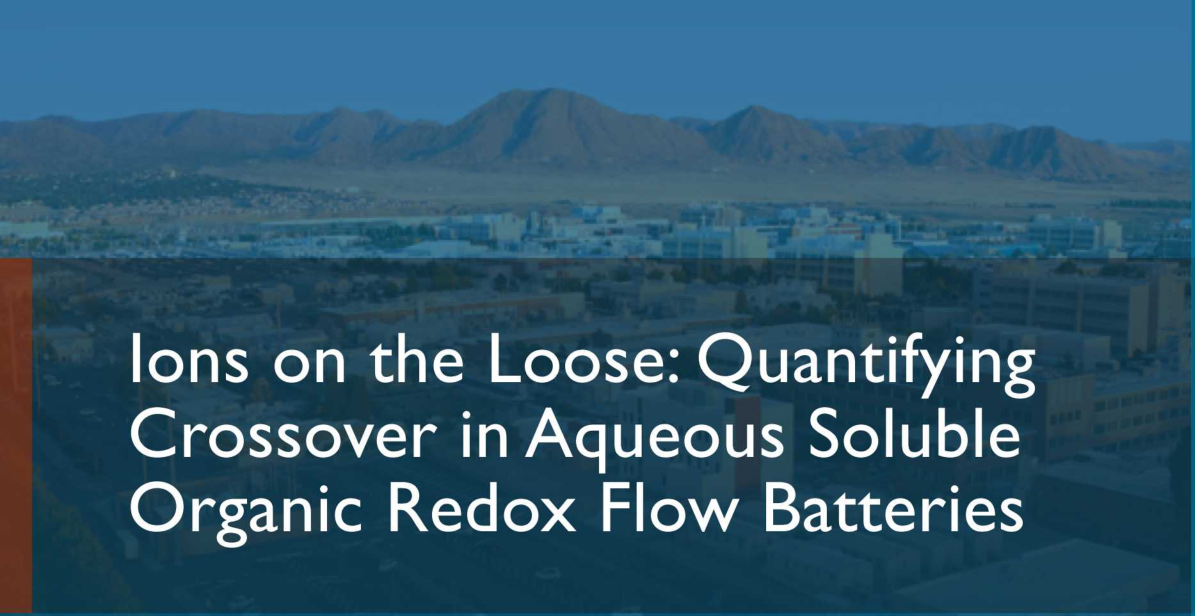

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DOE OE Energy Storage Peer Review

26 Sep 2018

PRESENTED BY

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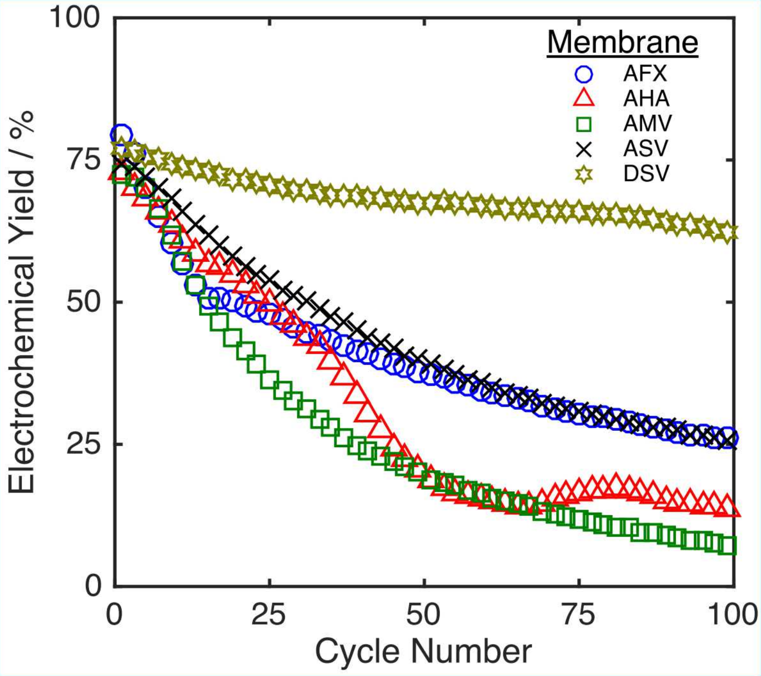
Choice of Membrane Greatly Influences Capacity Loss

- Compare performance of five commercial anion-exchange membranes in widely-studied aqueous soluble organic flow battery.
- Wide variation in capacity loss after 100 cycles at 50 mA cm^{-2} due primarily to crossover of redox-active species
- Measure >10 materials constants to predict crossover using a dilute solution model.



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

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