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Advanced Membranes for Vanadium Redox Flow Batteries (VRB) Cy Fujimoto

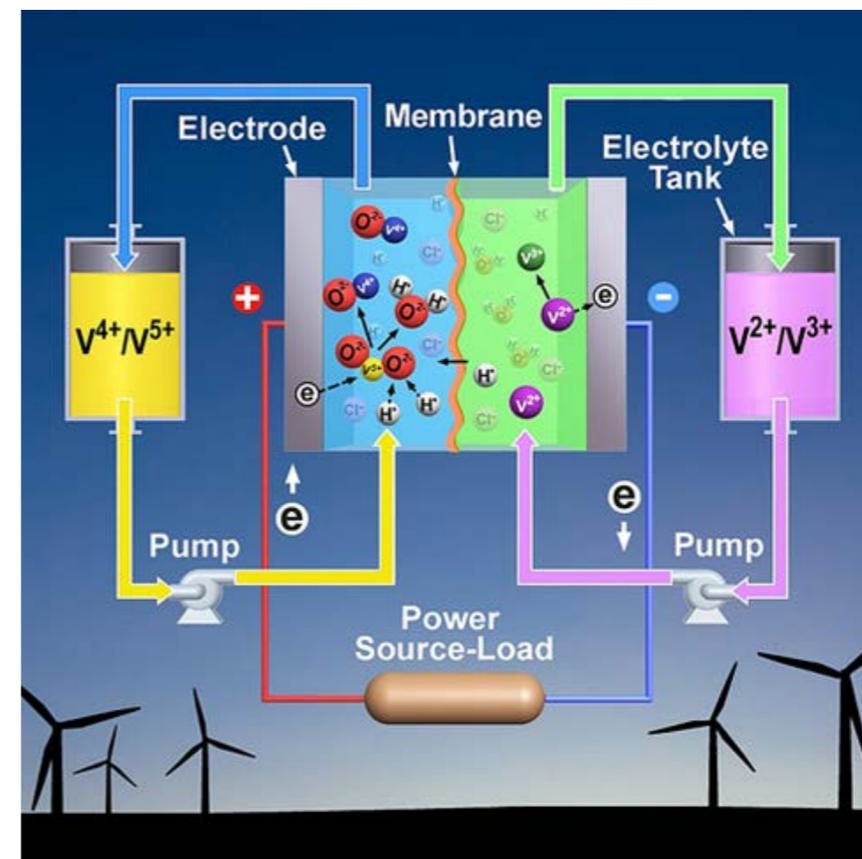
Travis Anderson and Harry Pratt @ SNL; Tom Zawodzinski and
Zhijang Tang @ ORNL; Wei Wang and Xiaoling Wei @ PNNL



Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Project

- Separation of energy and power
- Robust battery. Allows for deep discharge and long life cycles
- Several US companies looking to commercialize this technology

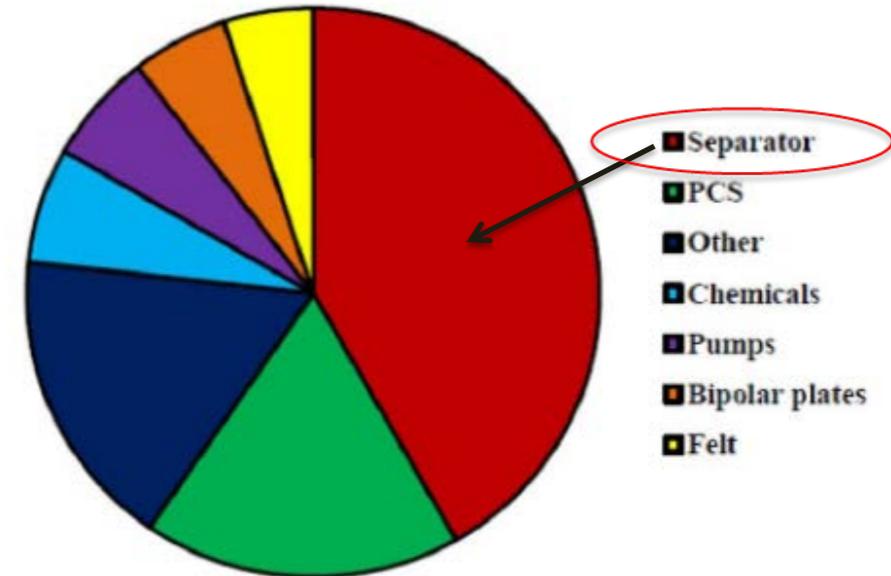


Cost is focus since current capital costs range between \$500-1000/kWh

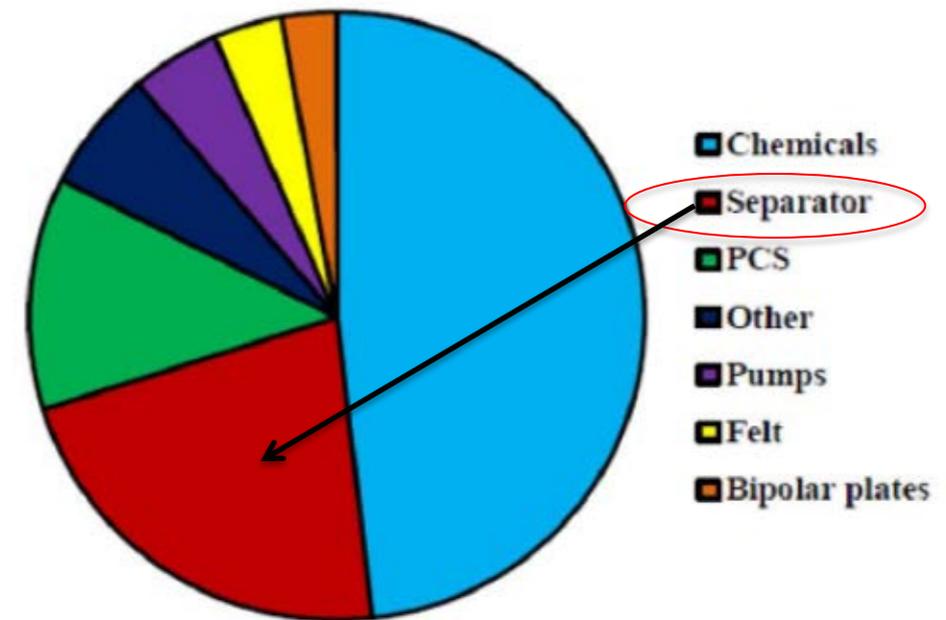
Cost of VRB

- Cost calculated based on shunt-pumping losses and delivered power and energy capacity.
- Two types of VRB configurations
 1. Power intensive: 1 MW/0.25 MWh (Power quality applications)
 2. Energy intensive: 1 MW/4 MWh (Load following)
- In both scenarios the membrane separator takes up a significant portion of total cost
- Nafion™ \$250-500/m²; Perfluorinated polymer (primarily C-F)

VRB capital costs¹



Power intensive case

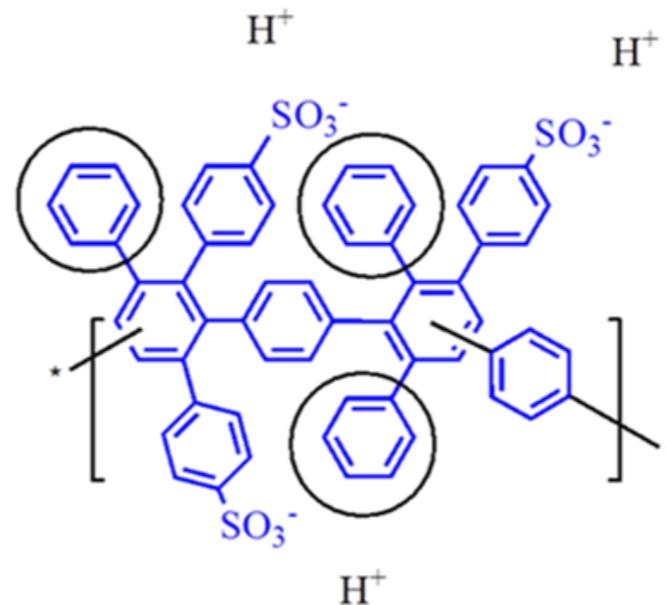


Energy intensive case

Sandia is developing low cost, hydrocarbon polymer (C-H) with better performances than Nafion

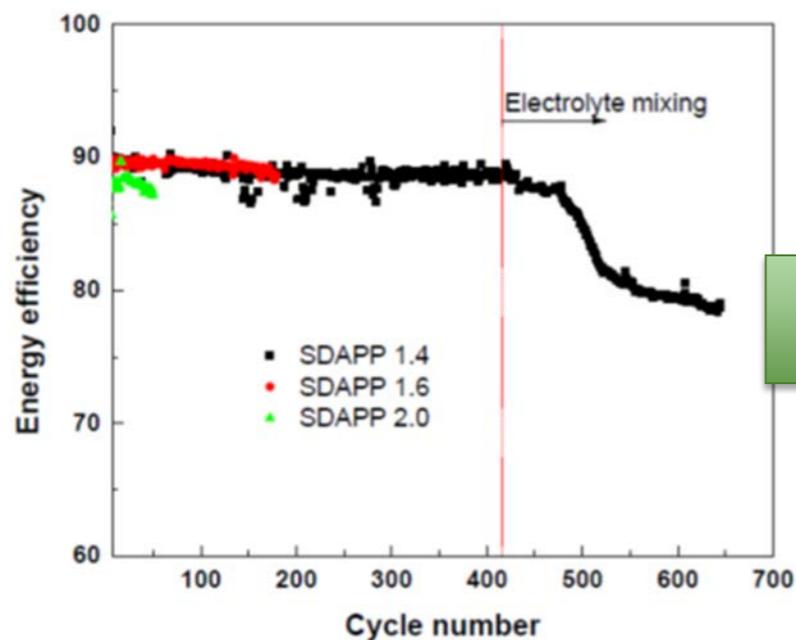
Evolution of VRB membranes

- GEN 1 material:
 - + Performance equivalent to PFSA
 - Durability, after 179 cycles oxidation of film



Test credit Soo-Han Kim 2012

In-situ

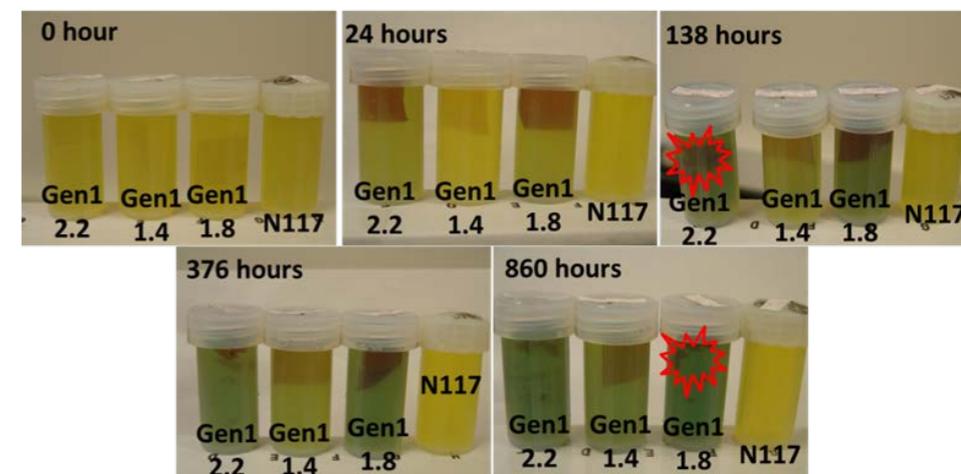


SDAPP1.6
179 cycles (27d)



Very brittle

Ex-situ: 0.1M V⁺⁵

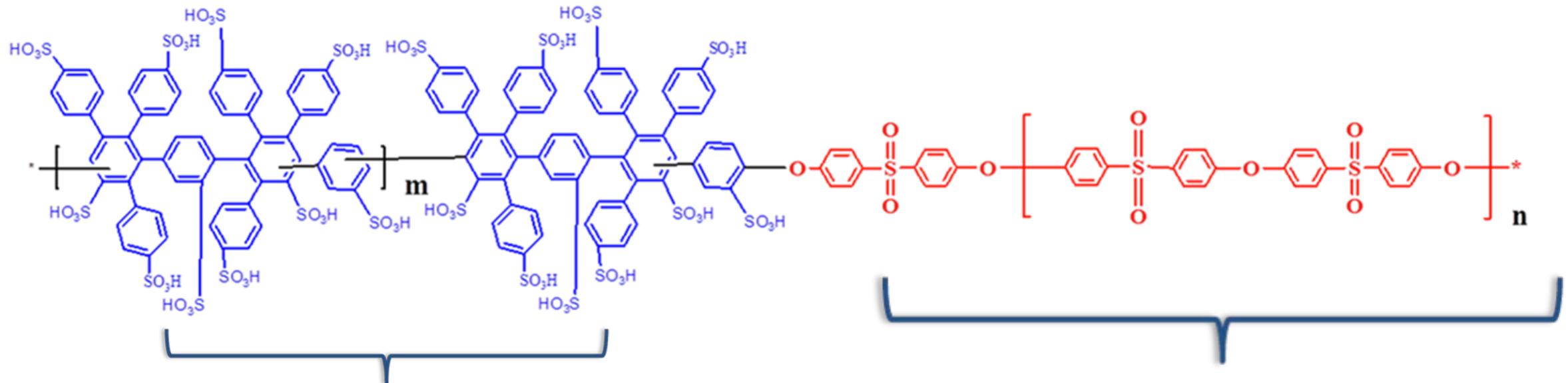


V⁺⁵ oxidizing un-substituted aryl rings

Evolution of VRFB membranes

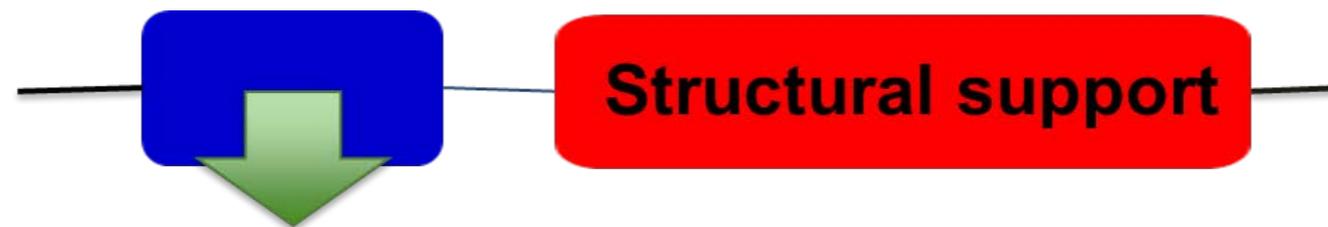
Substitute $-\text{SO}_3\text{H}$ on all aryl groups

GEN 4 material



Hydrophilic segment
Controls ions and water flow

Hydrophobic segment
Mechanical support



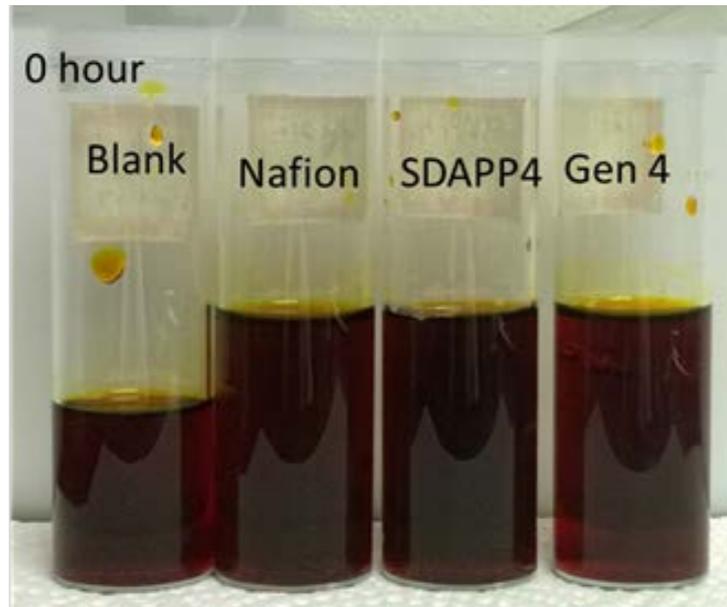
Ions and water transport

Structural support

Patent submitted Nov 2014 US 62/075,693

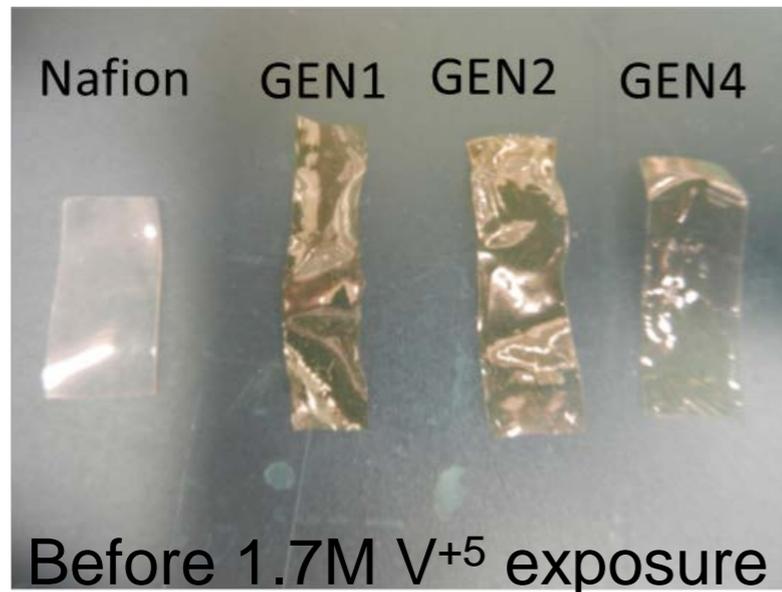
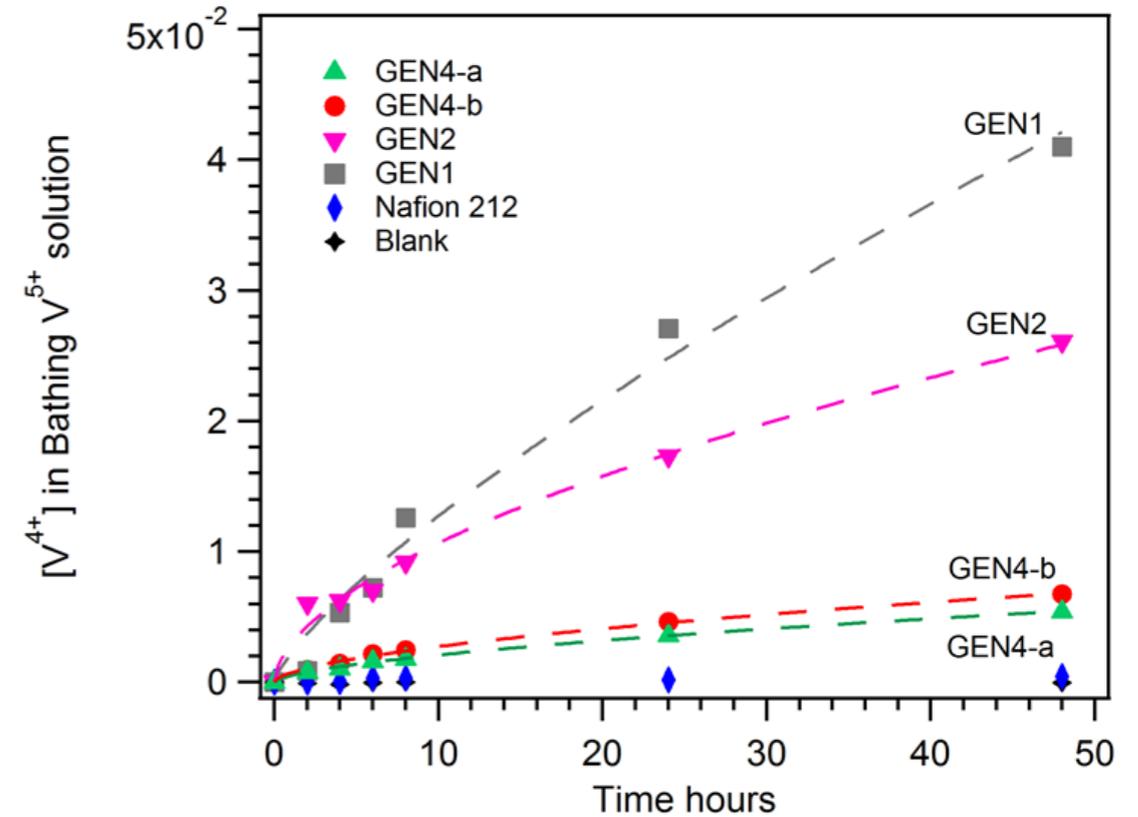
Membrane Durability

Ex situ durability

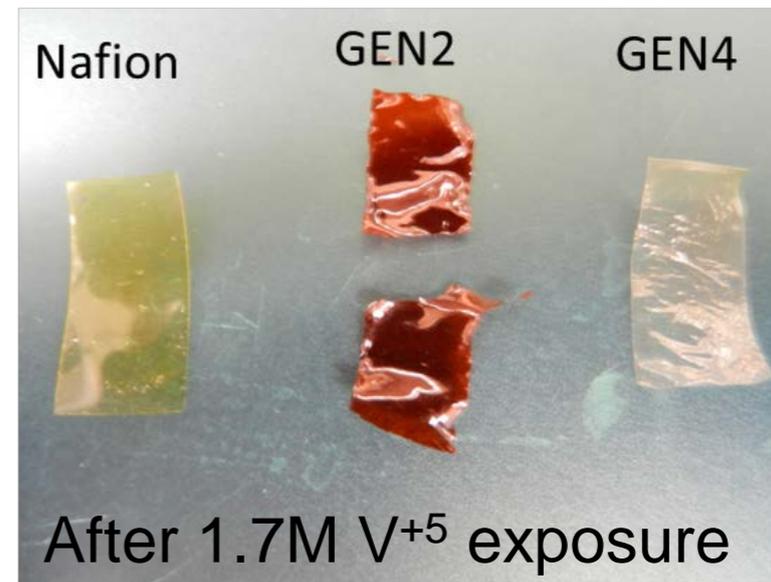


25 mL of 1.7 M V^{5+} , 5M SO_4^{-2}
200mg of membrane

Monitored V^{4+}
production by
UV-Vis



48 hrs

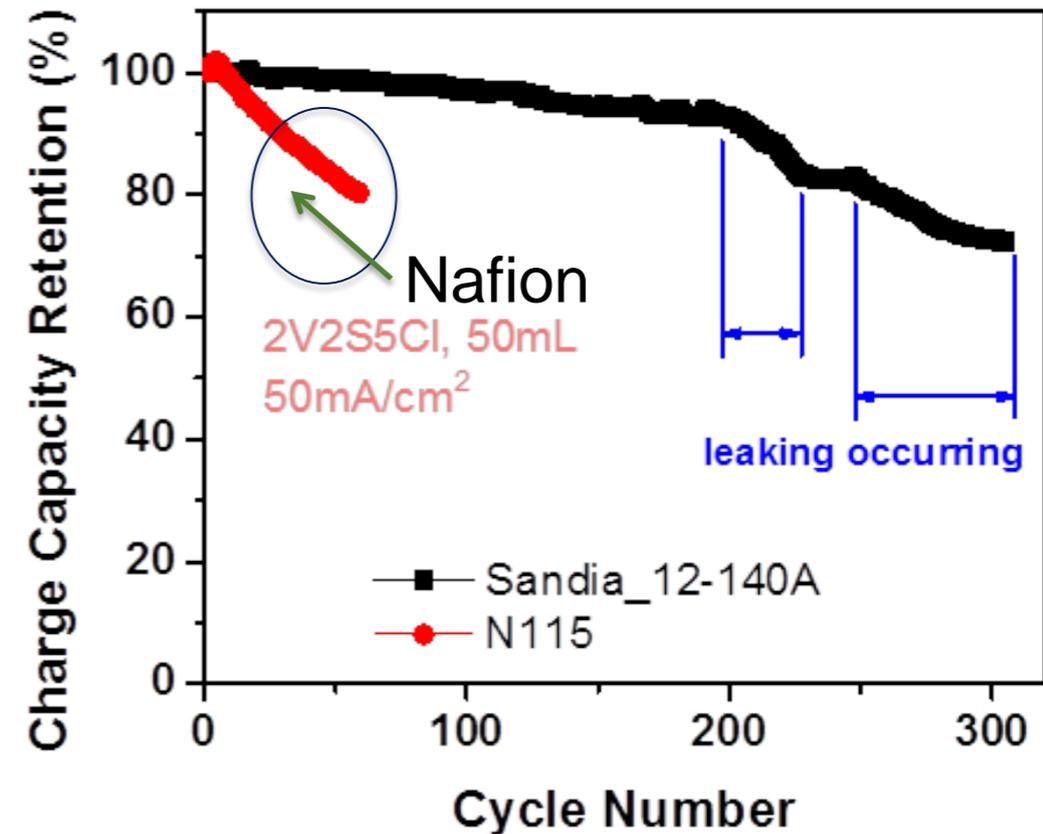
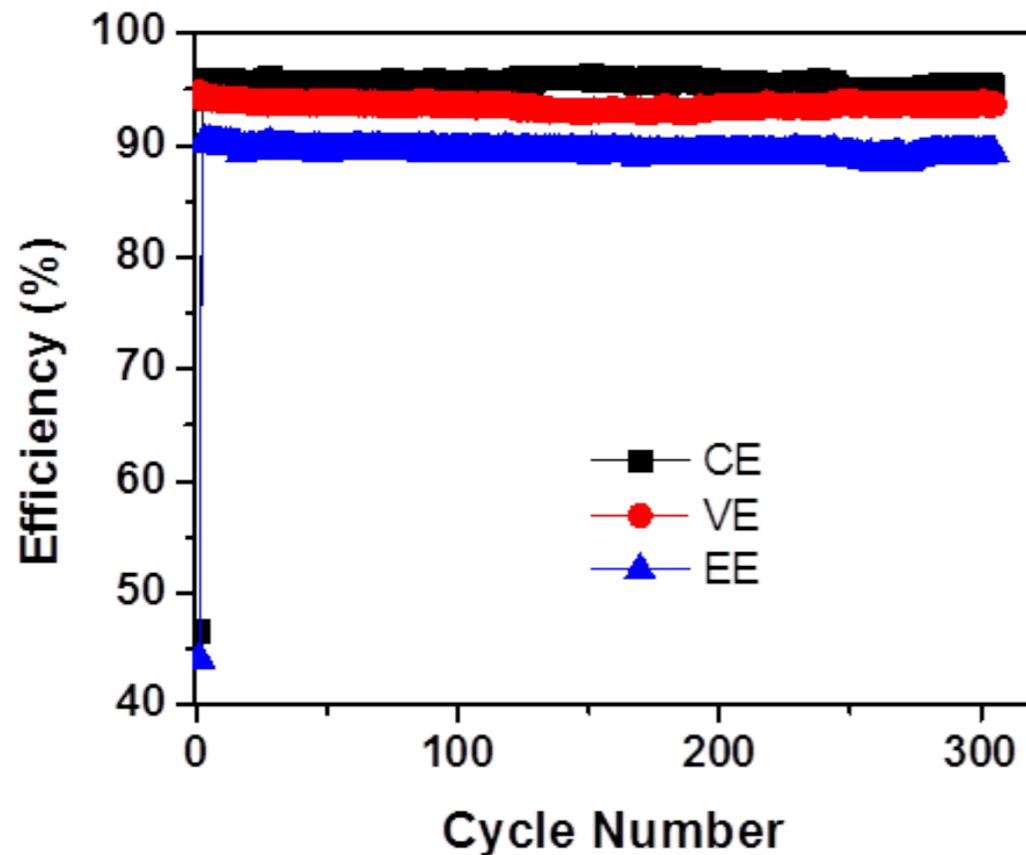


GEN4 stability greater than GEN1 and GEN2

Membrane Performance

Xiaoliang, PNNL

Tested in 2M mixed-acid VRB

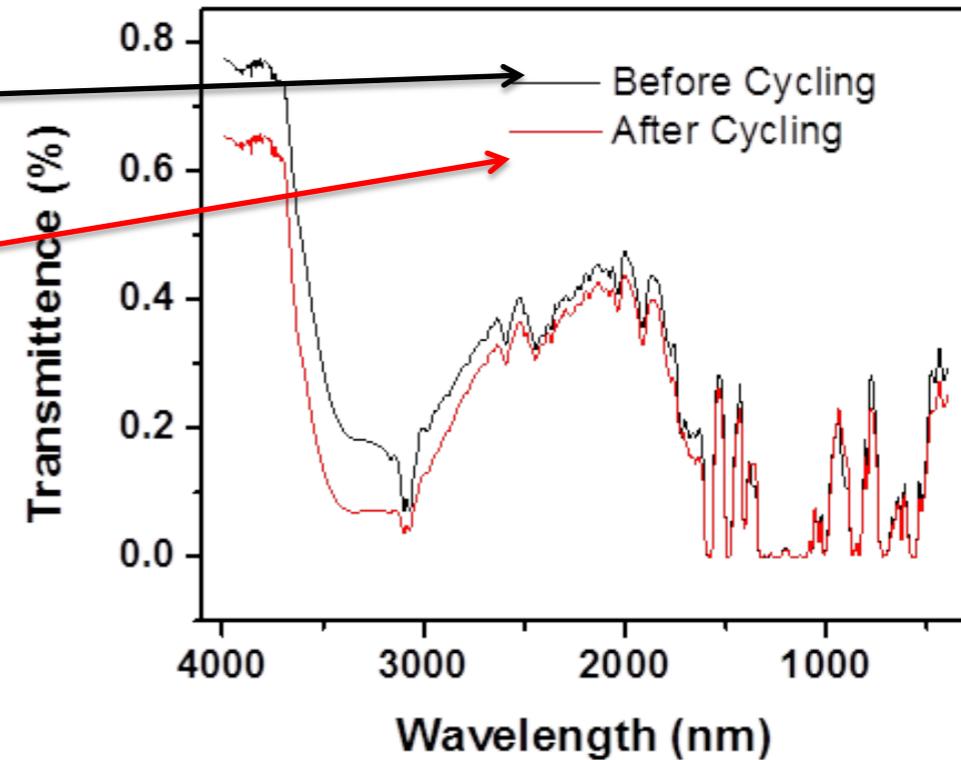
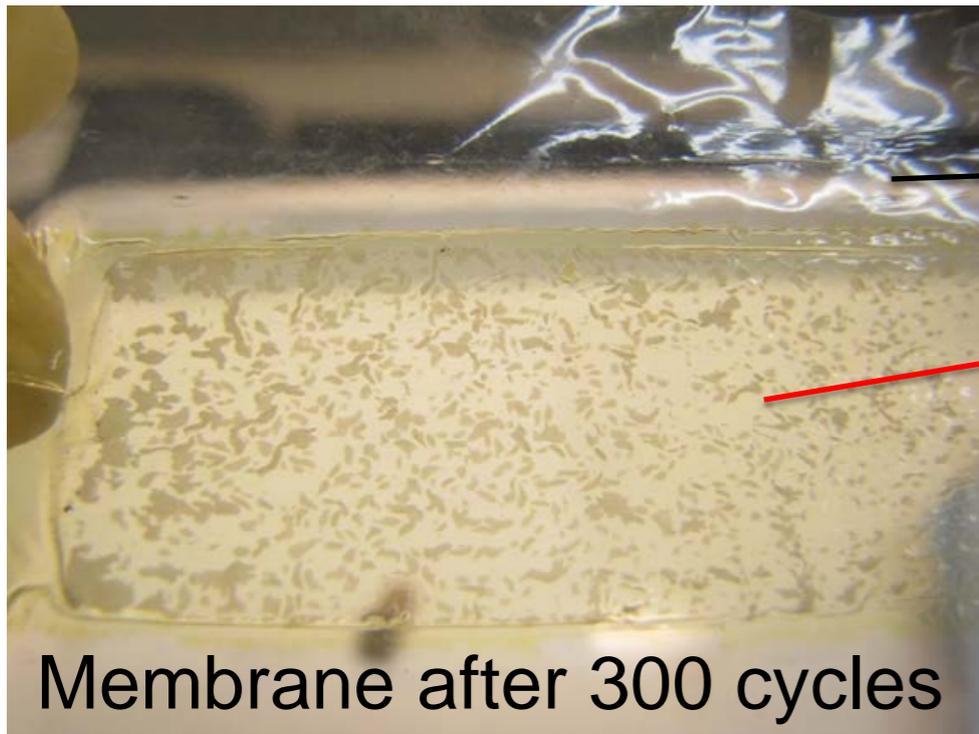


- Good performance: Columbic efficiency 95%, voltage efficiency 94% and energy efficiency 90%
- Much higher charge retention compared to Nafion
- Small capacity decay with time, but large drops in part to solution leaking [test run time nearly 4 months]

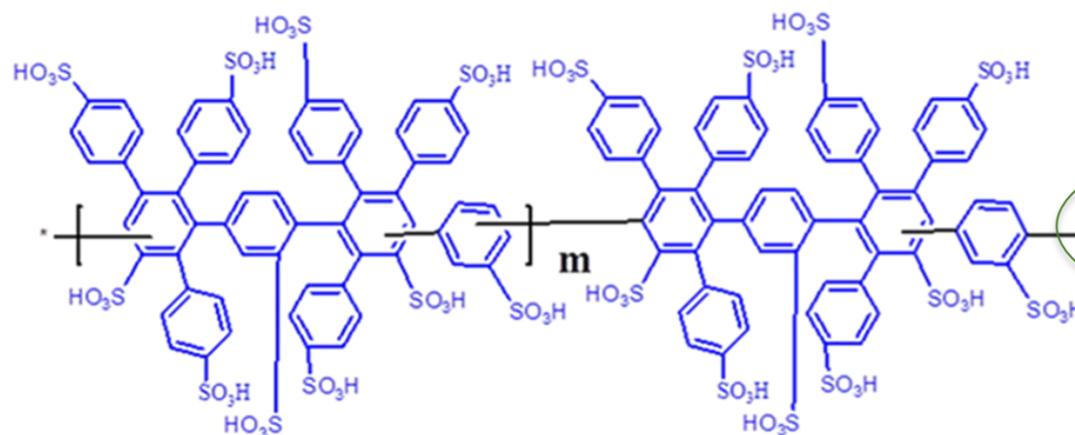
GEN4 good performance much better capacity retention than Nafion

Membrane Performance

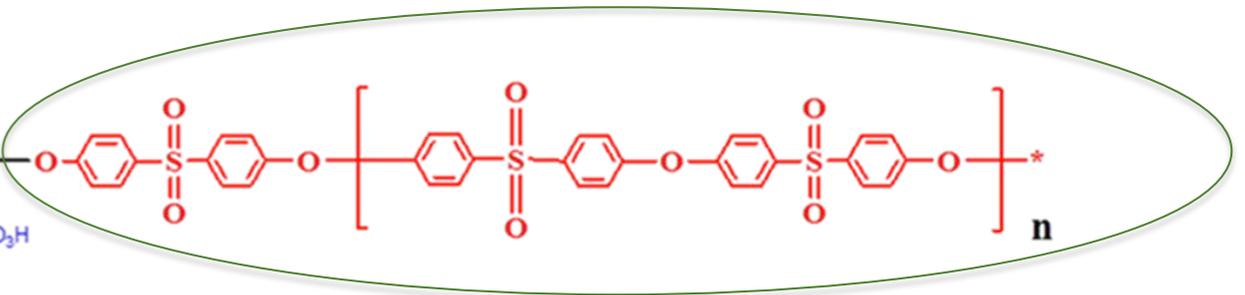
Xiaoliang, PNNL



- After cycling the membrane it shows some discoloration (white spots)
- IR analysis of active and non active area shows very little difference, suggesting little to no decomposition



We are looking into several alternatives



GEN4 may still need a few modifications, but almost there

Membrane Scalable, Cost?

SEMICONDUCTOR FAB MATERIALS



**Low K & Ultra Low K
Metrology comes to the rescue**

Don Frye, Carol Mohler
Semiconductor Fab Materials
1712 Building
The Dow Chemical Company
Midland, MI, USA



 2005 International Conference on Characterization and Metrology for ULSI Technology March 16, 2005

SEMICONDUCTOR FAB MATERIALS



Organic Dielectric Films

SiLK film- all organic dielectric



 2005 International Conference on Characterization and Metrology for ULSI Technology March 16, 2005

- Feasible to scale chemistry? Yes
- Cost? Silicon dioxide (low volume pricing Sigma-Aldrich \$64/kg) assume SiLk costs were not extremely far off from this value since cost was never an issue [Nafion \$5000/kg approximately \$250/m²]

Summary/Conclusions

- Gen4 significantly improved durability over Gen 1&2
- Gen4 VRB performance better than Nafion212
- Gen4 charge retention **much** better than Nafion 212
- Gen4 structure as presented, requires slight modification

Future Tasks

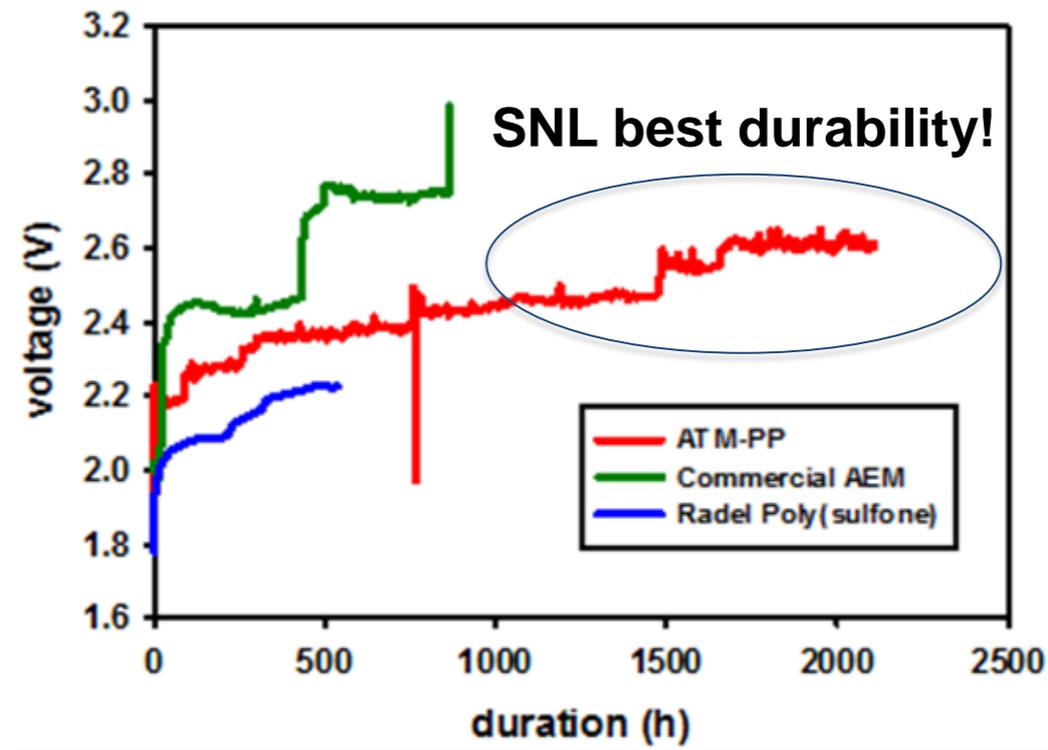
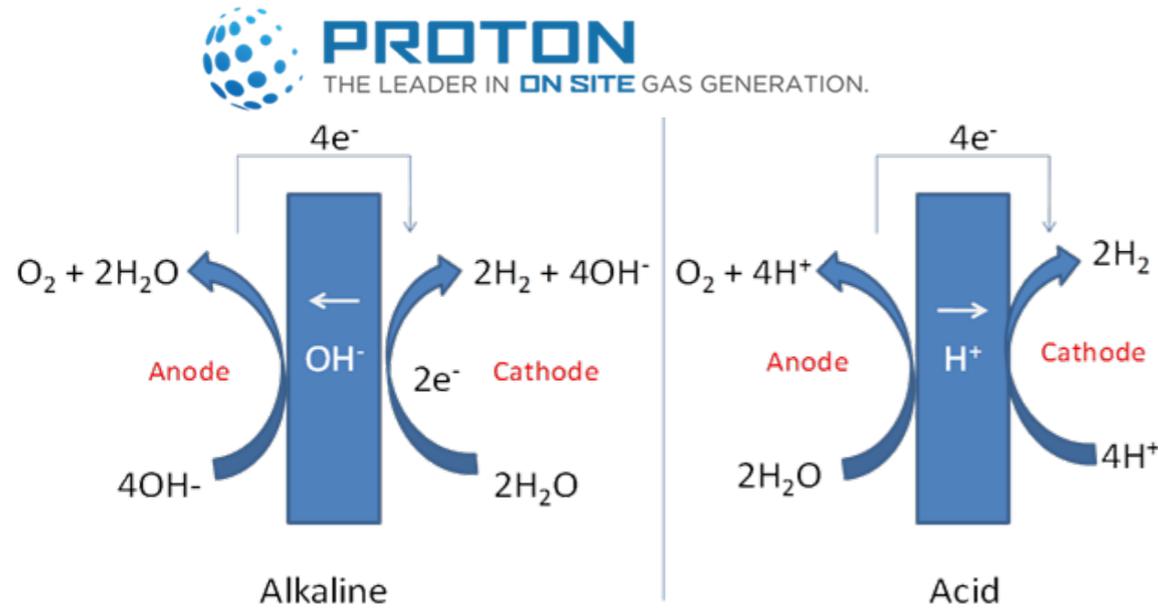
- Developing Gen4 with oxidative resistance hydrophobic domain
- Cost model development with external partner
- Further develop details in commercialization path forward

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?

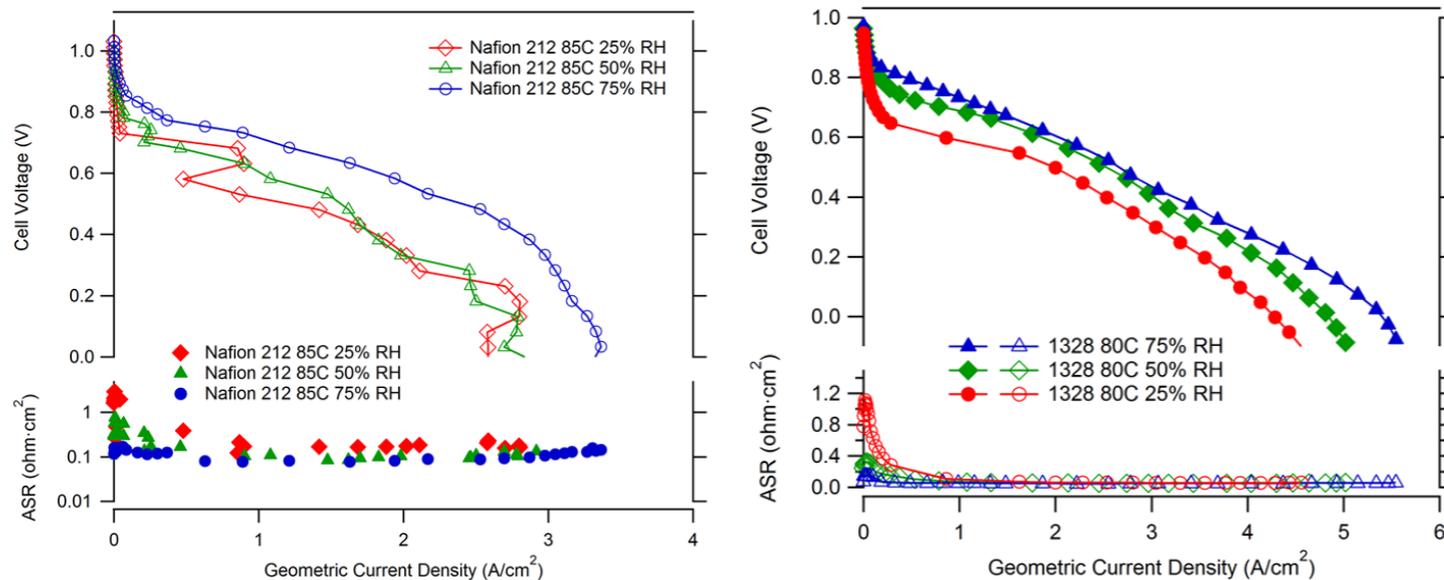
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Outside interest



With ProtonOnsite proved alkaline electrolysis is feasible

With IP developed in the OE program, EERE fuel cell awarded SNL incubator project for intermediate temperature PEM fuel cell – Results very promising



Lower ASR in SNL over Nafion
Higher power in SNL over Nafion

Work with Dr. Zawodzinski

Showing promising data for multiple applications