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Improving the durability of the Sandia flow battery membrane

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Collaborators, Professor Michael Aziz (Tommy George), Professor Michael Marshak (Brian Robb)

DOE Office of Electricity Energy Storage Peer Review

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Importance of the membrane in flow batteries:

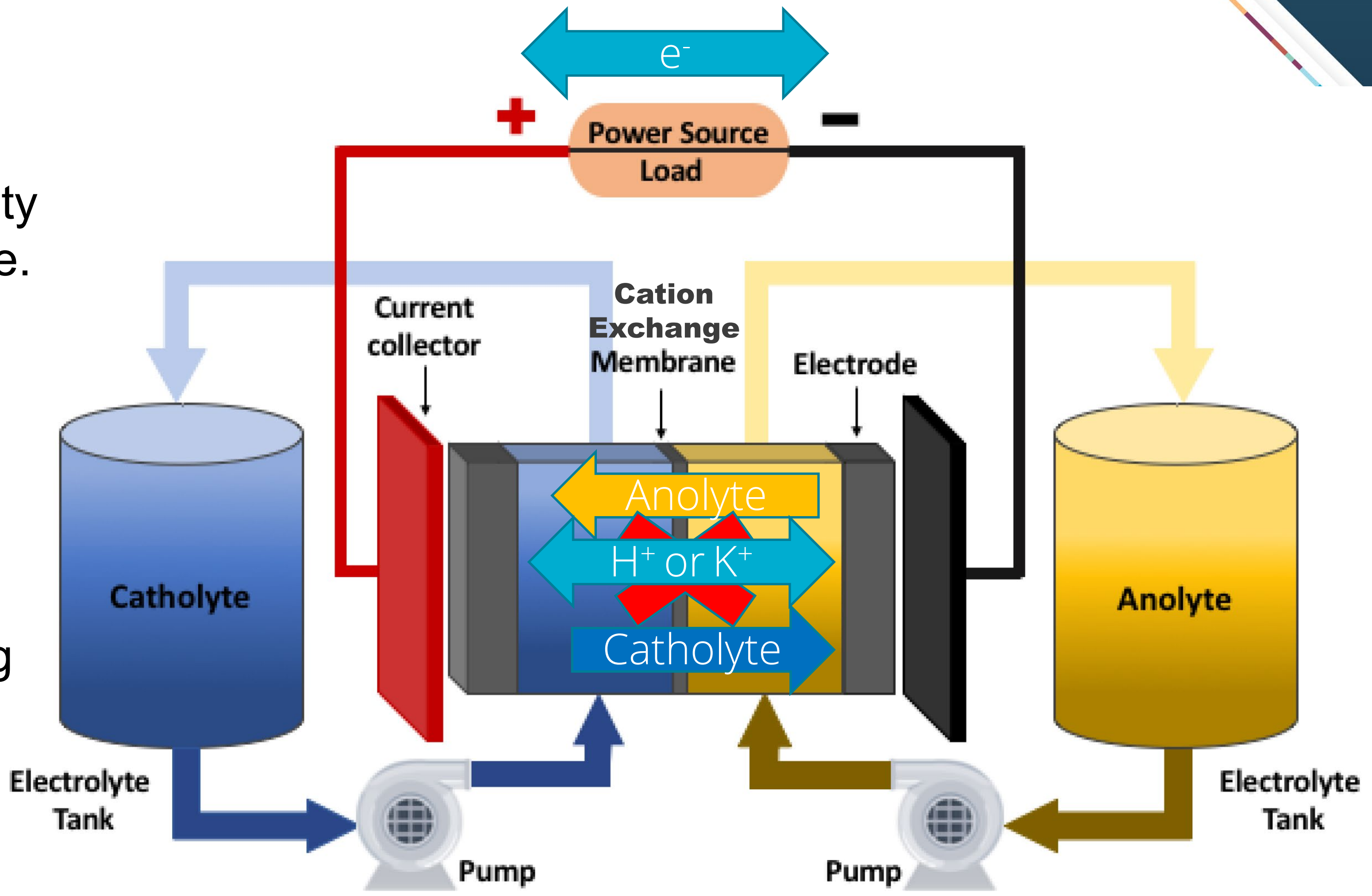
Desired Membrane Properties

1. Selective ion transport: Prevent electroactive species cross over. Results in maintaining battery capacity over time and improve battery lifetime.

   Current is coupled to ion migration. Membrane need to allow passage of specific ion. Results in lowering battery resistive losses.

2. Low cost $10m^{-2}. Results in lowering battery capital cost

3. Membrane required to survive highly oxidative/reductive and variety of pH environments.



Modified from Electronics 2020, 9(10), 1567 (2020)

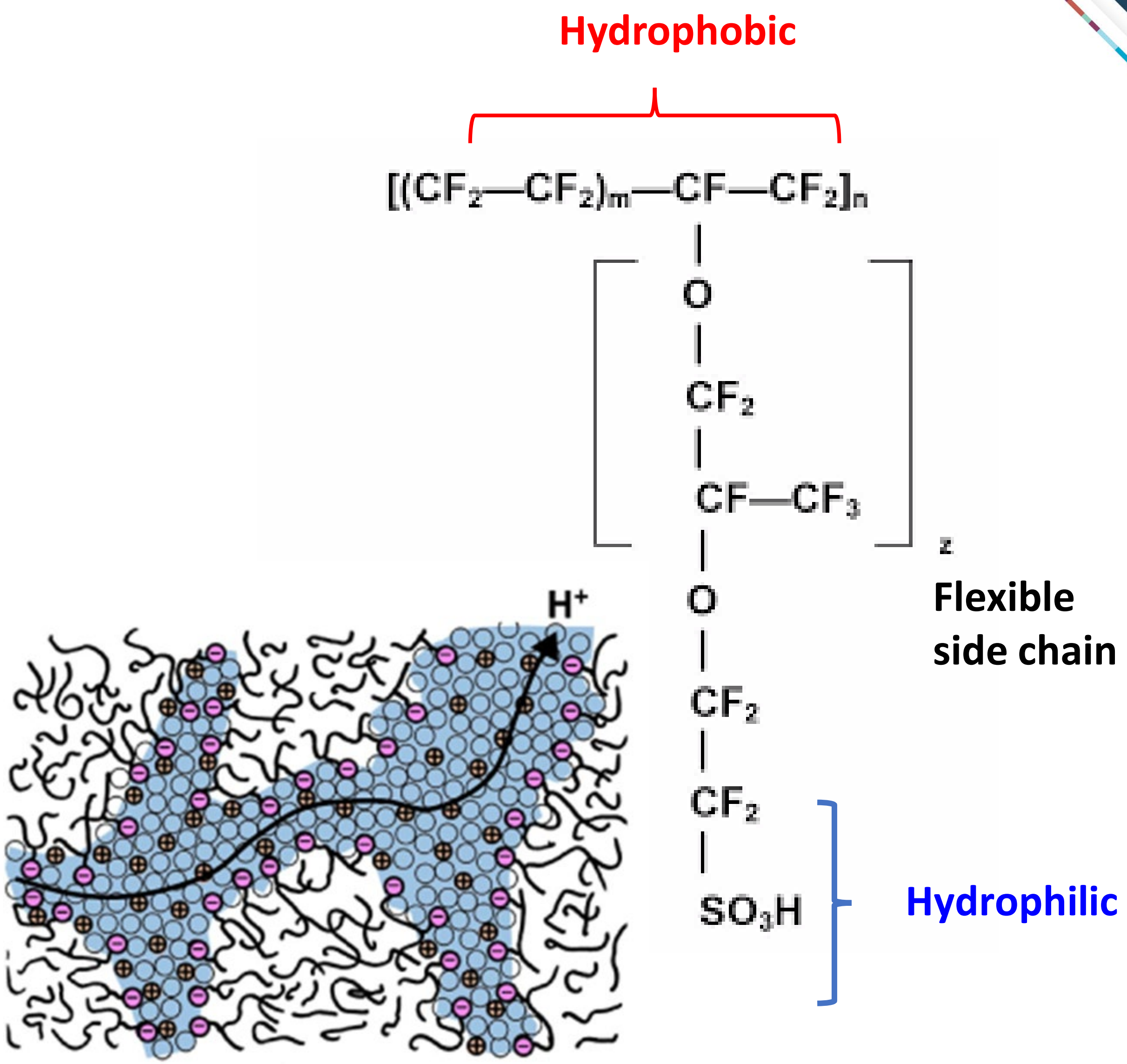
- **Objective: Develop ion selective, low cost, durable membrane for flow battery use.**

State of the art membrane: Perfluorinated sulfonic acid polymer (PFSA); Nafion, Aciplex, Flemion, etc.:

- PFSA developed by Dupont in the late 60s. Primary market is chloro alkali industry, but is used in early market devices (PEM fuel cells, electrolysers and flow batteries).

- PFSA high ion conduction (especially for protons) and excellent chemical durability. Unable to recycle/concerns of material disposal at end use (PFAS family) and high cost ($200-500 per m^2).

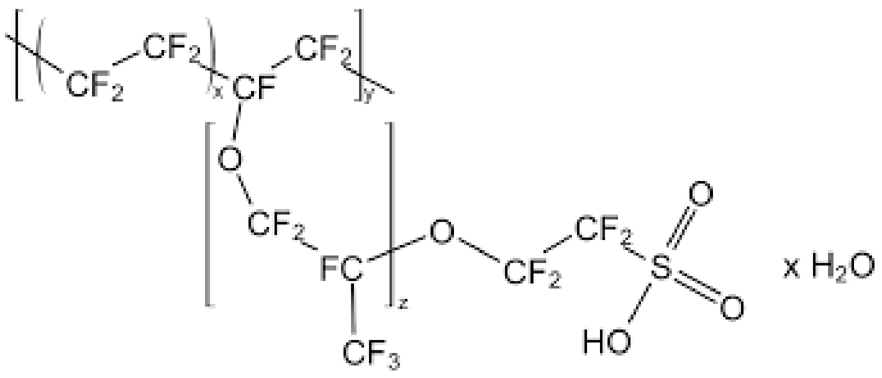
- Structure property relationship: Highly hydrophobic and hydrophilic functional groups tied together by chemical bonds.



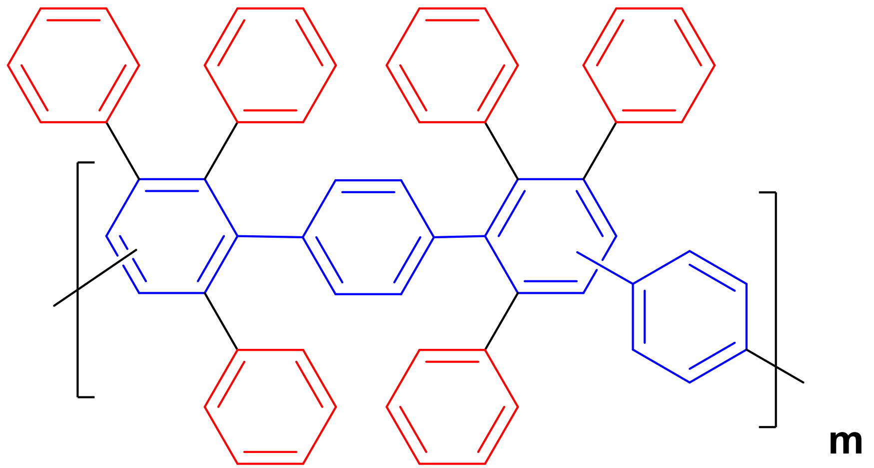
Development of PFSA alternatives:

PFSA materials are toxic and highly persistent if exposed in the environment. These factors are accelerating the need for an environmentally friendly replacement.

Bond type	Bond energy (kJ/mol)
C-F	485
C-C	342
C-O	380
C=C	606



Hydrocarbon alternative



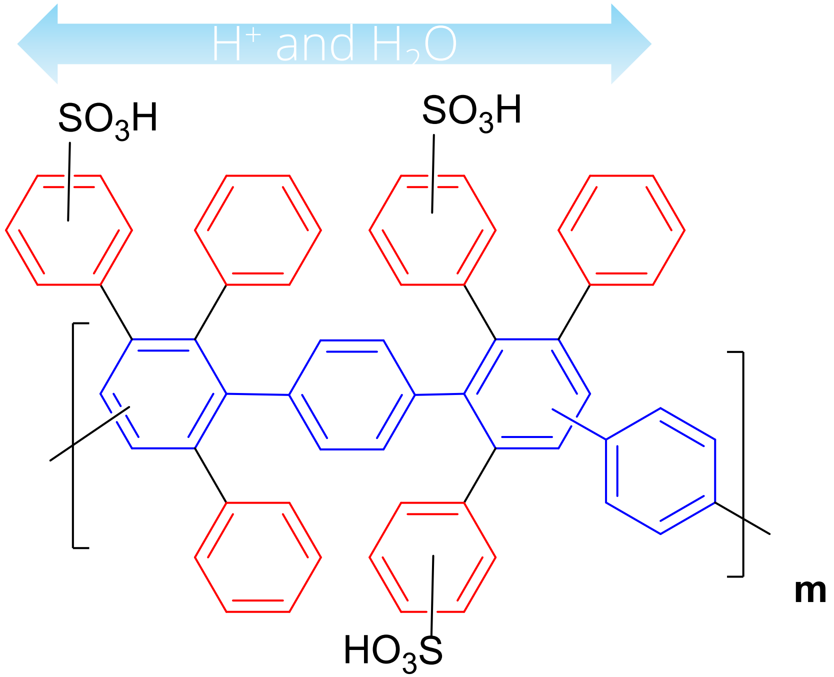
Required properties:

- Ion conducting: In PFSAs through sulfonic acid.
- Highly stable: In PFSAs through C-F bond (high bond energy).

- Hydrocarbon backbone no fluorine.
- Fully aromatic, highly stable polymer backbone.
- Two type of aromatic rings (external/pendant and internal/backbone).

Flow battery membrane development at Sandia:

Pendant sulfonation

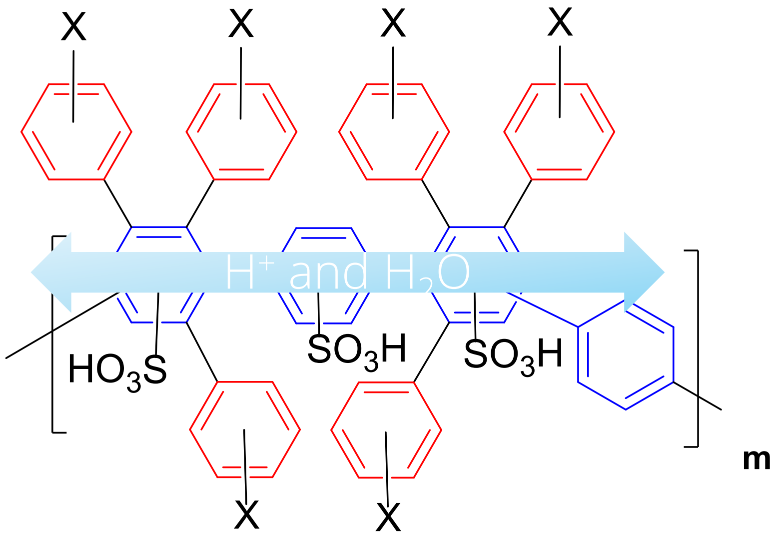


- Pendant sulfonation: external hydrophilic domains, through neighboring sulfonic aggregation.
- VRFB 5x higher selectivity of H^+/VO^{+2} compared Nafion.
- External unsubstituted aromatic rings susceptible to oxidation. Oxidized in dilute VO_2^+

Electrochemistry Communications (2012), 20, 48-51, Journal of the Electrochemical Society (2014), 161(12), A1860-A1868, 9 pp., Journal of the Electrochemical Society (2016), 163(1), A5154-A5162, Journal of the Electrochemical Society (2016), 163(1), A5229-A5235.

Backbone sulfonation

X = hydrophobic and electronwidthdrawing

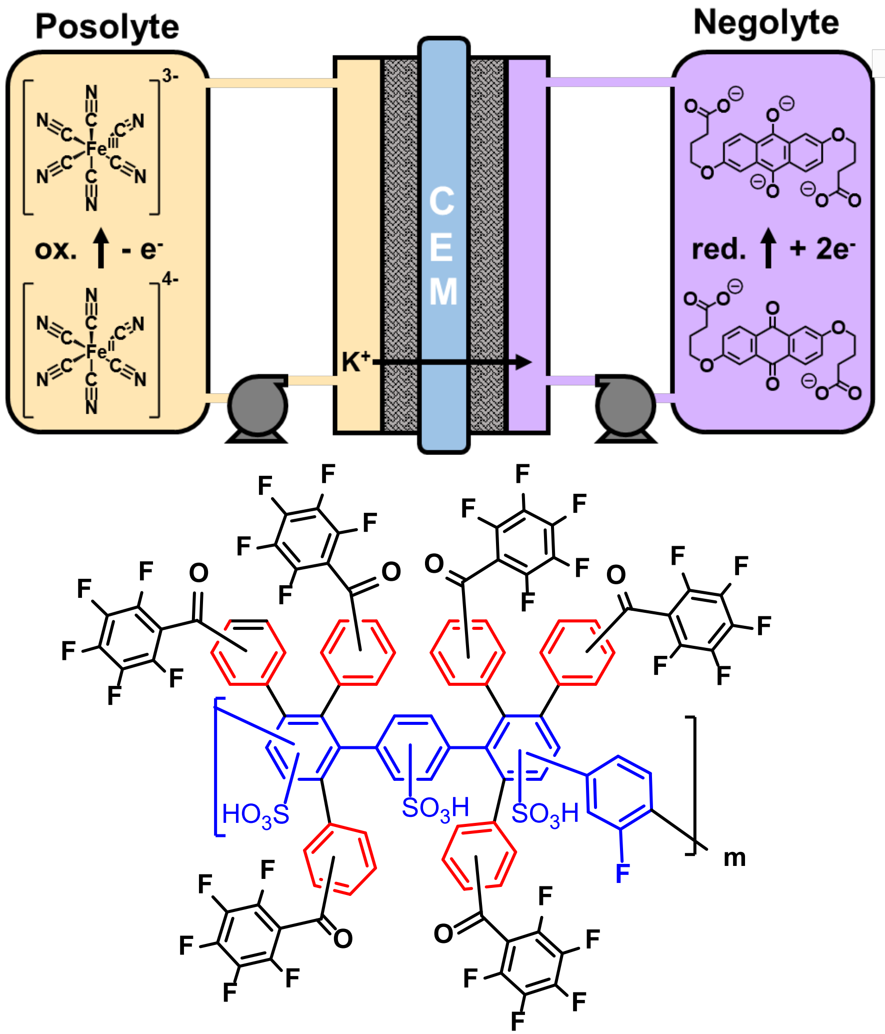


- Internal sulfonation: confinded hydrophilic domain, alignment of sulfonic acid.
- Pendant substitution requires group that is electron width drawing and hydrophobic.
- VRFB 10x higher selectivity of H^+/ VO^{+2} over Nafion, 5x high capacity retention. Stable towards concentrated VO_2^+

Journal of Power Sources (2022), 520, 230805.
Journal of Electrochemical Society (2023), 170, 030515

High ion selectivity of Sandia membrane in alternative flow batteries:

- Collaboration with Professor Michael Aziz from Harvard University (Tommy George).
- Aqueous organic electrolytes a potential low cost alternative to vanadium redox flow batteries.
- At neutral and high pH Nafion membranes are not ideal.



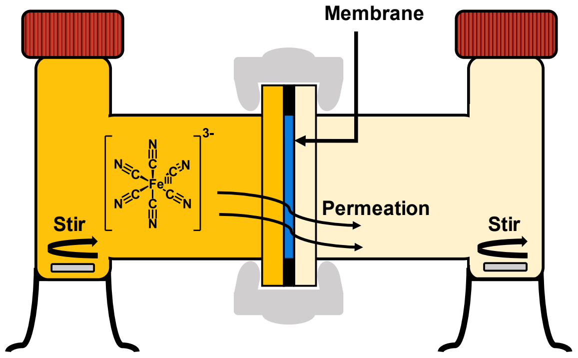
Journal of Electrochemical Society (2023), 170, 030515.

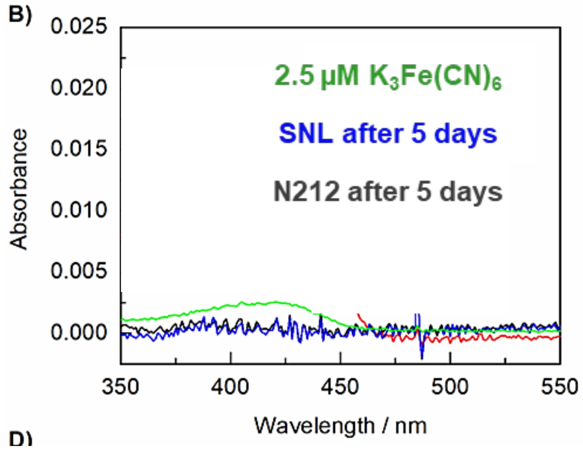
ASR in Ω cm^2 in 1M MCl

Membrane	H^+	Li^+	Na^+	K^+
Nafion 212	0.2	0.8	0.9	2.7
Sandia[d] 40	0.18	1.5	0.89	0.58

- **SNL membrane 4.5x less resistive to K+ than Nafion!**

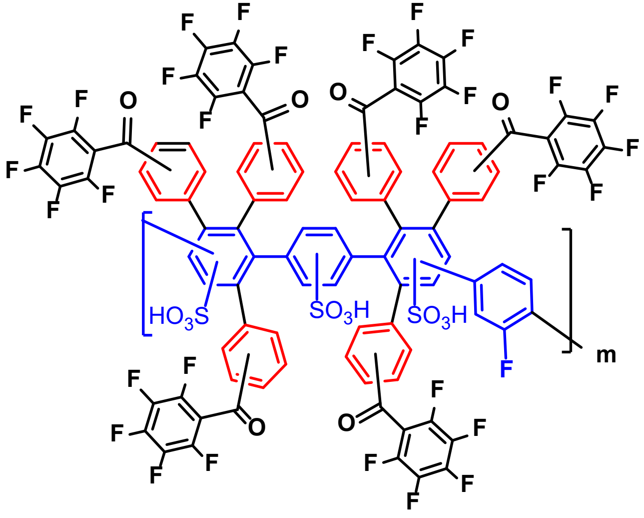
Diffusion of ferricyanide

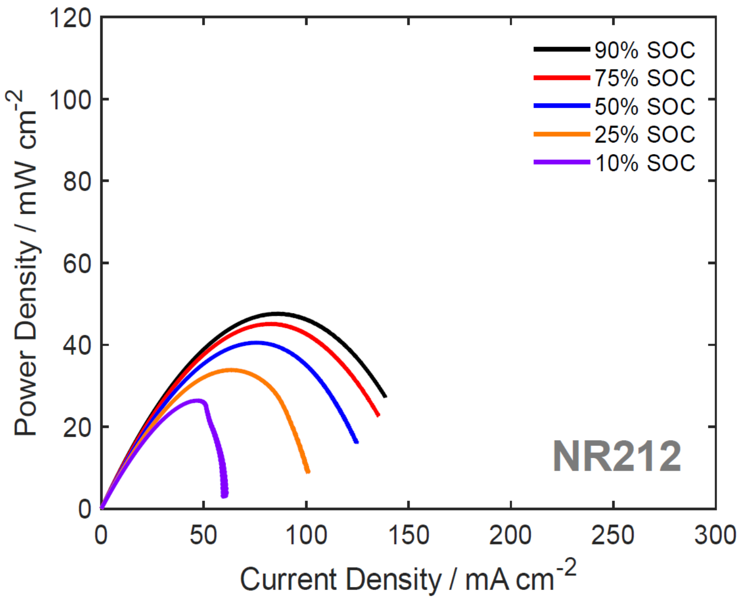


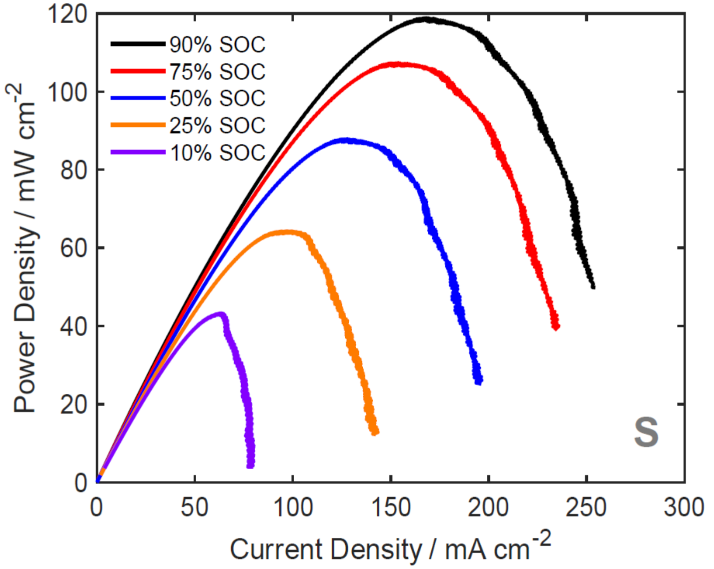


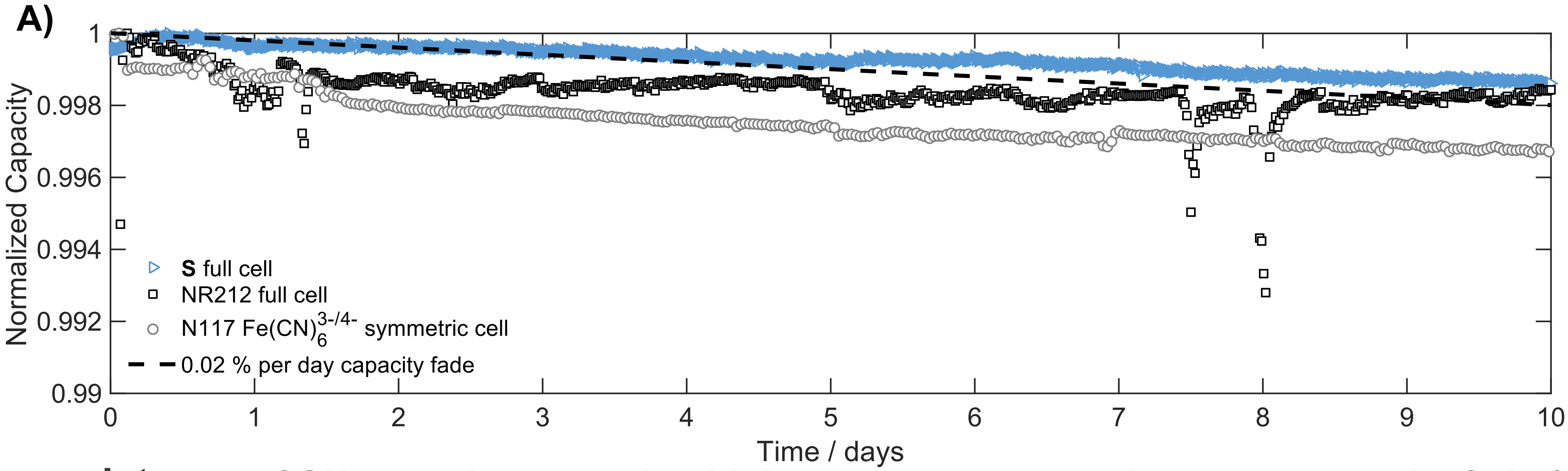
- **Nafion and SNL membrane no cross over of ferricyanide**

High ion selectivity of Sandia membrane in alternative flow batteries:







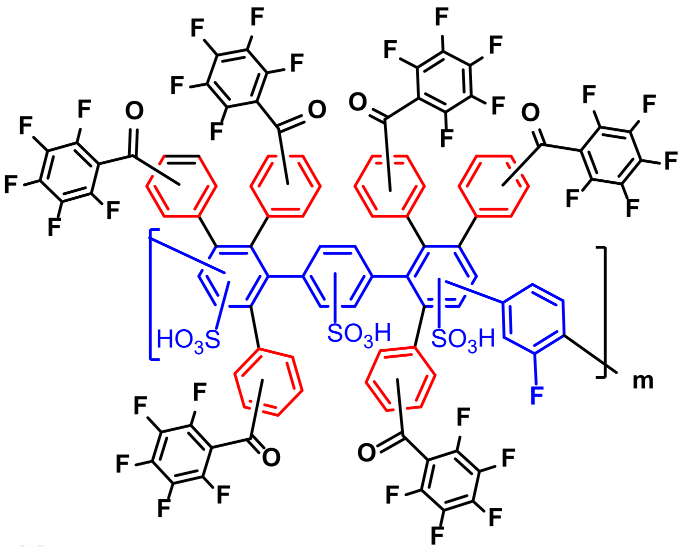


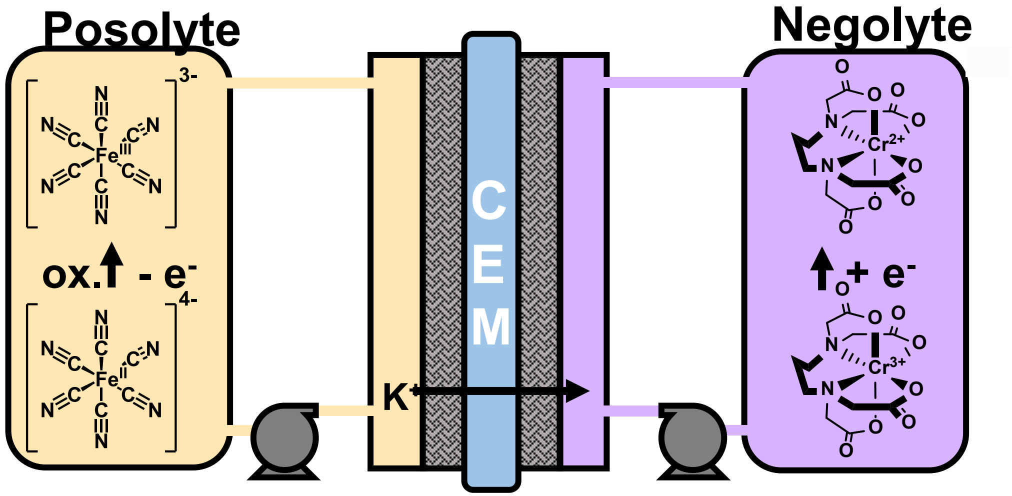
- **Low resistance of SNL membrane lead to higher power output and very low capacity fade (0.02% per day).**

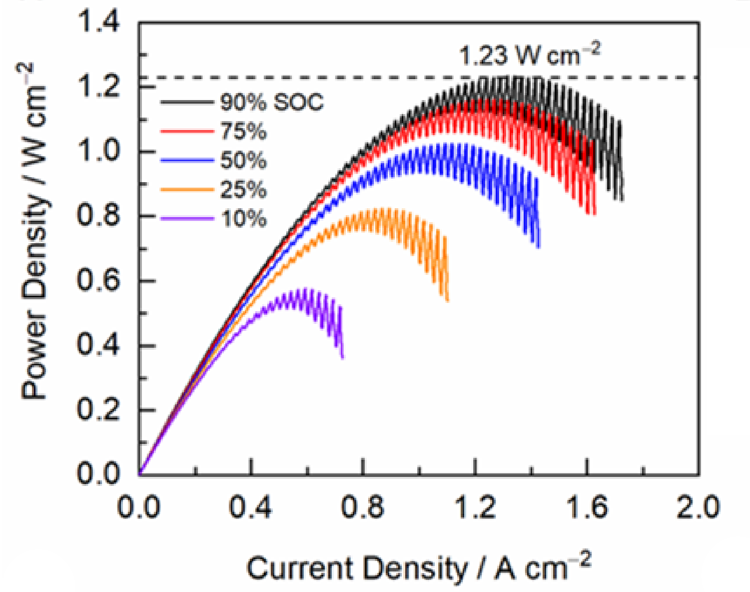
Journal of Electrochemical Society (2023), 170, 030515

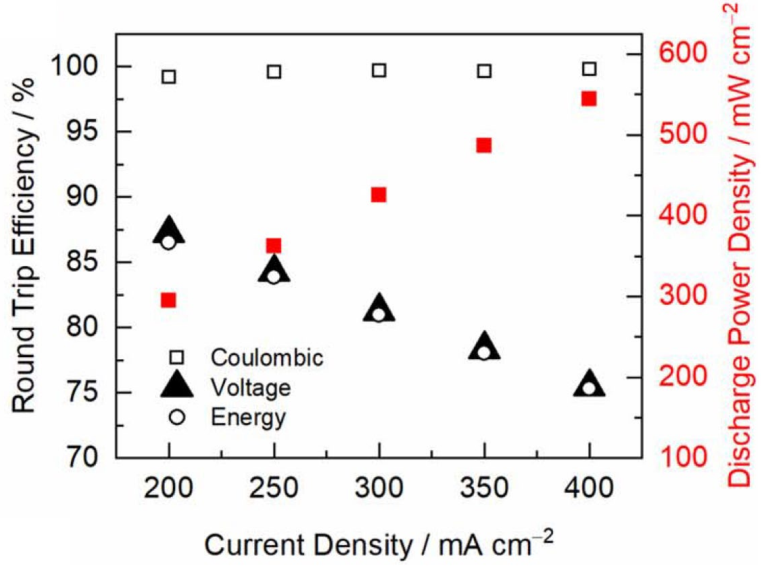
High ion selectivity of Sandia membrane in alternative flow batteries

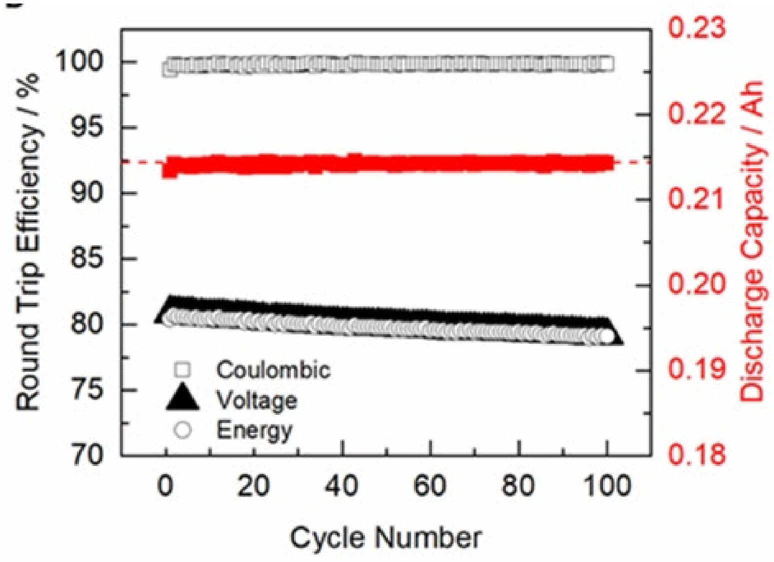
- Collaboration with Professor Michael Marshak from Colorado Boulder (Brian Robb)







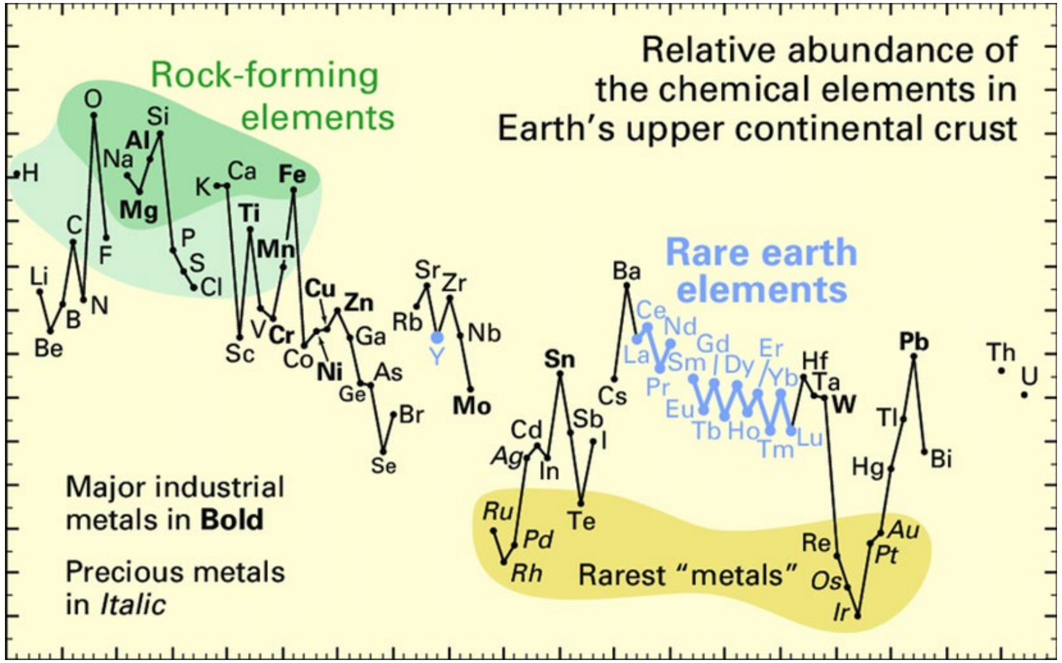




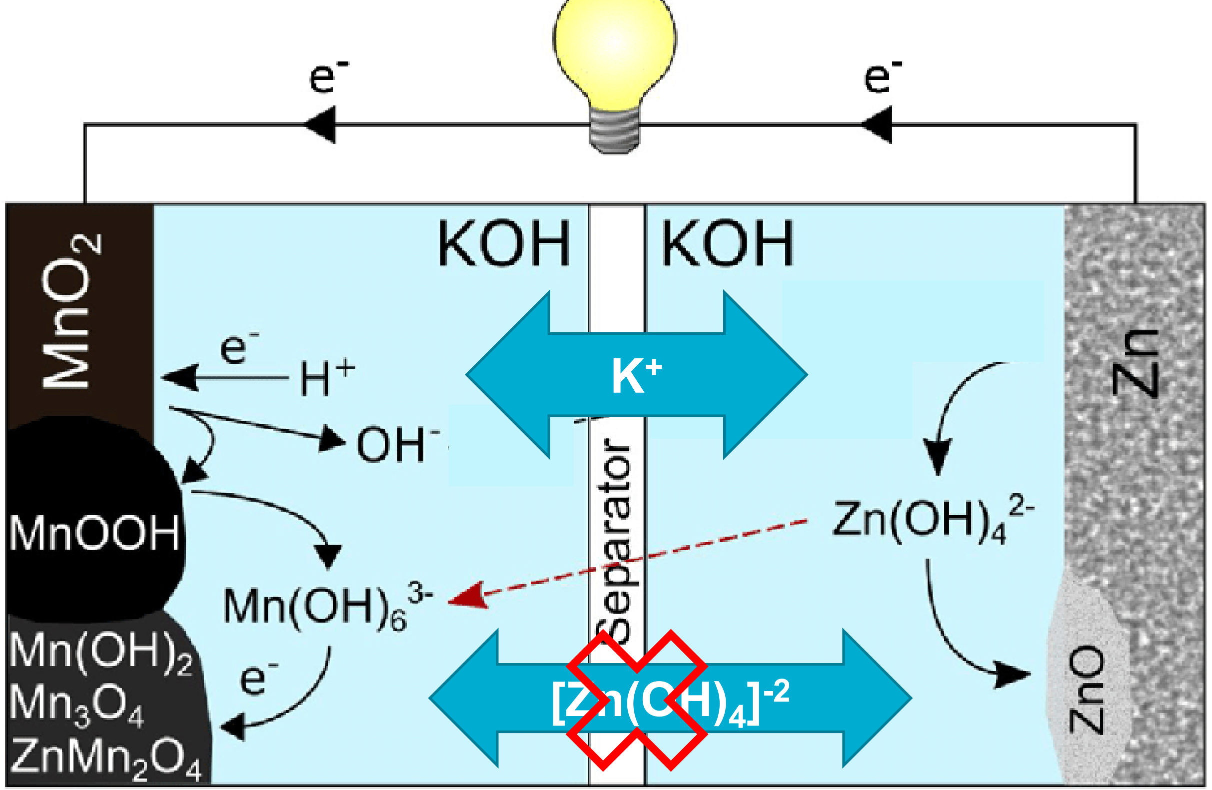
- **SNL membrane very high battery efficiency for Cr chelate battery chemistry.**

Exploring Rechargable Zn/MnO_2 batteries with the Sandia membrane

- Rechargeable Zn/MnO_2 batteries in deployed by Urban Electric Power and Tim Lambert.
- Employs materials abundant, low cost ($20 per kWh) and existing supply chain.
- Technical challenge impacting high DOD in rechargeable batteries is membrane selectivity.



From Haxel, Gordon & Hedrick, James & Orris, Greta. (2002). Rare Earth Element Resources: A Basis for High Technology.

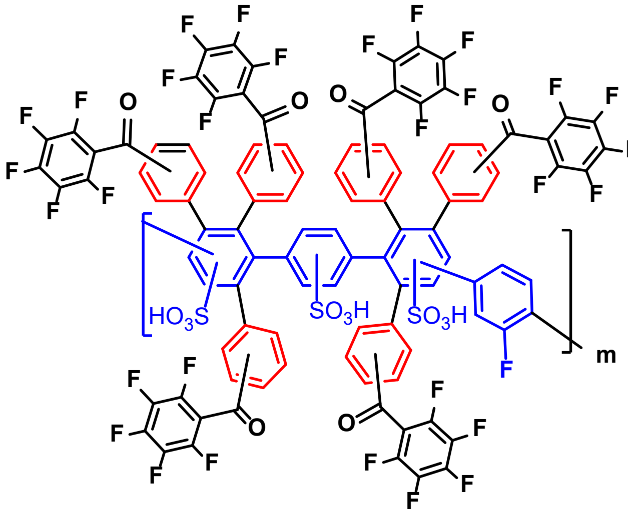


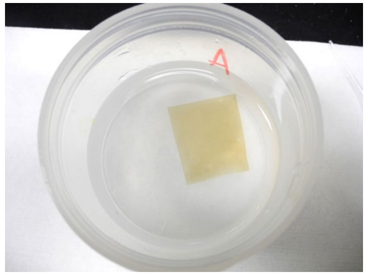
From Lim, Matthew & Lambert, Timothy & Chalamala, Babu. (2021). Rechargeable alkaline zinc–manganese oxide batteries for grid storage. Materials Science and Engineering: R: Reports. 143. 100593.

- **Membranes needs in Zn/MnO_2 are allow K^+ migration/diffusion, block $Zn(OH_4)^{-2}$ and stability under highly alkaline conditions, 30% KOH or > 6M KOH!**

Exploring Zn/MnO_2 batteries with the Sandia membrane

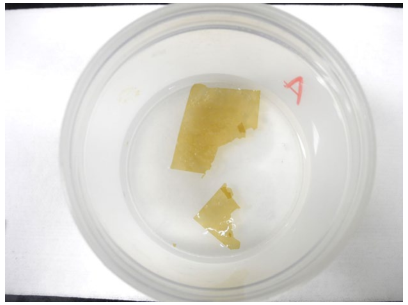
- Discovered current version of Sandia membrane not stable in 6M NaOH.
- Stability issues attributed to pendant functionalization.

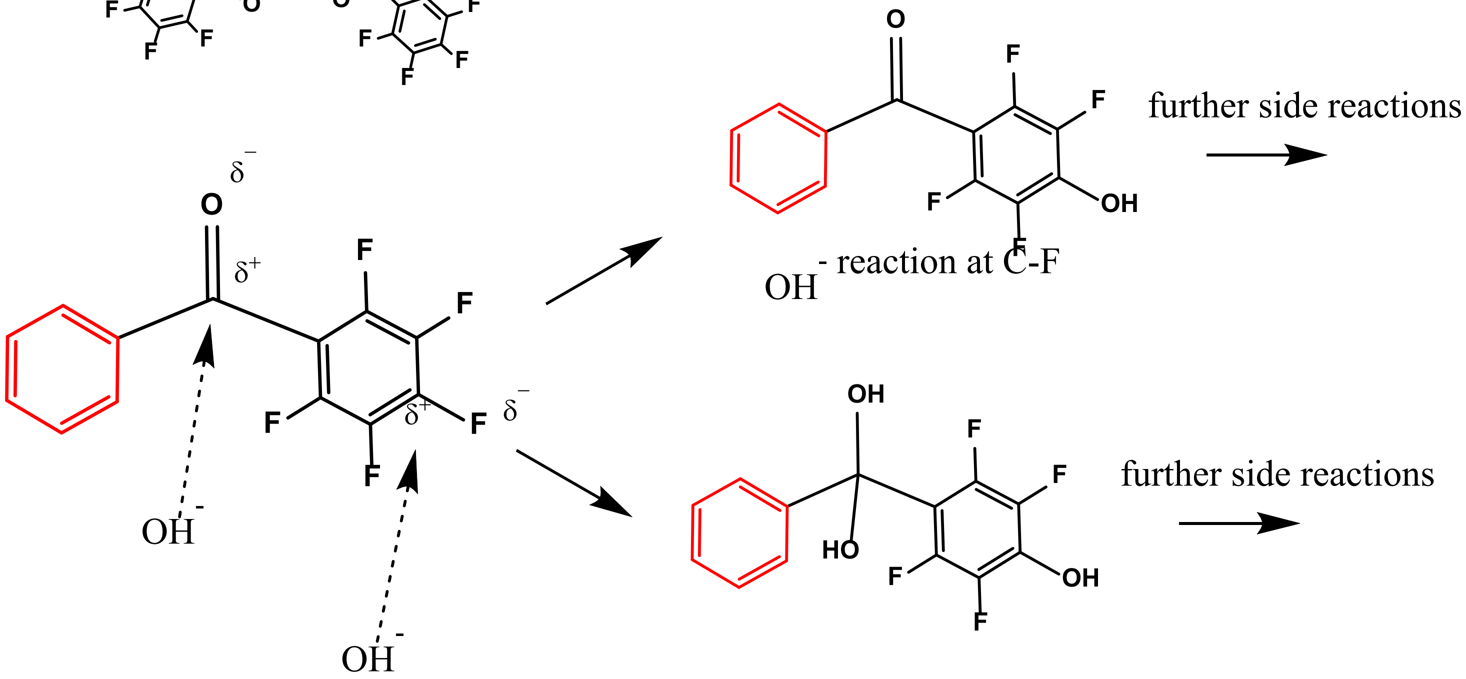




6M KOH

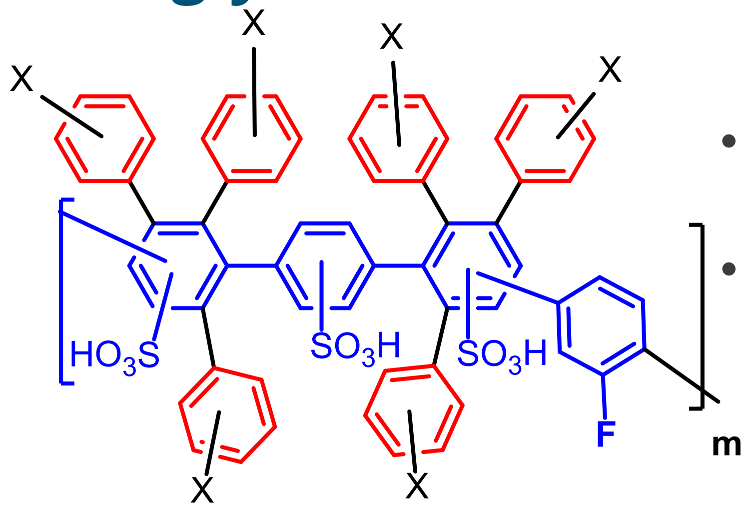
Membrane embrittlement





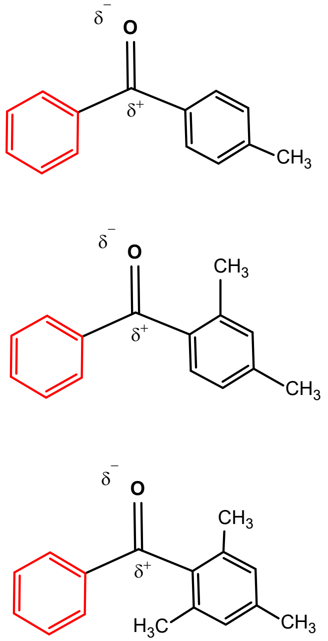
- **The combination of the ketone and highly fluorinated aryl group are highly reactive in strongly alkaline conditions.**
- **Look to replace pendant functionalization with alkaline stable group.**

Improving the stability of the Sandia membrane in highly alkaline strongly oxidative environments.



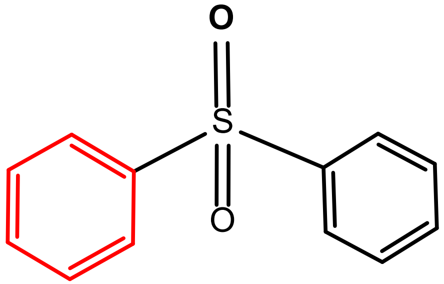
- Sulfonated backbone for ion selectivity (allow K^+ and block $[Zn(OH)_4]^{-2}$).
- Identify X group which is stable in highly alkaline/oxidative environments.

X =



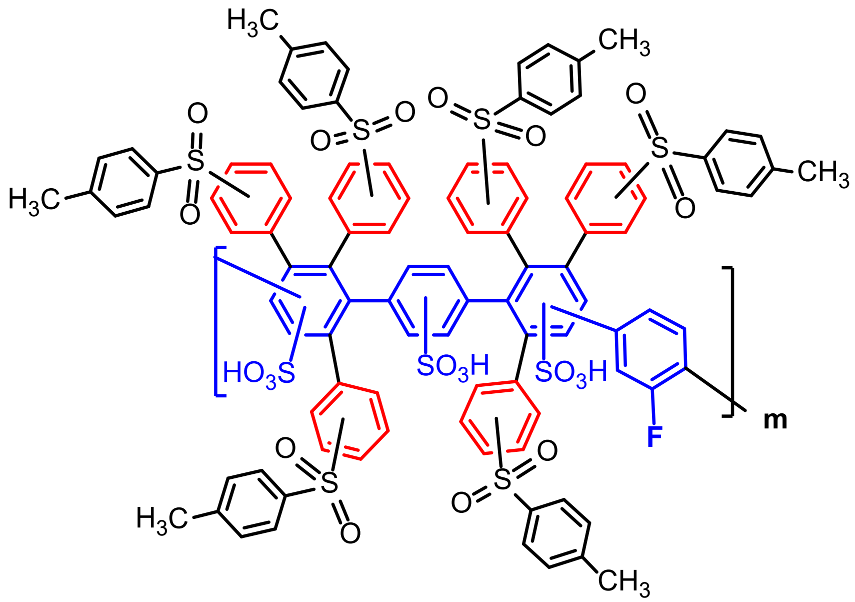
- First replaced highly fluorinated aryl group with methyl groups.
- Methyl (alkyl) groups donate e- density towards aryl ring.
- Increasing alkyl groups should prevent ketone from alkaline attack.
- Unfortunately, not stable after weeks to months in 6M KOH. Ketone cannot be stabilized at high pH.

X =



- Sulfone is an excellent replacement for ketone, since highly alkaline/oxidatively stable.
- Actively investigated this attachment off/on years.

Improving the stability of the Sandia membrane in highly alkaline strongly oxidative environments.



6M KOH

Membrane mechanically intact after 2 weeks and temperatures up to 40 ^oC.

Before 6M KOH

	1	2	3
Water uptake	45.9	48.5	47.6
Ion exchange capacity	1.82	1.76	1.83

After 2 weeks in 6M KOH

	1	2	3
Water uptake	46.5	47.7	47.0
Ion exchange capacity	1.79	1.72	1.80

- **New sulfone functionalized polymer has shown good chemical durability in highly alkaline environments.**
- **Working with Tim Lambert to begin investigating zincate diffusion, K^+ conductivity and Zn/MnO_2 battery testing.**

Conclusions:

- SNL developed a unique polymer structure which has shown very good flow battery performance in aqueous organic flow and metal chelate flow battery where K^+ is conducting ion.
- Pentafluorobenzoyl functionalization was found to be unstable in highly alkaline environments; used in Zn/MnO_2 rechargeable batteries.
- Discovered synthesis method of attaching alkaline stable, sulfone onto poly(phenylene) backbone.
- In initial accelerated alkaline durability studies, the sulfone poly(phenylene) does not change in after soaking in 6M KOH for two weeks.

Accomplishments:

- Three OE funded membrane patents commercially licensed in Spring 2023.
- Publication: "Sulfonated Diels Alder Poly(phenylene) membrane for efficient ion-selective transport in aqueous metalorganic and organic redox flow batteries. Journal of Electrochemical Society (2023), 170, 030515.
- Presentation: "Efficient Ion-Selective Transport in Sulfonated Diels-Alder Poly(phenylene) Membrane Enables Aqueous Organic Flow Batteries with Undetectable Crossover" 243rd Electrochemical Society Meeting, Boston, MA, May 28 – June 2, 2023.
- Technical advance of new flow battery membrane (1st step in SNL patent process)

Next Steps:

- In situ/Ex situ of sulfone poly(phenylene) membrane towards Zn/MnO_2 battery.

THANK YOU!

- Audience for your attention.
- Collaborators, Professor Michael Aziz, Professor Michael Marshak, Tommy George and Brian Robb.
- Office of Electricity for support this work.