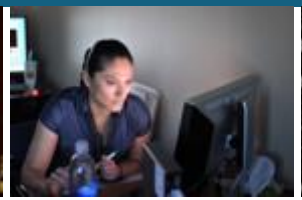
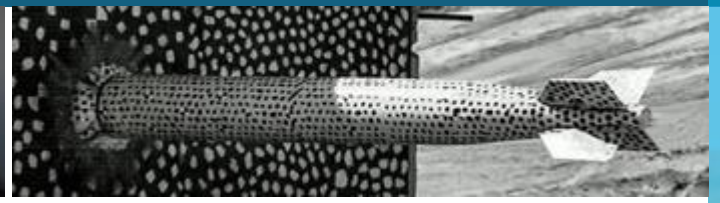
Advanced Membranes for Flow Batteries:





PRESENTED BY

Cy Fujimoto

SAND2020-9987 C

Team: Ehren Baca, Harry Pratt and Travis Anderson @ Sandia National Laboratories

Sandip Maruya @ Los Alamos National Laboratory

Tom Zawodinski @ Oak Ridge National Laboratory

Professor Michael Aziz @ Harvard School of Engineering and Applied Sciences

2020 Budget = $375k

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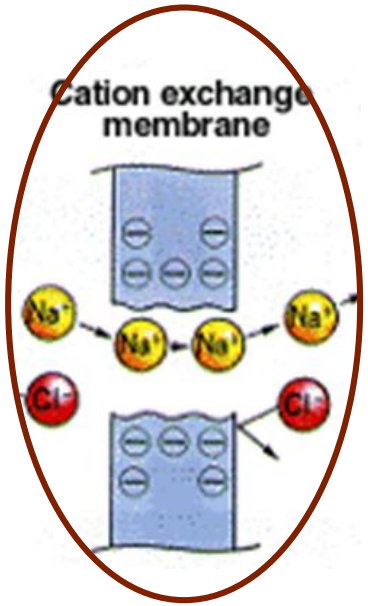
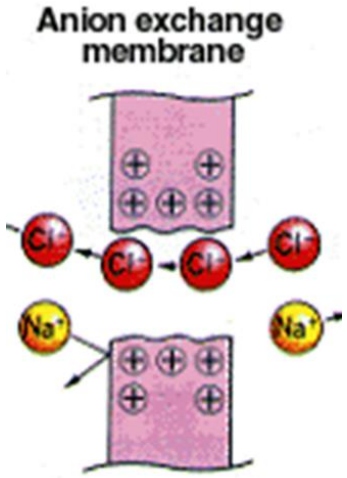
Membrane Basics

Objective: To develop membranes for flow batteries to lower cost and improve performance which will facilitate commercialization.

- *Cost: Developing hydrocarbon based membranes.*
- *Performance: Flow batteries are influenced by membrane properties. Membrane conductivity determines battery resistance and membrane selectivity regulates capacity retention.*
- **Focus: Most commercial interest still lies in cation exchange membrane; PFSA replacement.**



In acidic environments (VRFB)
CEM used pH < 7



In alkaline environments
AEM used pH > 7

Licensed Membrane Patents

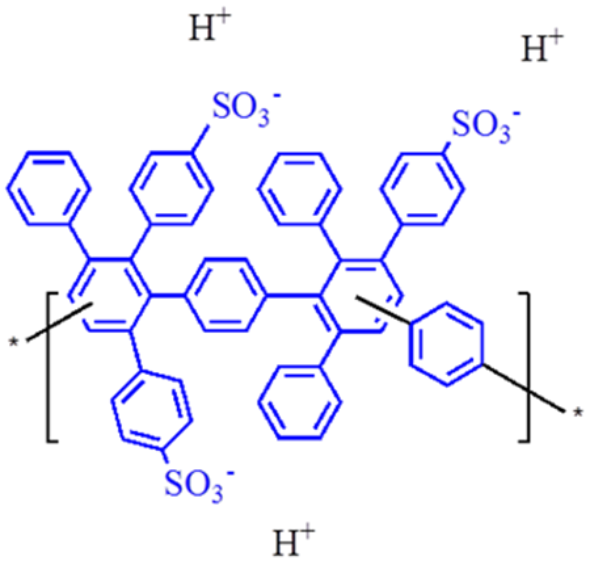
XERGY®

In June, Xergy Inc. a Delaware based material company, was granted non exclusive licenses of several patents that were developed in the OE program.

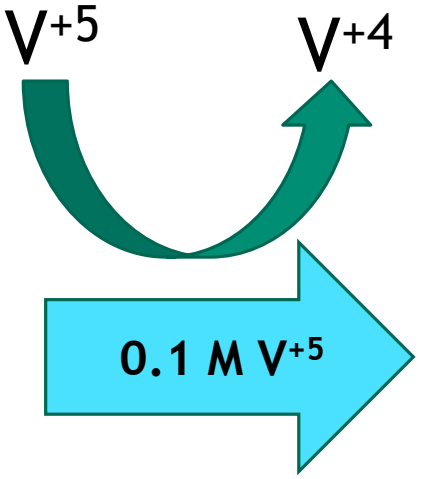
1) U.S. Patent No. 7,301,002, entitled Sulfonated Polyphenylene Polymers, issued on November 27, 2007. (SD#7565.1)
2) U.S. Patent No. 9,580,541, entitled High Performance, Durable Polymers Including Poly(Phenylene), issued on February 28, 2017. (SD# 12691.1)
3) U.S. Patent No. 7,888,397, entitled Polyphenylene 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)

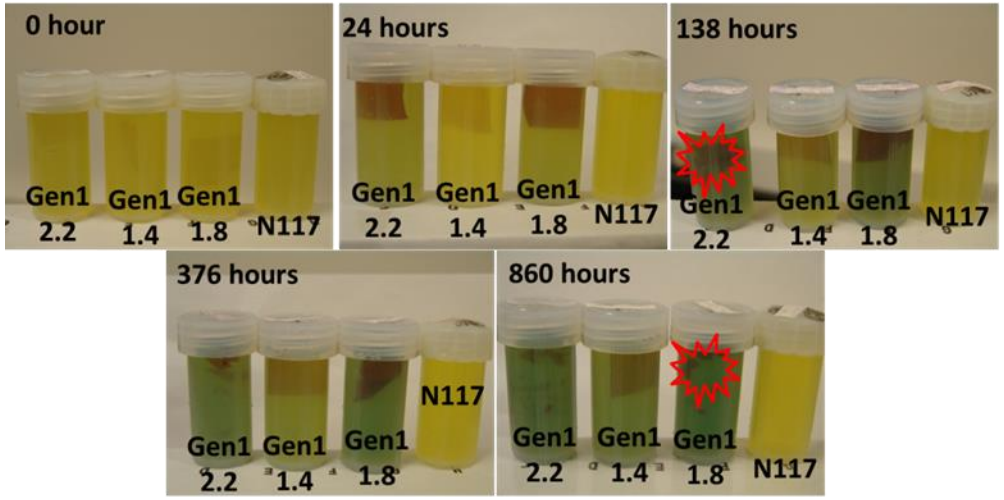
Earlier CEMs Degradation/Oxidation by V^{+5}

Aryl groups can be oxidized by $V^{+}5$ = Durability issues

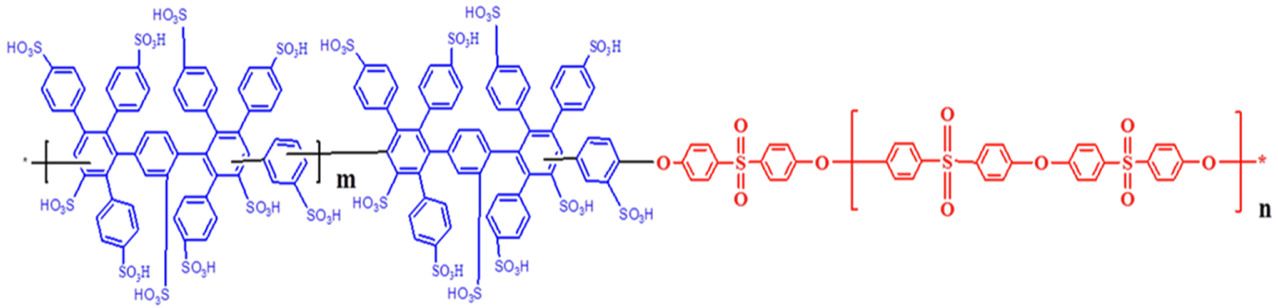


1st Gen: SDAPP

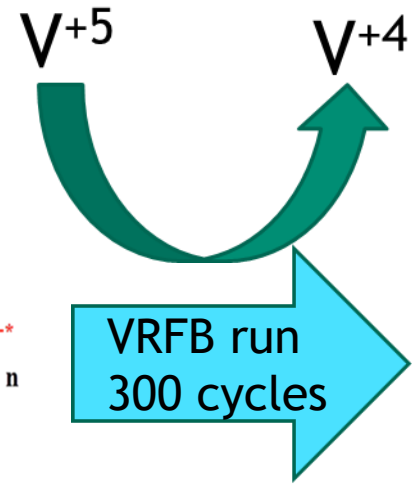




Even with dilute V+5 membranes oxidize!



4th Gen: Block SDAPP

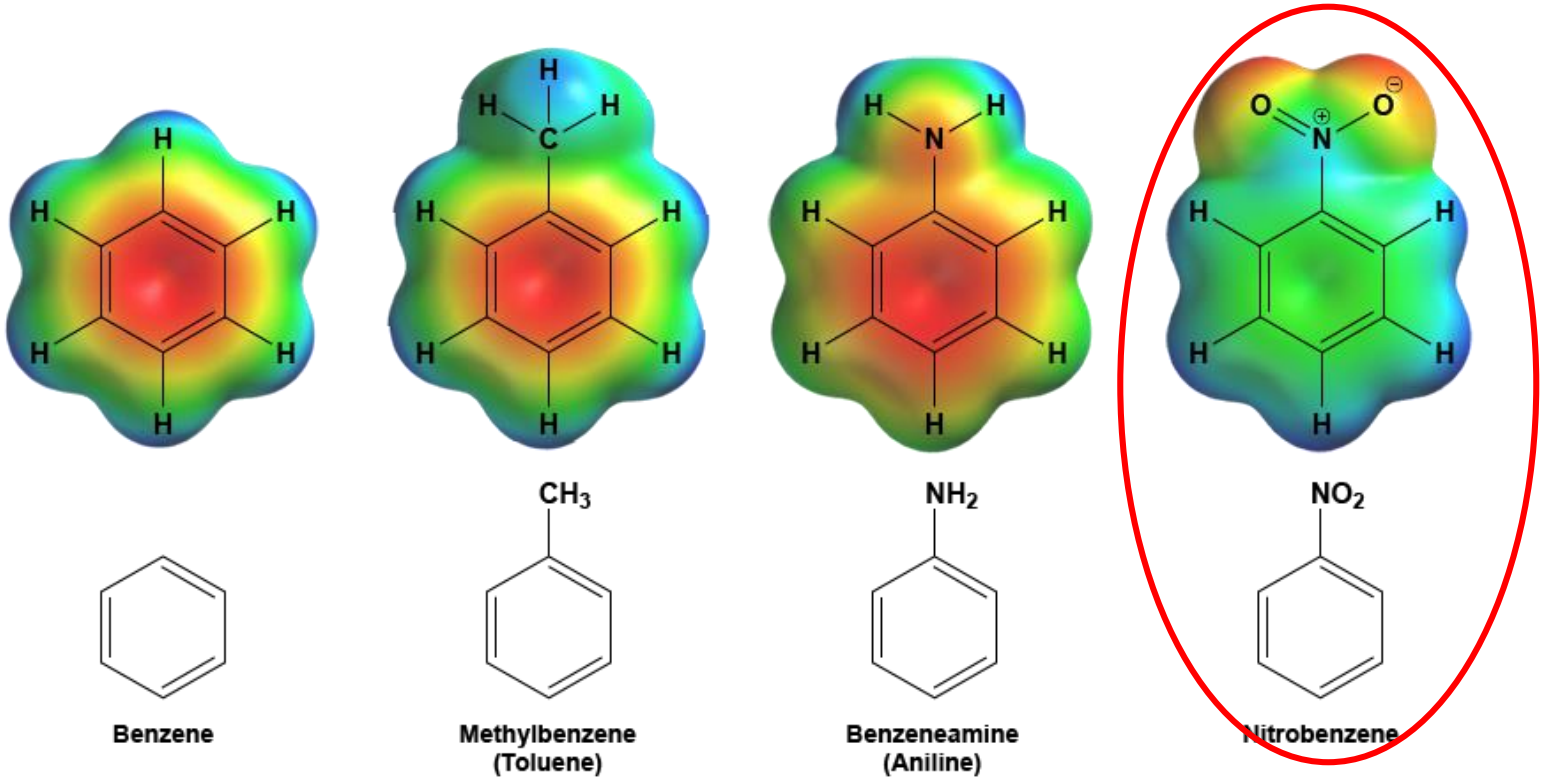


Innovated Approach

Problem is: Oxidation process that removes electrons and aryl groups have high density of electrons.

Electrostatic potential maps:
Models that indicate electron/charge density

- Red high density of electrons
- Blue low density of electrons

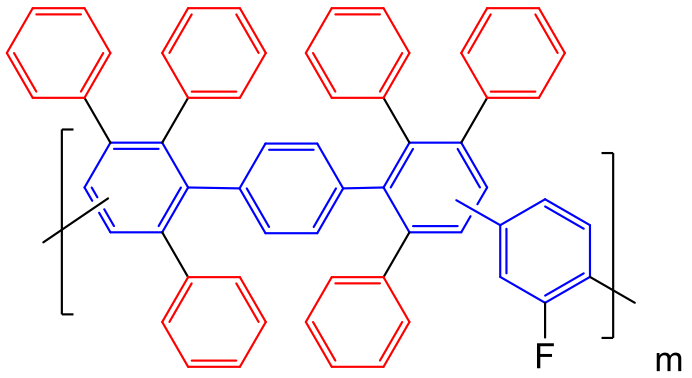


Electron donating

Electron withdrawing

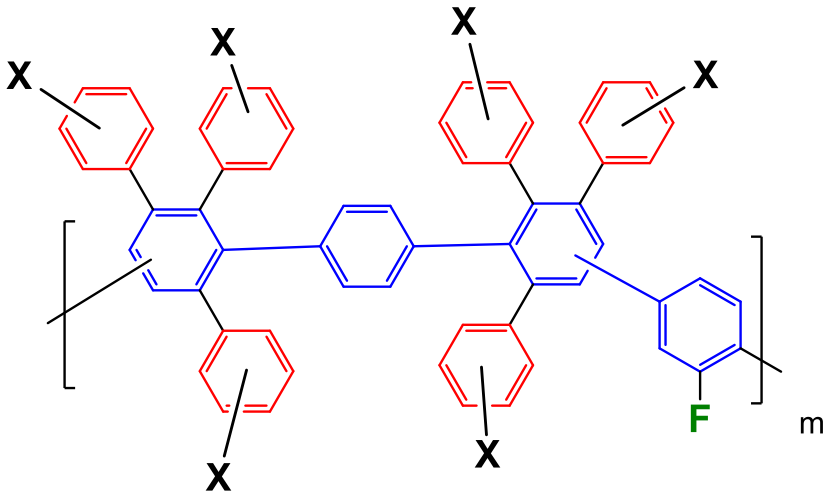
Possible solution is: Attach electron withdrawing groups to all aryl rings to prevent V+5 oxidation.

Implemented Approach to the Membrane



DAPP

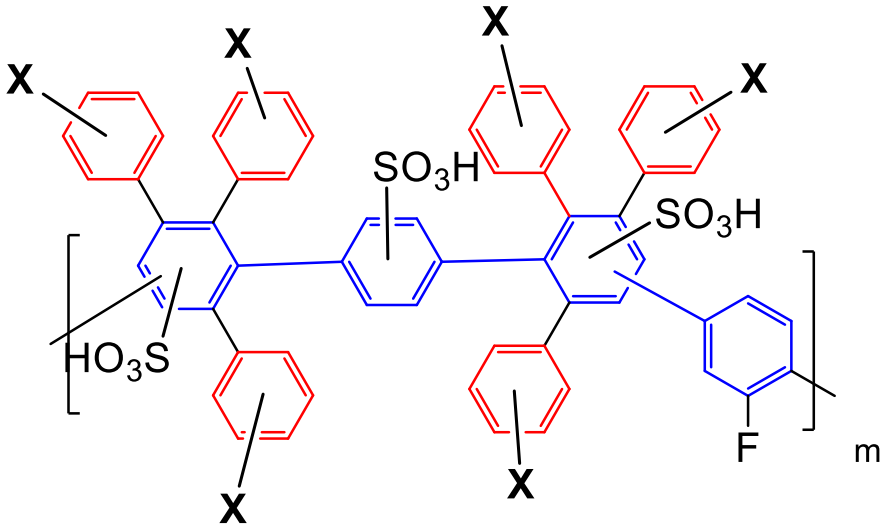
Red pendant aryl group:
Pendant most likely oxidized initially by V^{+5}.
Blue backbone aryl group.



X = electron withdrawing group

FDAPP

Attach electron withdrawing, hydrophobic moiety on pendant rings.



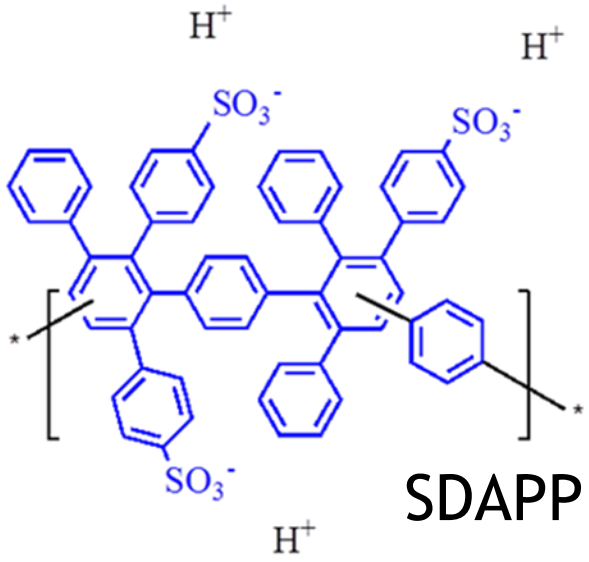
SFDAPP

Sulfuric acid is used to sulfonate backbone, electron withdrawing and ion source.

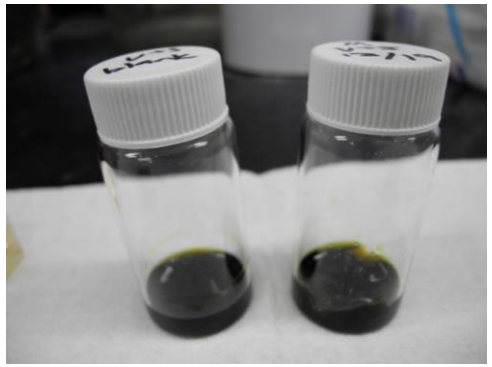
Water uptake: 25%
IEC_{theory}: 1.35 meq/g
$IEC_{experimental}$: 1.4 meq/g

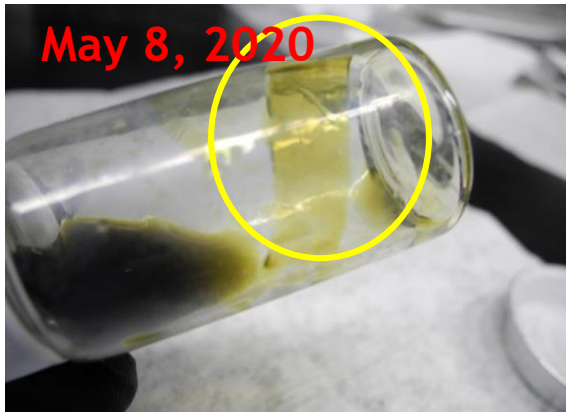
New IP, TA 15330, patent filed Aug. 20, 2020

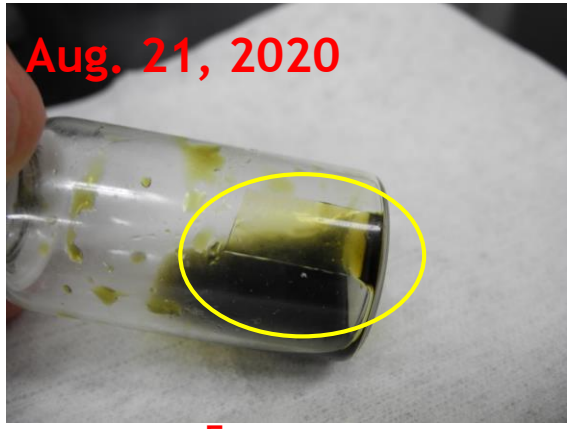
Initial-Small Scale Durability Probe



Initially probed durability on small scale: Soaked small strips of film in 1.5M V^{+5} in 2M H_2SO_4





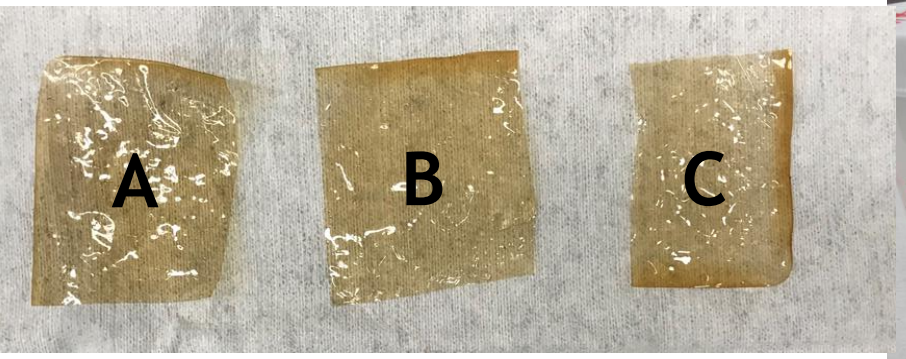


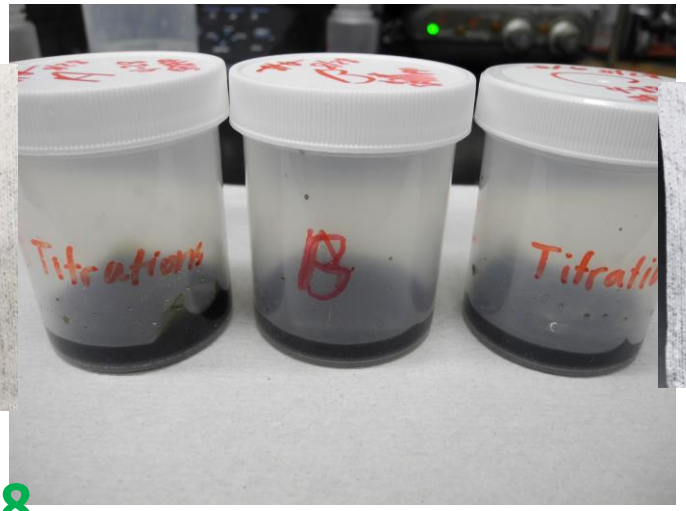
After 246 days FSDAPP still intact in contact of 1.5 M V^{+5}

Larger Scale Durability

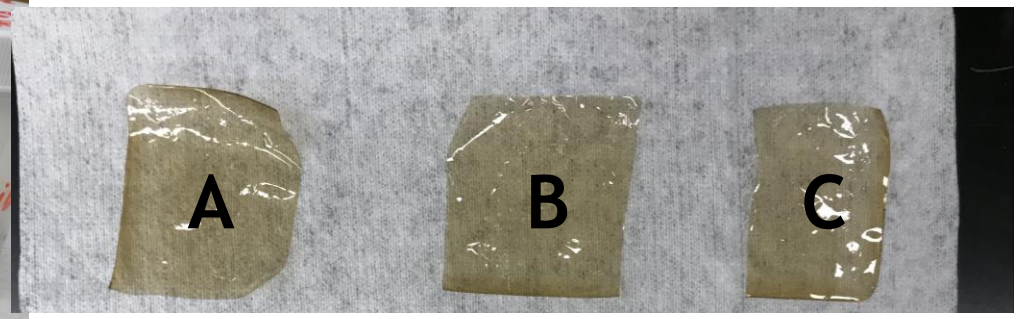
Larger scale durability in 1.5M V^{+5} in 2M H_2SO_4 to track changes in weight, IEC and water uptake

Aug. 6, 2020





Aug. 26, 2020



$Wt_{a,b,c}$(mg): 75.6, 76.2, 57.8
IEC_{ave}(meq/g): 1.3
Water $uptake_{ave}$: 23.5%

$Wt_{a,b,c}$(mg): 75.4, 76.2, 57.8
IEC_{ave}(mg): 1.3
Water $uptake_{ave}$: 23.5%

No change after 20 days, promising! Continuing soaking studies…

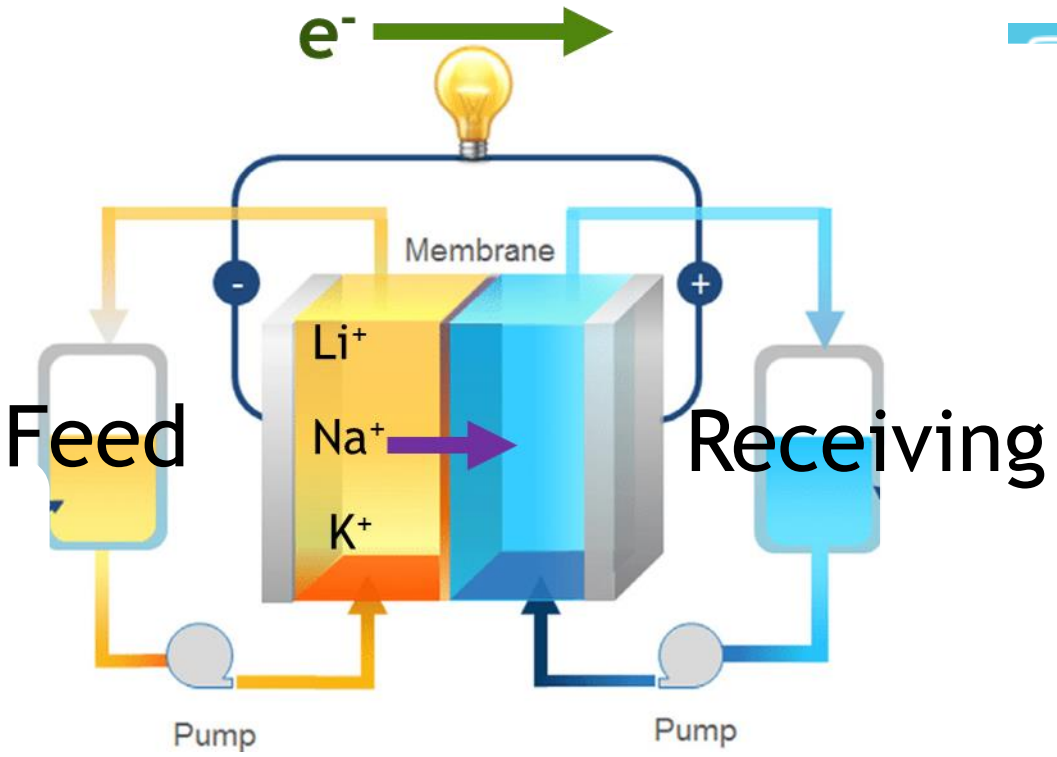
Ion Selectivity

Electrosynthesis

Measured by Josh Sun

Wanted to see the selectivity of SFDAPP between Li+, Na+ and K+

Ion	Bare ion radius (nm)	Hydrated radius (nm)	Hydration number (±1)
Li^+	0.068	0.38	5
Na^+	0.095	0.36	4
K^+	0.133	0.33	3



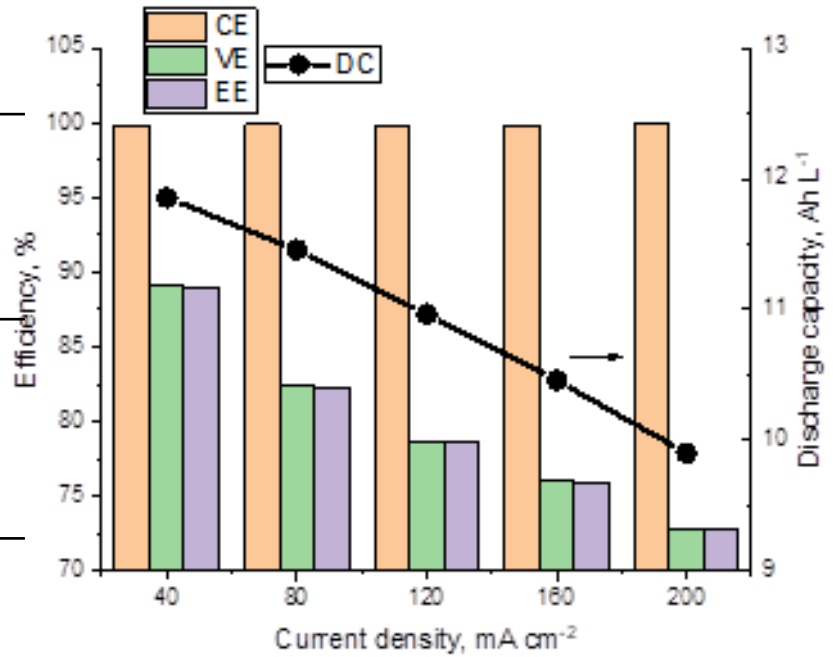
Feed	Receiving	current density mA/cm2	Charge carried by Li	Charge carried by Na	Charge carried by K
0.25M Li/K/Na Cl	0.1M HCl	113	24%	34%	43%
0.25M Li/K/Na Cl	0.1M HCl	191	28%	32%	40%

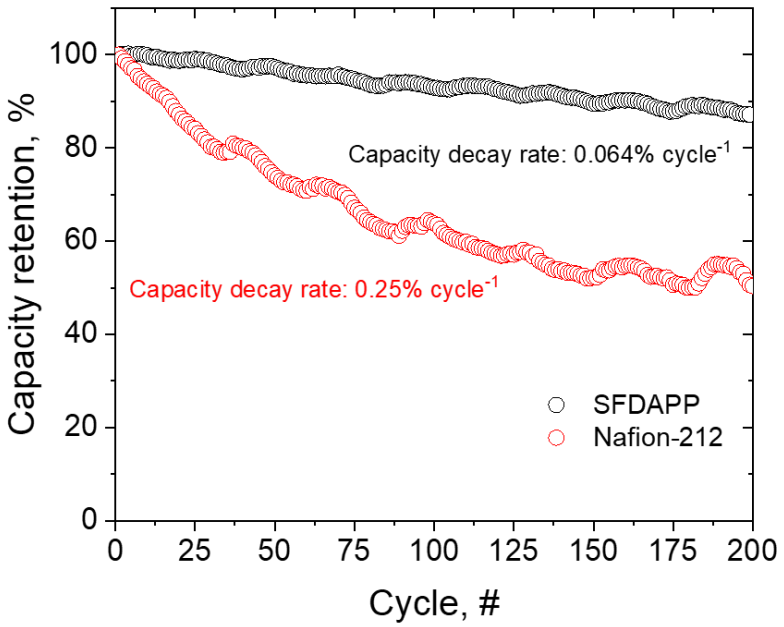
FSDAPP does shown selectivity down to 0.3 Å difference in ion size!
Stokes radius of Li = 0.38 which is smaller than vanadium ion Stokes radius +0.6nm.

Vanadium Redox Flow Battery: Collaboration with Los Alamos NATIONAL LABORATORY EST. 1943

Measured by Sandip Maurya

Membrane	VO^{2+} Permeability, cm^2/min
SFDAPP	4.25×10^{-8}
Nafion 212	6.0×10^{-6}





VRFB testing by LANL look very promising!

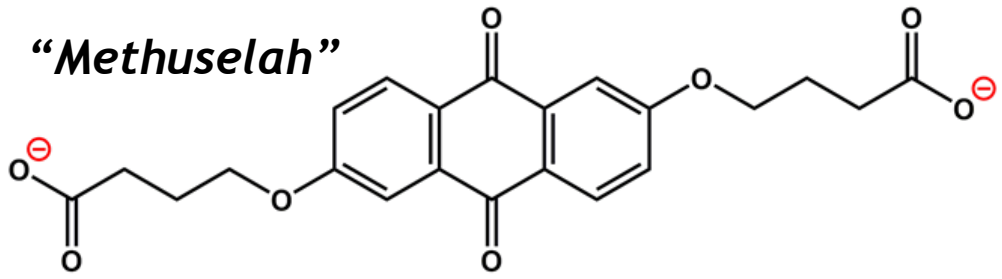
- **SDAPP 100 x less permeable to VO^{+2}.**
- **Near 100% CE and high VE.**
- **Higher capacity retention than Nafion.**
- **Long term testing is underway.**

Aqueous Organic Flow Battery: Collaboration with Professor Aziz's Group

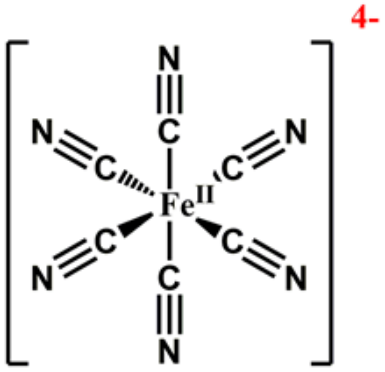
Measured by Tang Zhijiang

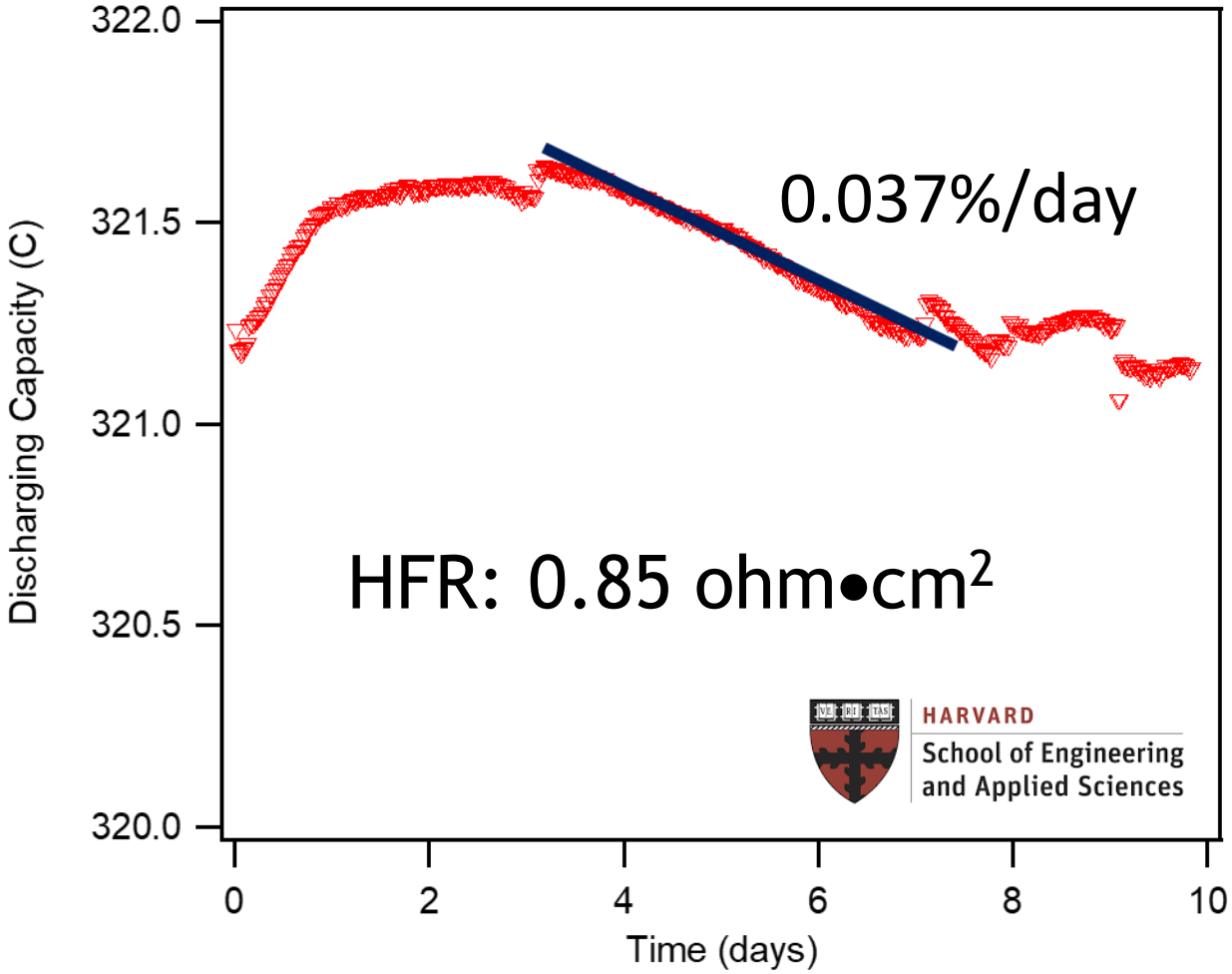
Negolyte: DBEAQ

"Methuselah"



Posolyte: Ferricyanide





Low capacity loss per day and low high frequency resistance. Test performed right before shut down, restarting testing.

Conclusions

- Seven membrane patents licensed.
- Developed new cation exchange membrane; SFDAPP.
- SFDAPP has shown very good stability in concentrated V^{+5} and ion selectivity.
- SDFAPP is showing very good VRFB and aqueous organic flow battery performance.

Future Tasks

- Continue flow battery testing of SFDAPP.
- Open for new collaborators interested in testing our new membrane.

IP Patents

- Patent published, US Appln. No. 16/597,279 “Block Copolymers including Poly(phenylene) and methods thereof”, Feb. 6, 2020.
- TA submission C. Fujimoto and E. Baca “High ion selective membranes for flow battery applications” SD#15330, filed for patent Aug. 20, 2020

Thank You

Thank You to the DOE OE and especially Dr. Gyuk for his dedication and support to the ES industry and Sandia's ES Program.

Questions?

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