Comparison of Membrane Performance for Vanadium Redox Flow Batteries

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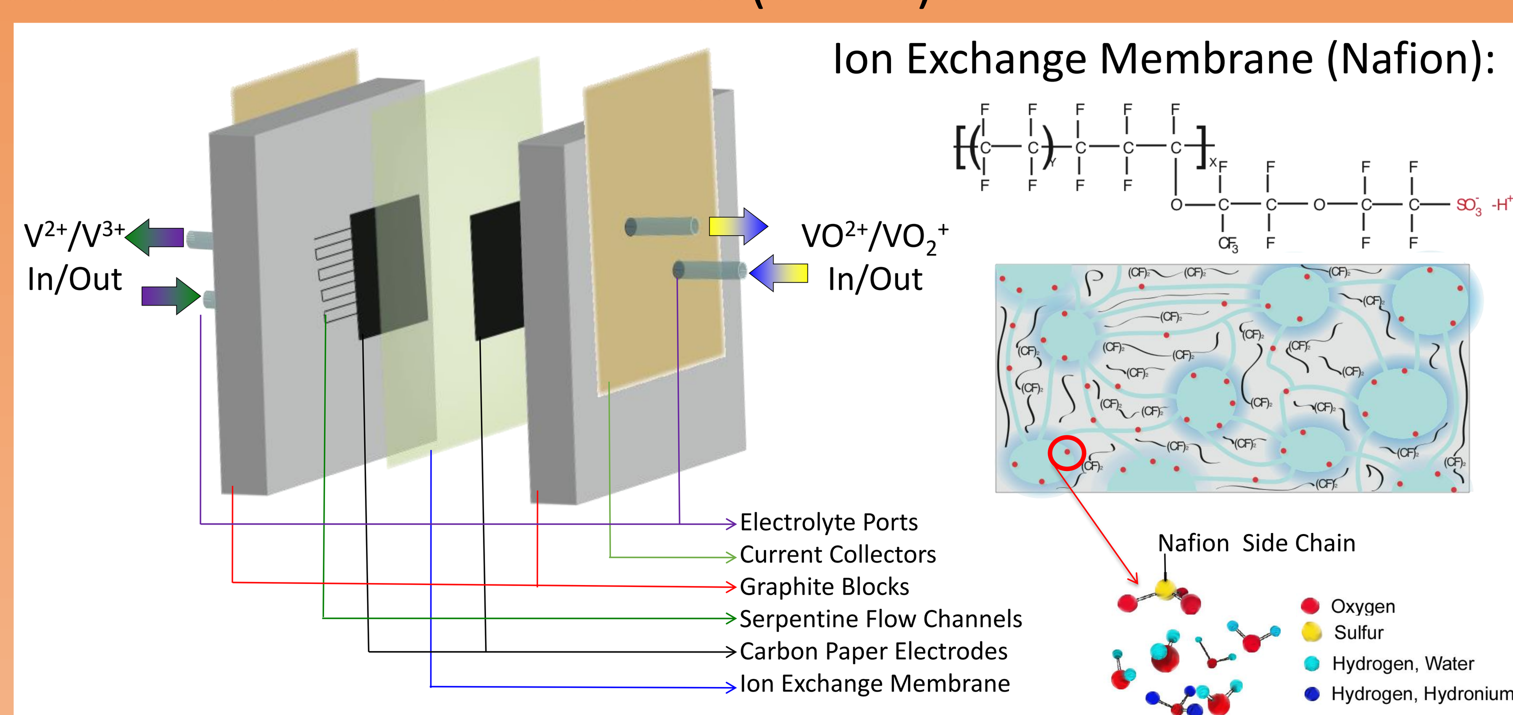
Abstract:

The vanadium redox flow battery (VRFB) is a promising solution for large-scale energy storage. VRFBs consist of positive and negative cells operating with VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox couples. Ion diffusion across the membrane, known as crossover, is a problem that causes battery self-discharge. Electron Paramagnetic Resonance (EPR) is a sensitive technique able to detect VO^{2+}. By flowing battery electrolyte through the EPR cavity, the concentration of VO^{2+}can be monitored. This method is used to characterize vanadium transport in VRFB membranes. Data from such experiments is useful in guiding membrane development as well as comparing the performance of membranes. Cost, chemical stability, vanadium permeability, and ion conductivity are important factors to consider when selecting an appropriate membrane for battery operation. The Sulfonated Diels-Alder Polyphenylene (SDAPP) membrane is a possible alternative membrane for VRFB applications. Characterization of SDAPP membranes with different ion exchange capacities (IEC) allows for a better understanding of the effect of sulfonation level on the transport properties of the membrane.

Vanadium Redox Flow Batteries (VRFBs) :



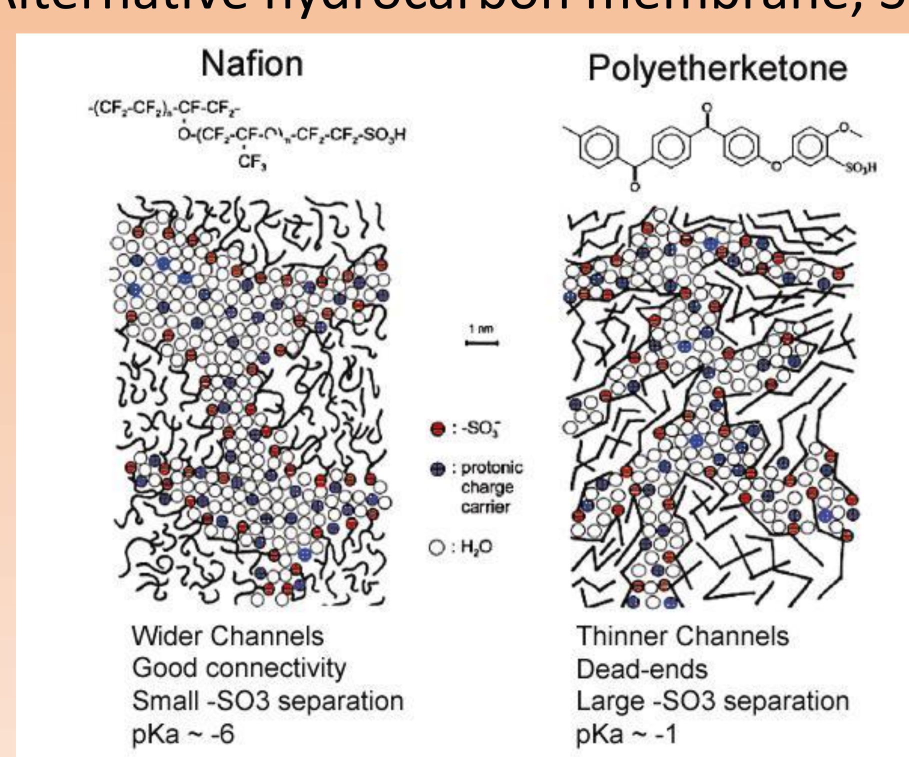
Positive Side Rxn:

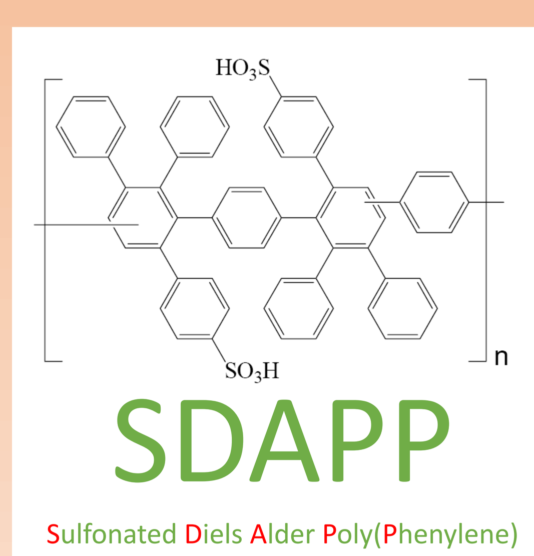
$VO^{2+} + H_2O \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} VO_2^+ + 2H^+$ E= 1.000 V

Negative Side Rxn:

$V^{3+} + e^- \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} V^{2+}$ E=-0.255 V

Alternative hydrocarbon membrane, SDAPP[1]:





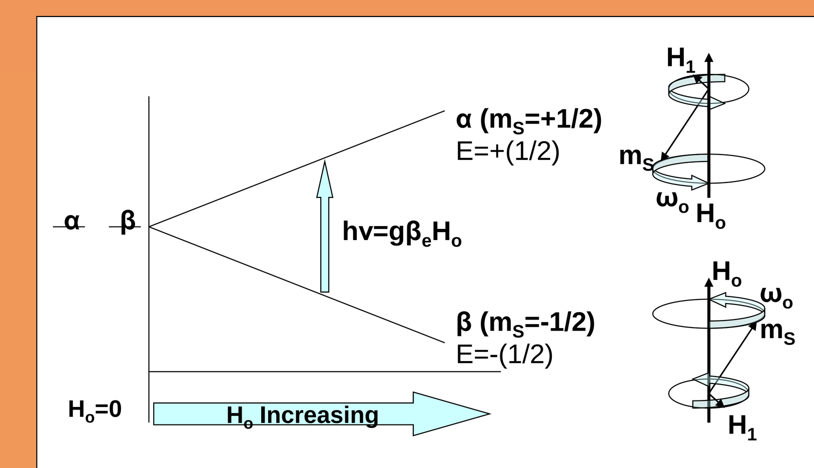
➢The number of sulfonate groups (IEC) in SDAPP is controllable. Higher IEC generally results in higher conductivity and water uptake

References:

Fujimoto, C.H, Hickner, M.A., Cornelius, C.J., Loy, D.A. *Macromolecules* **2005**, 38(12), 5010-5016.

Kreuer, K. D. On the Development of Proton Conducting Polymer Membranes for Hydrogen and Methanol Fuel Cells. *J. Membr. Sci.* **2001**, 185: 29-39

Electron Paramagnetic Resonance (EPR):



EPR detects the transitions of unpaired electrons in an applied magnetic field (H_o) caused by a resonant microwave frequency (H_1)

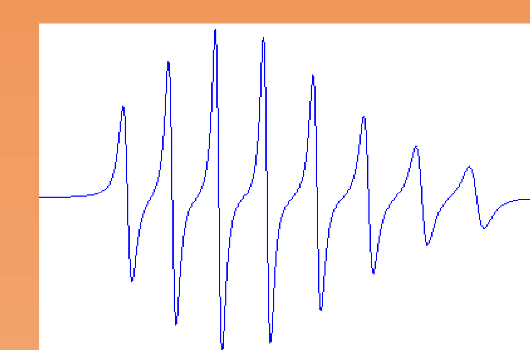
Vanadium Ion Electron Configuration:

VO_2^+: $1s^22s^22p^63s^23p^6$

VO^{2+}: $1s^22s^22p^63s^23p^64s^03d^1$

V^{3+}: $1s^22s^22p^63s^23p^64s^03d^2$

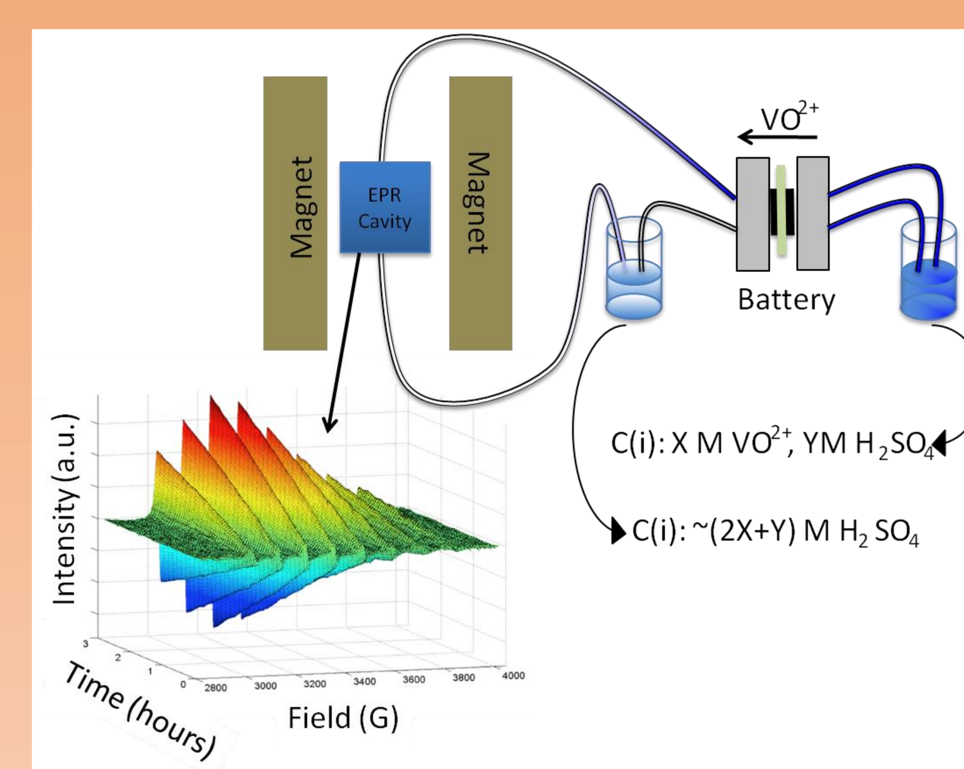
V^{2+}: $1s^22s^22p^63s^23p^64s^03d^3$



Flow-Through EPR Method:

➢Electrolyte flows through the battery and then through the EPR cavity

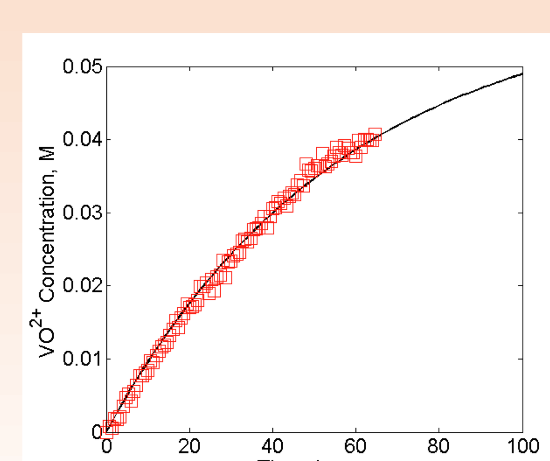
➢When monitoring the blank side, vanadium signal increases with time



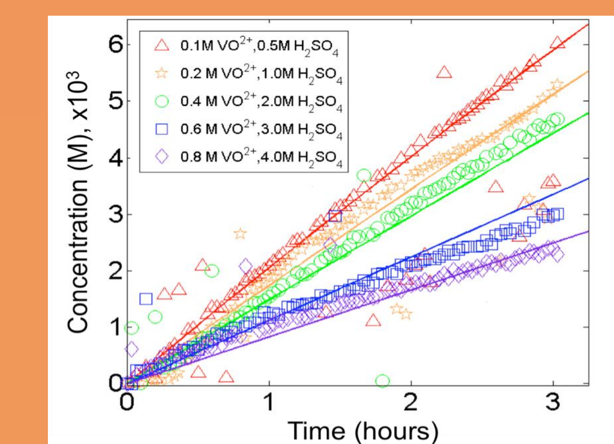
Permeability Determined by Fick's Second Law:

$$C(t) = C_{t=\infty} + (C_{t=0} - C_{t=\infty}) e^{\frac{-PAt}{Vl}}$$

➢Where P is the permeability (m^2/s), V is the volume of the electrolyte, l is the thickness of the membrane, A is the electrode area, t is time, and C is concentration from the initial point ($C_{t=0}$) to equilibrium ($C_{t=\infty}$)



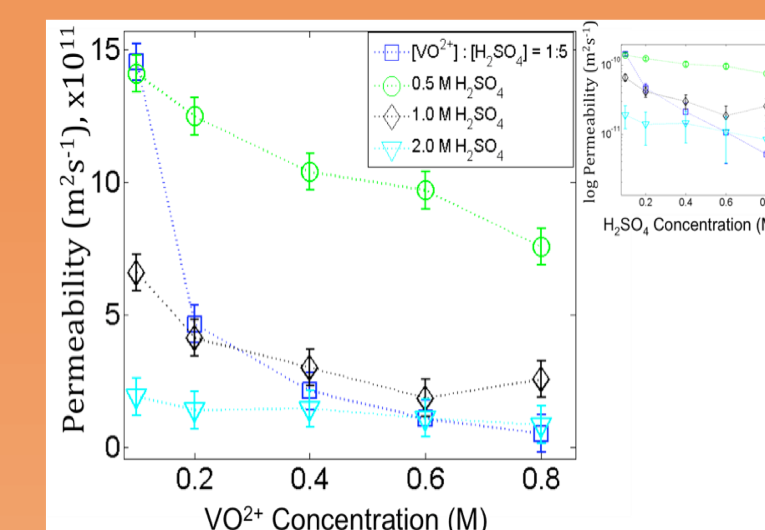
VO^{2+} Crossover in Nafion :



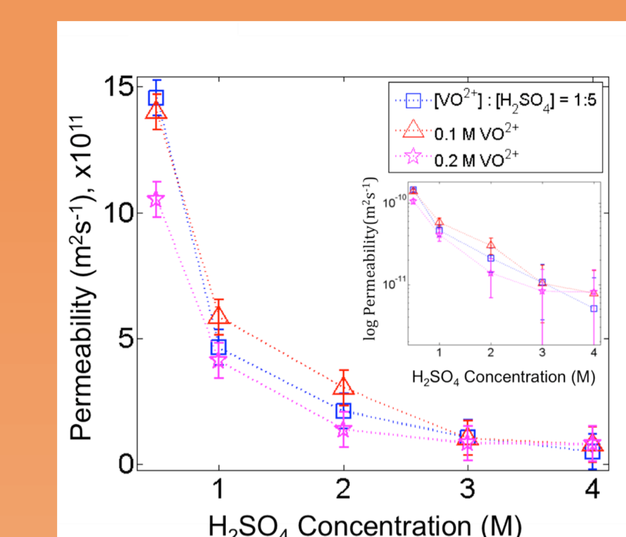
➢Concentrations observed when $[VO^{2+}]$:$[H_2SO_4]$ ratio is maintained at 1:5

➢The highest VO^{2+} concentration accumulated on the blank side after 3 hours resulted from the lowest initial VO^{2+} and H_2SO_4 concentrations on the vanadium rich side

Permeability Values:

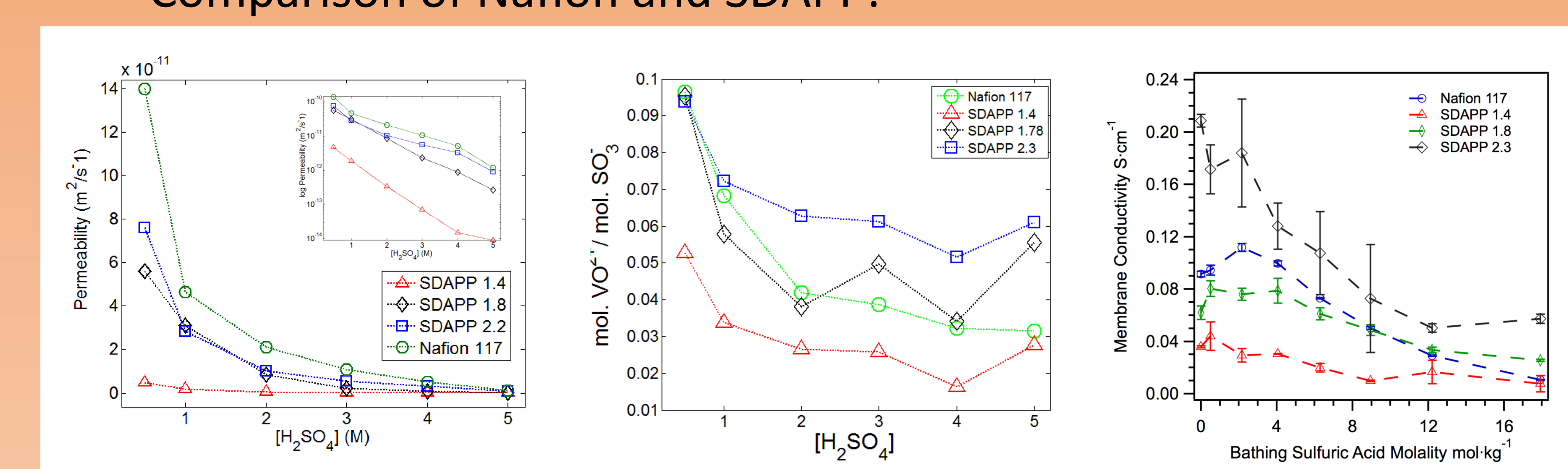


➢VO^{2+} permeability values calculated for changing VO^{2+} concentrations



➢VO^{2+} permeability values calculated for changing H_2SO_4 concentrations

Comparison of Nafion and SDAPP:



➢VO^{2+} crossover is lowest in SDAPP 1.4 due to fewer acid groups in the membrane

➢VO^{2+} uptake in the membrane, which affects crossover

➢VO^{2+} conductivity is also lowest in SDAPP 1.4. Low crossover is desirable, but low conductivity is not.

Conclusions:

➢Intensity of EPR signal can be used to determine VO^{2+} concentration

➢Permeability can then be calculated from concentration change

➢VO^{2+} permeability decreases with both increasing H_2SO_4 concentration and increasing VO^{2+} concentration

➢As H_2SO_4 concentration increases, the effect of VO^{2+} concentration on permeability is significantly diminished

➢This method can be extended to monitor other vanadium species and provide the data necessary for modeling VRFB cell and membrane processes

➢The most suitable membrane for VRFB applications should have low vanadium permeability but maintain a high conductivity

Acknowledgements:

➢ We would like to gratefully acknowledge the support of the NSF-funded TN-SCORE program, NSF EPS-1004083, under Thrust 2