The Evolution of Membrane Development @ SNL

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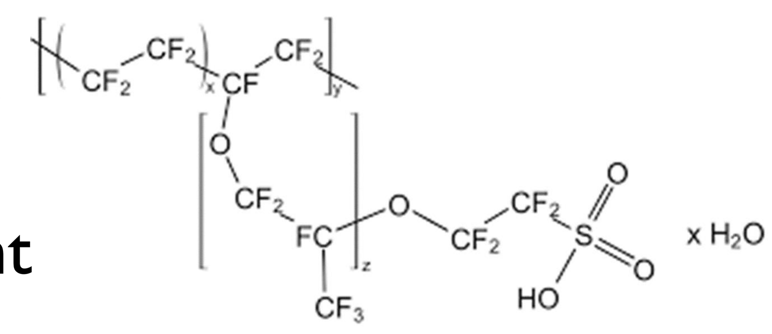
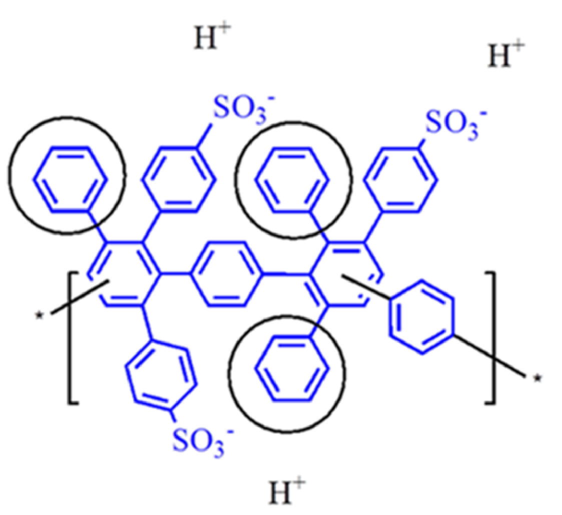
Objective: Membrane separators in flow batteries play a vital role in influencing battery lifetime (by blocking electroactive species crossover) and round trip efficiency (allow fast counter ion migration). Perfluorinated sulfonic acid (PFSA) such as Nafion™ are commonly used in these devices (e.g. vanadium flow batteries). However, the high cost of PFASs and moderate ion selectivity has led to the development of synthetically engineered alternatives. Recently, awareness that perfluorinated aliphatic substances (PFAS) are toxic and highly persistent is driving the need for an environmentally friendly replacement. Here we describe the evolution of SNL's non PFSA membrane development and demonstrate that structural control can influence battery performance.

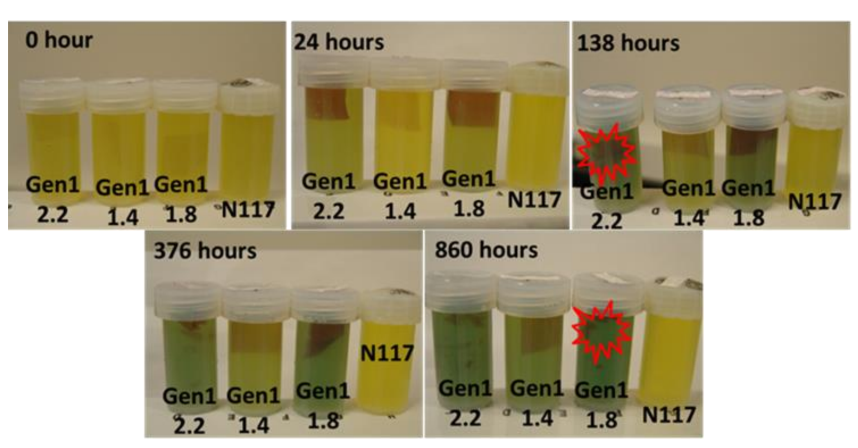


Generic structure of PFSA material

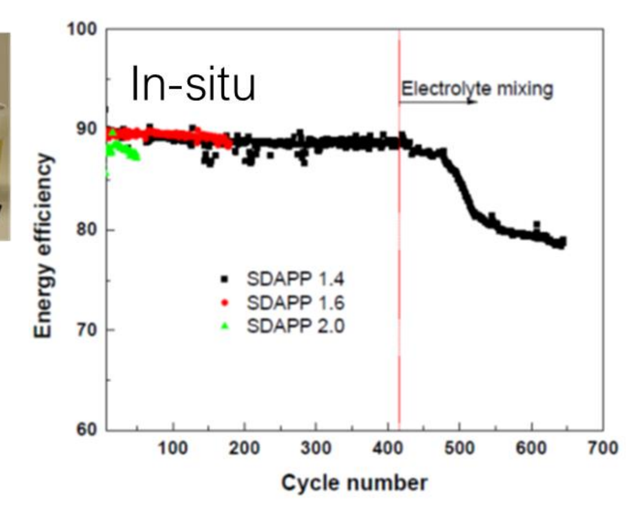
Materials Innovation:

I. Pendant Sulfonation:

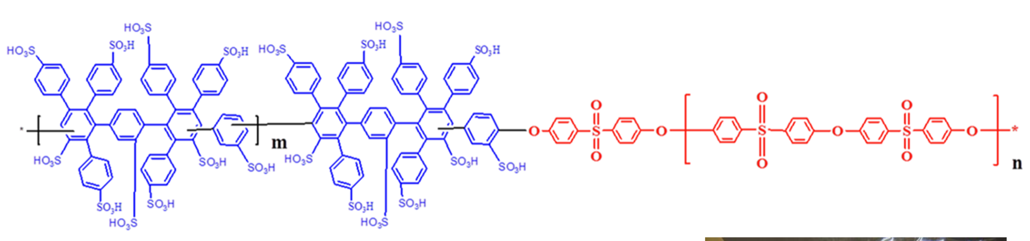




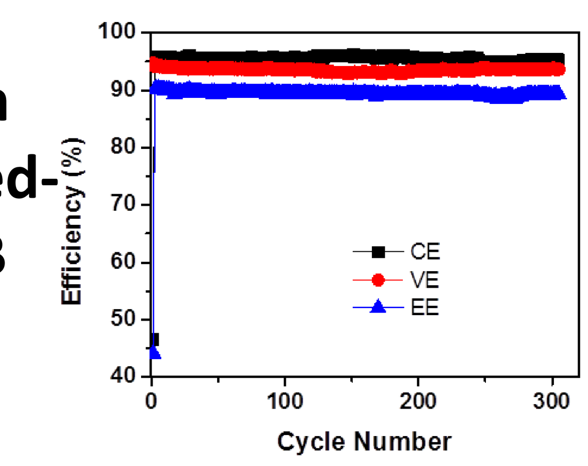
Ex-situ: 0.1M VO_2^+

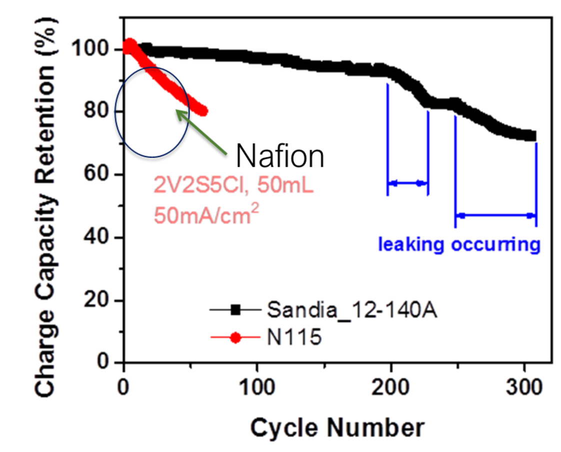


II. Block Polymers:



Tested in 2M mixed-acid VRB

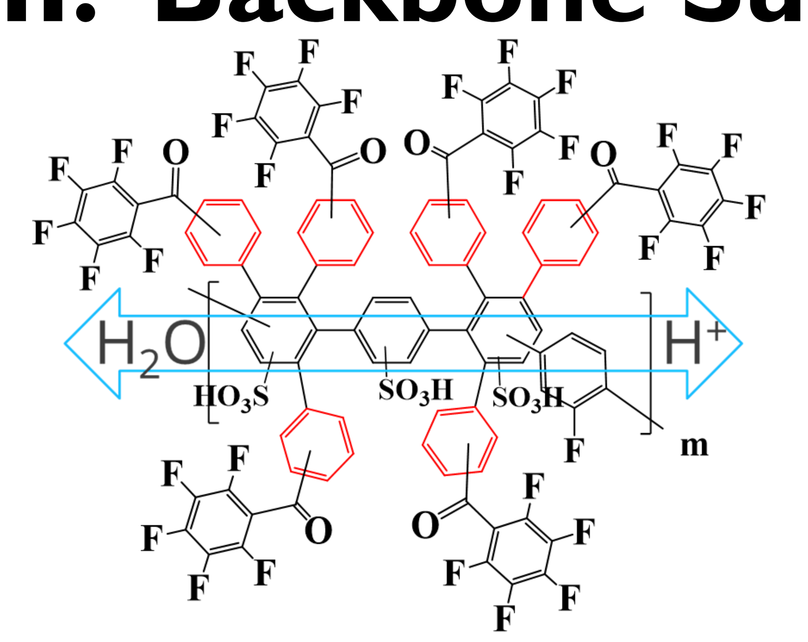


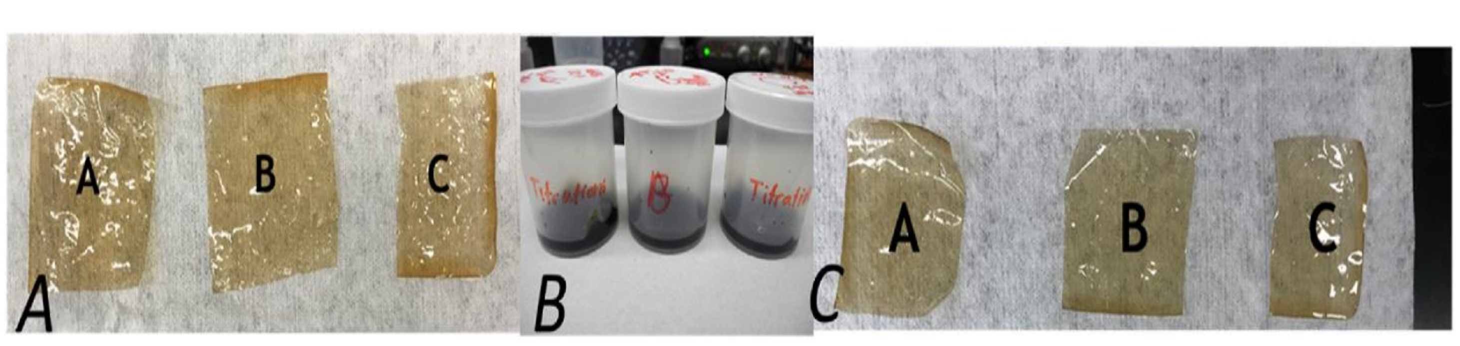


Membrane after cell testing

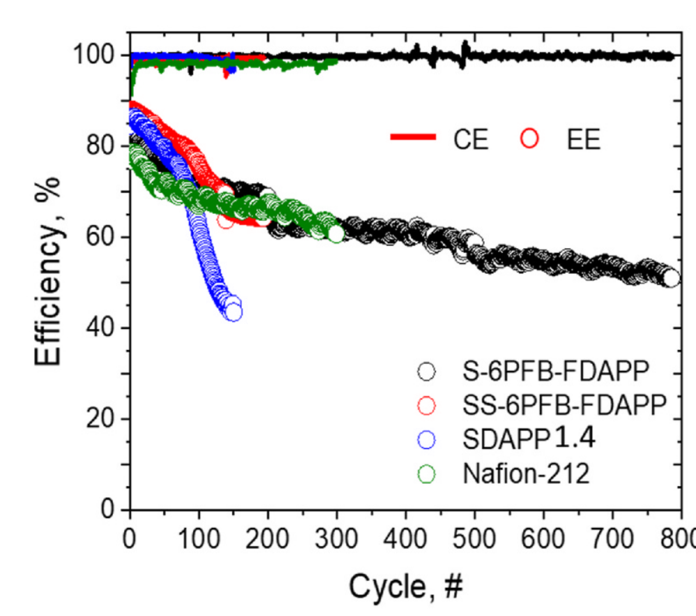
By attaching acidic functional groups on aryl pendant rings (structurally mimic PFSA), found membrane had near equivalent performance to PFSA but displayed poor durability (ex-situ and in-situ). The likely source of oxidative instability was believed to be unsubstituted aryl rings. To eliminate unsubstituted aryl rings, we employed a fully sulfonated poly(phenylene) unit that was coupled to poly(sulfone) in a block co-polymer. Optimized block lengths led to high performance, low capacity loss and higher durability than pendant sulfonated poly(phenylene). However, there was still durability issues which potentially stemmed from the heteroatom containing poly(sulfone) segment.

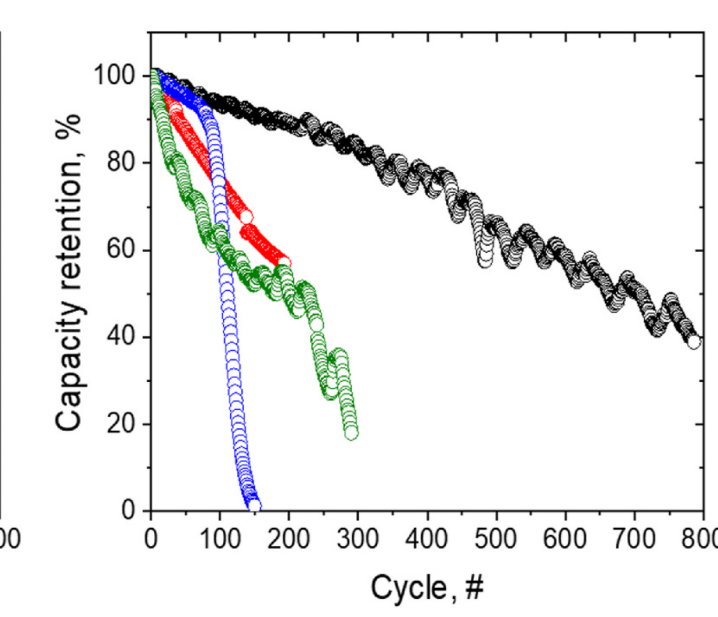
III. Backbone Sulfonation:





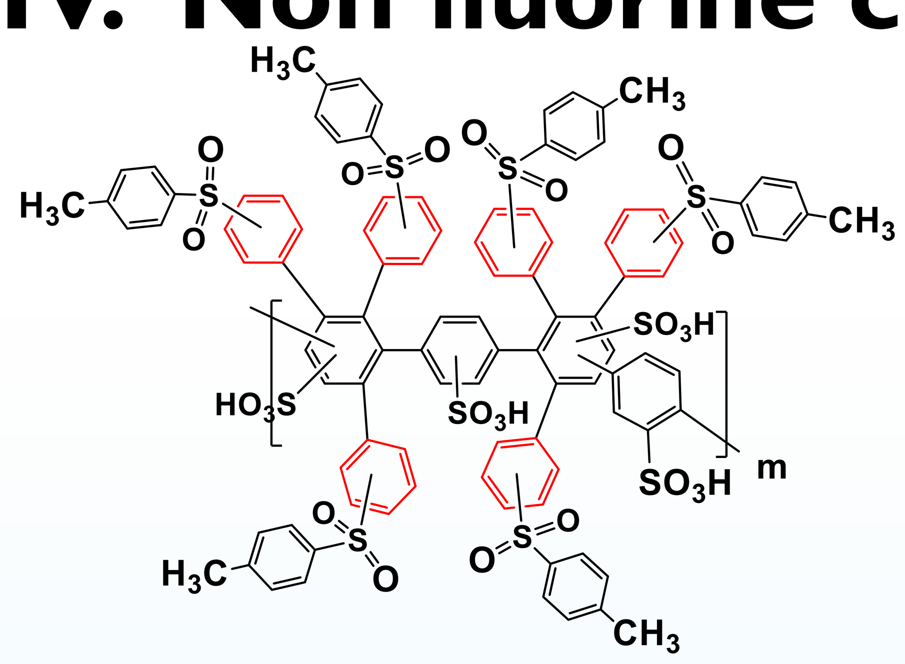
Ex-situ: 1.5 M VO_2^+ for 60 days





To improve oxidative stability, we targeted a polymer structure that eliminated both unsubstituted aryl rings and aryl heteroatom bonds. This resulted in a poly(phenylene) with perfluorobenzoyl groups attached on the pendant rings and sulfonic acid groups functionalized onto the backbone aryl rings. This arrangement led to films that are stable in 1.5M VO_2^+ for 60 days (length of test) and higher capacity retention than Nafion212.

IV. Non fluorine containing membrane:



Backbone Sulfonation discussed above has two structural issues that are the result of the perfluorobenzoyl group. One is heavy fluorination of the aryl ring and the other is the ketone functional group. Both pentafluorobenzene and ketones are known to react in highly alkaline environments which are employed in some Zn battery chemistry; which would preclude the use of these membranes. We are currently exploring removing all fluorine and replacing the ketone with a sulfone group. Sulfones are alkaline stable and are resistant to oxidation. Removing the fluorine will also ensure an environmentally friendly processing and disposal.

Conclusions/Future:

The SNL membrane has evolved and tuned to improve both performance and durability. By controlling the positioning of the sulfonic acid group in the polymer backbone we have found this restricts the permeation of larger electroactive compounds, while still allowing the passage of smaller, charge balancing ions such as H^+ and K^+. In addition, by attaching electron withdrawing groups onto the pendant rings increase oxidative stability. We are exploring this architecture for use in Zn hybrid batteries which are typically highly alkaline.

Acknowledgements: *This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.*