

## Advanced Membranes for Flow Batteries

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**Objective:**

To develop low cost, high performance ion-exchange membranes to replace costly state of the art fluorocarbon membranes limiting widespread commercialization. This work specifically addresses shortcomings in current state-of-the-art membranes, critical to flow battery deployment and utilization.

- Cost:** Developing hydrocarbon based membranes.
- Performance:** Flow batteries are influenced by membrane properties. Membrane conductivity determines battery resistance and membrane selectivity regulates capacity retention.

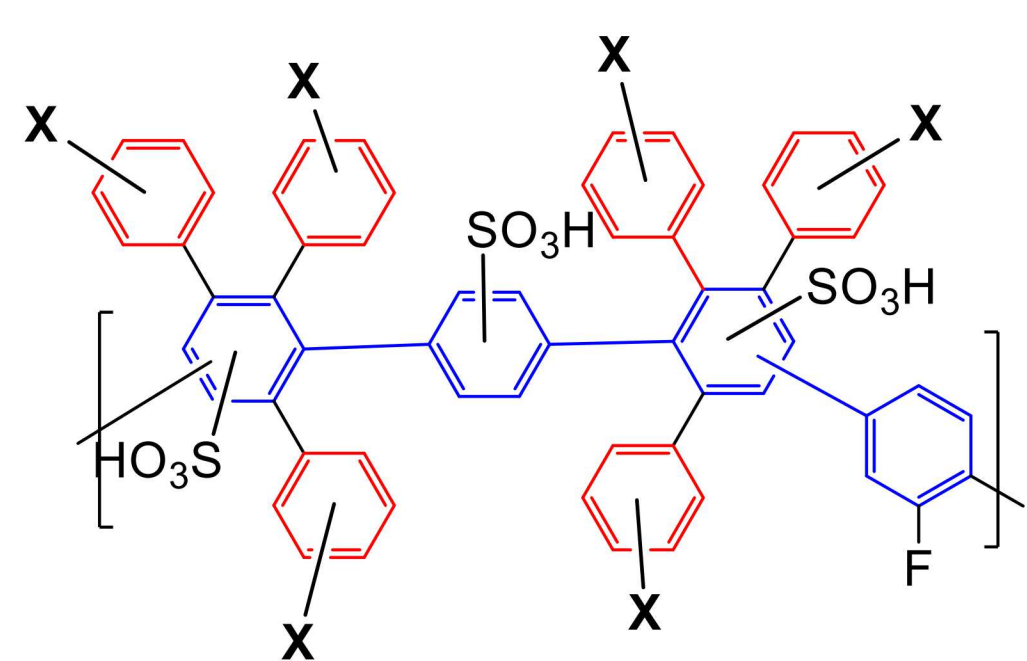
**Licensed Membrane Patents:**

Xergy, a Delaware based materials company licensed several OE funded patents.

- 1) U.S. Patent No. 7,301,002, entitled Sulfonated Polyphenylene Polymers, issued on November 27, 2007. (SD#7565.1)
- 2) U.S. Patent No. 9,580,541, entitled High Performance, Durable Polymers Including Poly(Phenylene), issued on February 28, 2017. (SD# 12691.1)
- 3) U.S. Patent No. 7,888,397, entitled Polyphenylene Based Anion Exchange Membrane, issued on February 15, 2011. (SD# 10987.0)
- 4) U.S. Patent No. 8,809,483, entitled Functionalization of Polyphenylene by Attachment of Sidechains, issued on August 19, 2014 (SD# 12299.0)
- 5) U.S. Patent No. 10,053,534, entitled Functionalization of Diels-Alder Polyphenylene, issued on August 21, 2018 (SD#13592.1)
- 6) U.S. Patent No. 10,442,887, entitled Functionalization of Diels-Alder Polyphenylene, issued on October 15, 2019 (SD#13592.5)
- 7) U.S. Patent No. 10,294,325, entitled Halo Containing Anion Exchange Membranes & Methods Thereof, issued on May 21, 2019 (SD#14264.0)

**Focus:** Cation exchange membrane in vanadium redox flow battery (VRFB). Main concern is hydrocarbon oxidation by  $\text{VO}_2^+(\text{V}^{+5})$ . Also, requires high  $\text{H}^+$  conductivity and low vanadium permeability.

**Innovation:** Used electron withdrawing substituents on aryl rings to improve oxidative stability.



SFDAPP  
X = electron withdrawing group

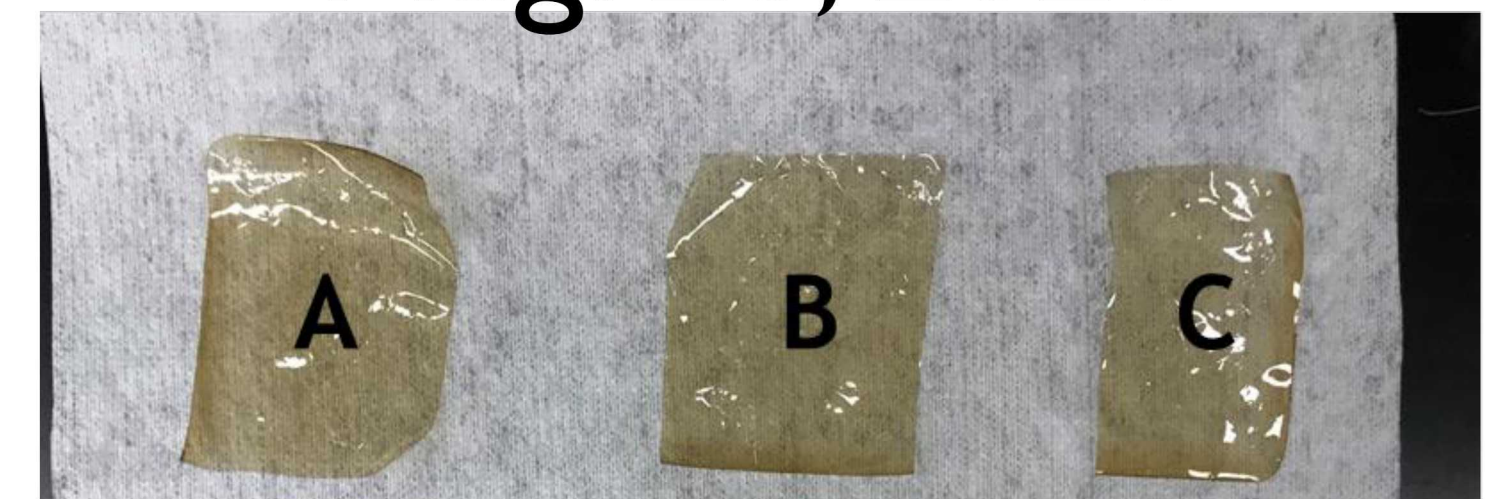
**Durability Results:** Soaked films in 1.5 M  $\text{V}^{+5}$  for 20 days, no change!

Aug. 6, 2020



Wt<sub>a,b,c</sub>(mg): **75.6, 76.2, 57.8**  
IEC<sub>ave</sub>(meq/g): 1.3  
Water uptake<sub>ave</sub>: 23.5%

Aug. 26, 2020



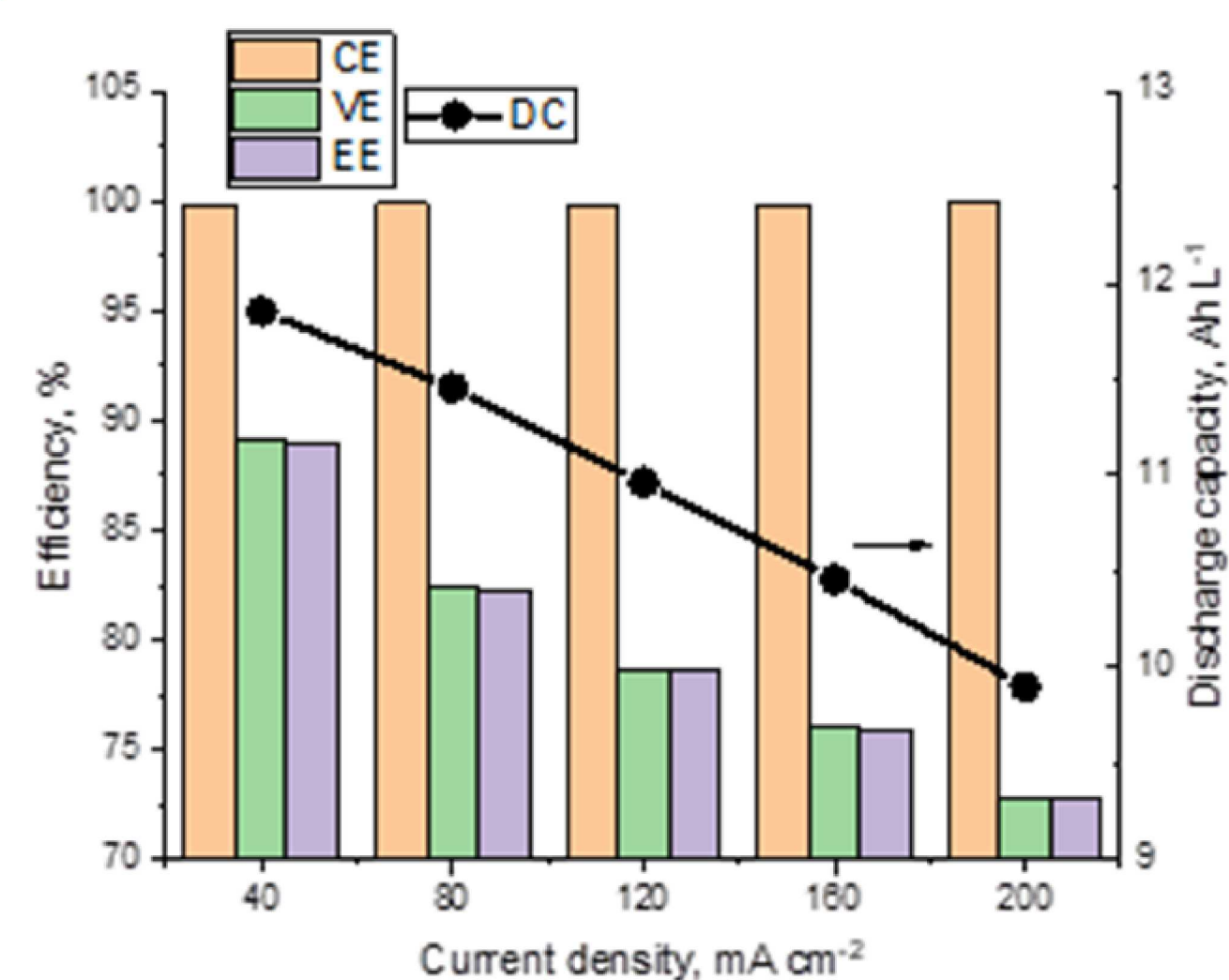
Wt<sub>a,b,c</sub>(mg): **75.4, 76.2, 57.8**  
IEC<sub>ave</sub>(mg): 1.3  
Water uptake<sub>ave</sub>: 23.5%

Soaking continues.....

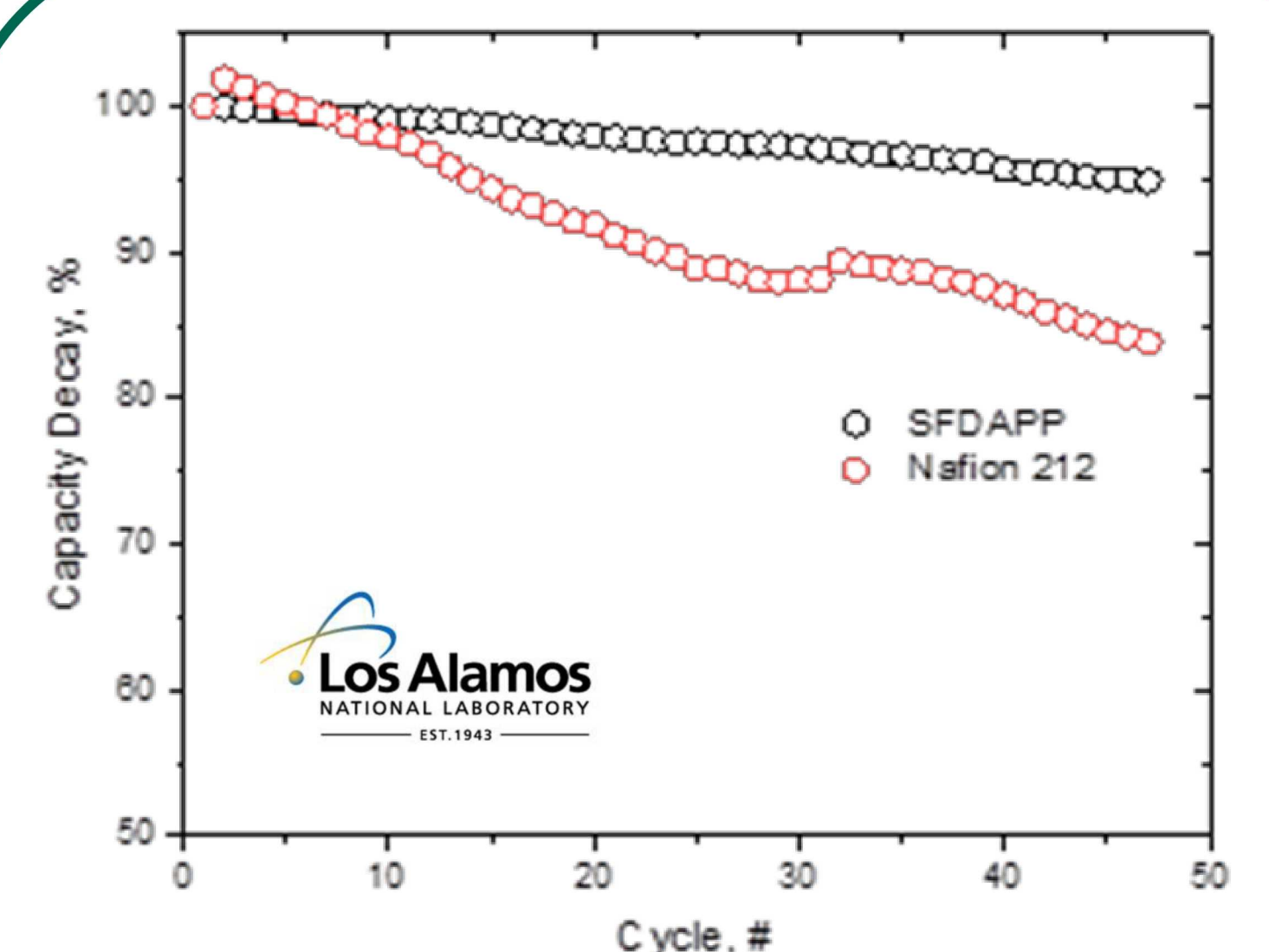
**VRFB Results:** Through collaboration with Sandip Maury at LANL.

Membrane	$\text{VO}_2^+$ Permeability, $\text{cm}^2/\text{min}$
SFDAPP	$4.25 \times 10^{-8}$
Nafion 212	$6.0 \times 10^{-6}$

**SFDAPP 100x less permeable than Nafion**



**SFDAPP nearly 100% CE and high VE at all currents.**



**SFDAPP high capacity retention than Nafion.**

**Conclusions/Future:**

These membranes promise a significant improvement over other systems, including our own polyphenylene systems. Based on the high conductivity and the drastic improvement in ionic selectivity seen in vanadium redox flow batteries, if this system proves sufficiently durable, it stands to significantly improve VFRB performance and lifetime.

1. Seven membrane patents licensed.
2. Developed new cation exchange membrane; SFDAPP.
3. SFDAPP has shown very good stability in concentrated  $\text{V}^{+5}$  and ion selectivity.
4. SDFAPP is showing very good VRFB and aqueous organic flow battery performance.
5. Long term flow battery testing of SFDAPP.
6. Open for new collaborators interested in testing our new membrane.