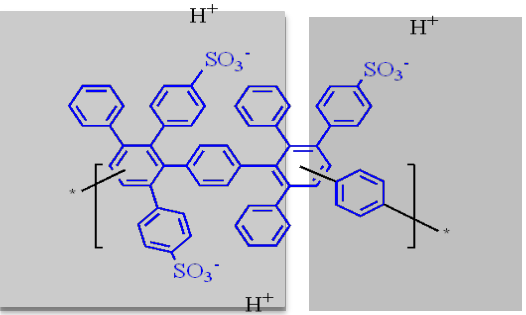
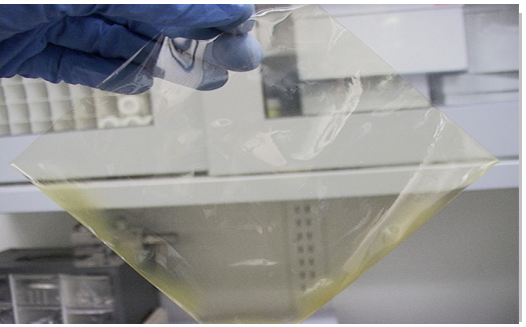




Advanced Membranes for VRFB. A Collaboration with SNL, PNNL and ORNL

September 28, 2012

Cy Fujimoto

Sandia National Laboratories

Exceptional service in the national interest

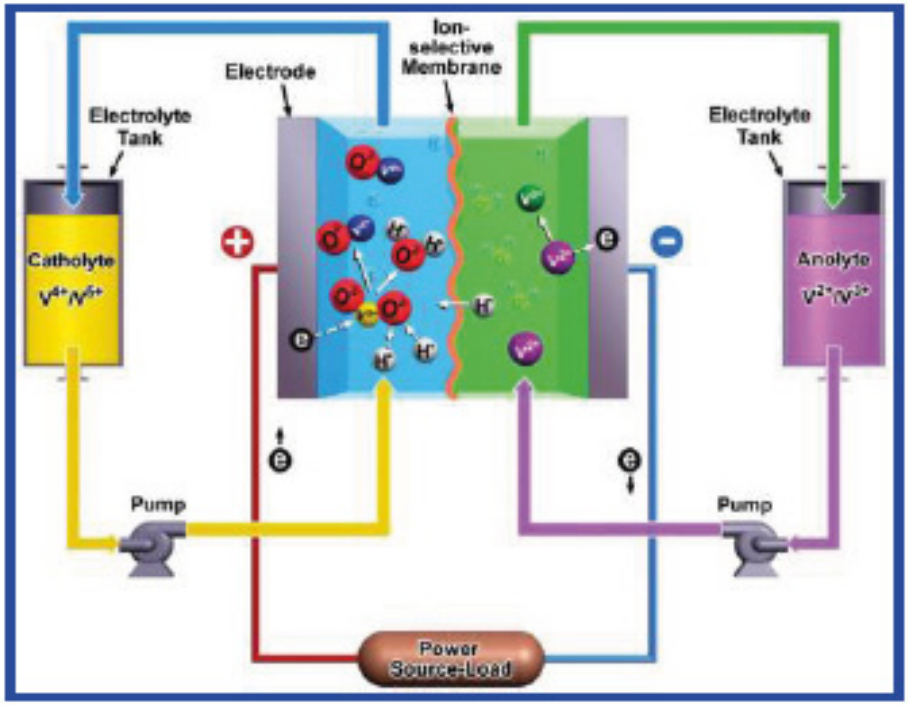
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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

- VRFB Proven technology; 6MWh VRB on a 32 MW wind farm in Japan.
- Near Commercialization; Prudent Energy and UniEnergy Technologies
- Separation of energy and power
- At the electrodes only electron transport is occurs. Allows for deep discharge, long life cycles and little capacity fade



The problem is cost, DOE capital cost target $100/kWh[1]
According to a recent study,[1] current capital costs is $380/kwh

1. M. Zhang, M. Moore, J.S. Watson, T.A. Zawodzinski, R.M. Counce; J. Electrochem. Soc., 159, A1184-A1188, 2012.

Cost of VRFB

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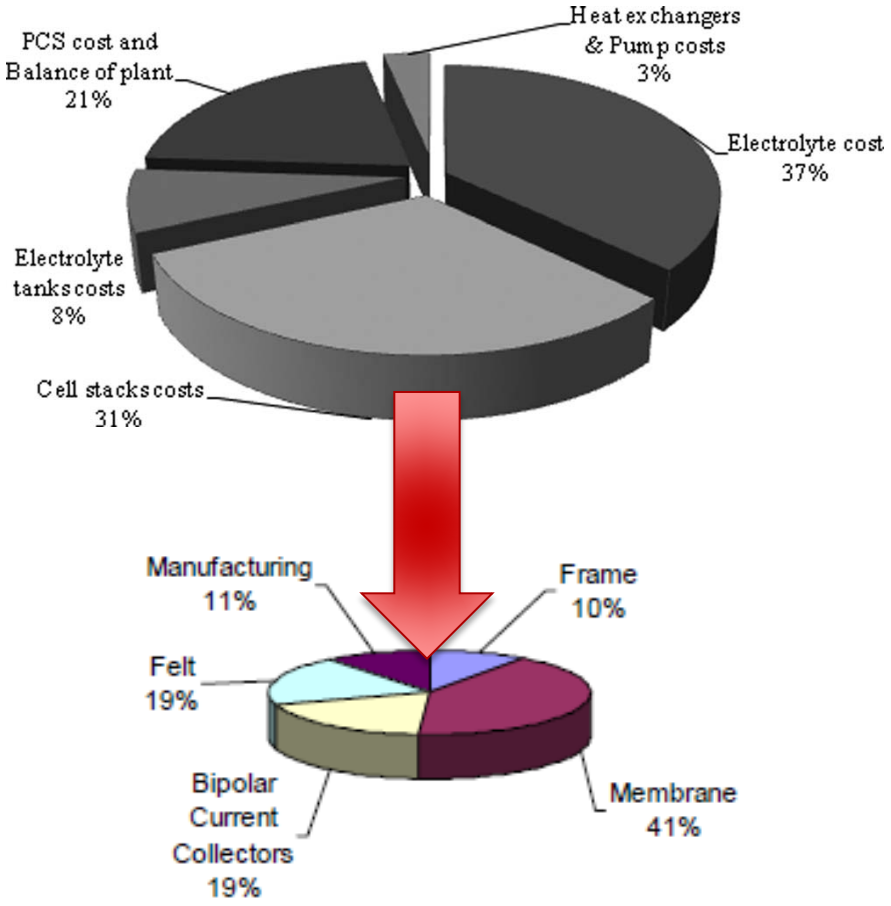
VRFB capital costs[1]



VRFB stack costs[2]

Base capital cost of VRFB, largest cost stems from vanadium. The stack costs is the second largest expense.

The membrane separator accounts for 40% of the cost of the stack.

Nafion™ $250-500/m^2
Perfluornated polymer (primarily C-F)

Developing hydrocarbon polymer (C-H) with equal or better performances to Nafion at a price target of $40/m^2

2. Vanadium Redox Flow Batteries: An In-Dept Analysis. EPRI, Palo Alto, CA: 2007. 1014836.

Membrane Considerations

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Performance

- High current efficiency
- High voltage efficiency
- High energy efficiency [CE x VE = EE]

Durability

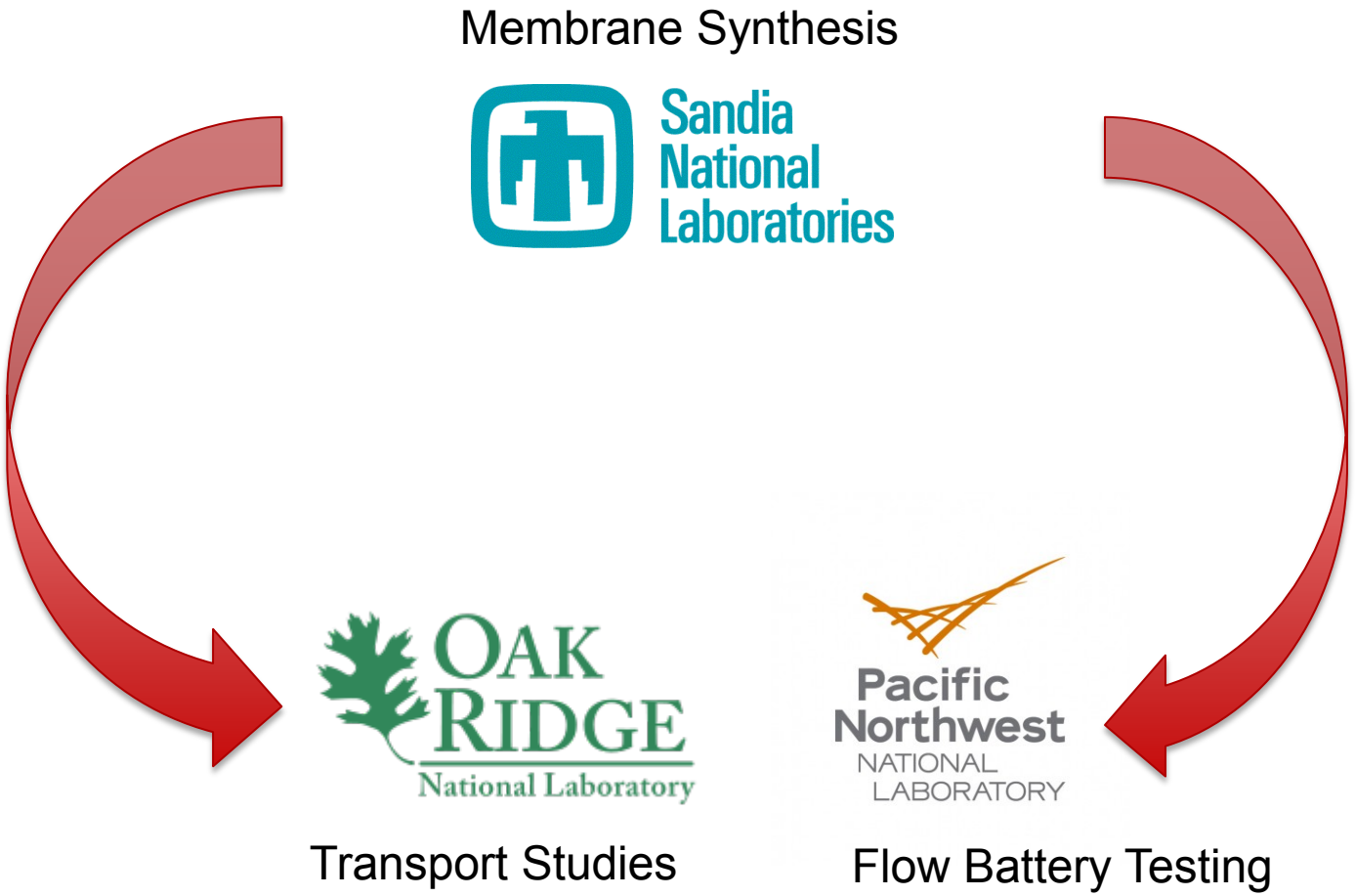
- Charge-Discharge cycles: >4,000 cycles
- Accelerated Durability: Vanadium +5 soaking studies

Cost [Membrane impacts more than material costs]

- More durable = Less maintenance
- More efficient = smaller stack

Collaboration Structure:

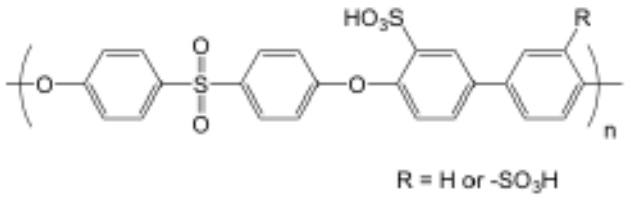
To more effectively utilize our R&D resources by tasking each lab on their respective strengths and to prevent work duplication (leverage – no duplication)

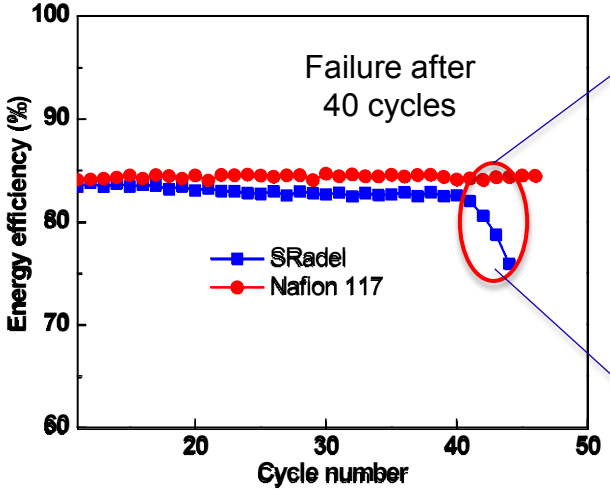


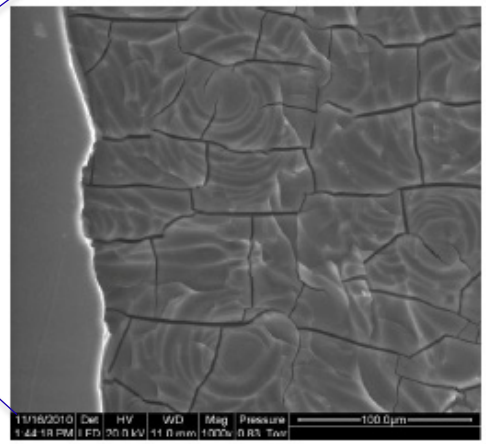
State of Hydrocarbon polymers in VRFB

One of the more common type of polymer backbone being explored for alternative VRFB membranes

S-Radel (SPAE)[3]



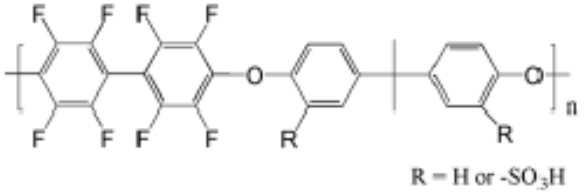


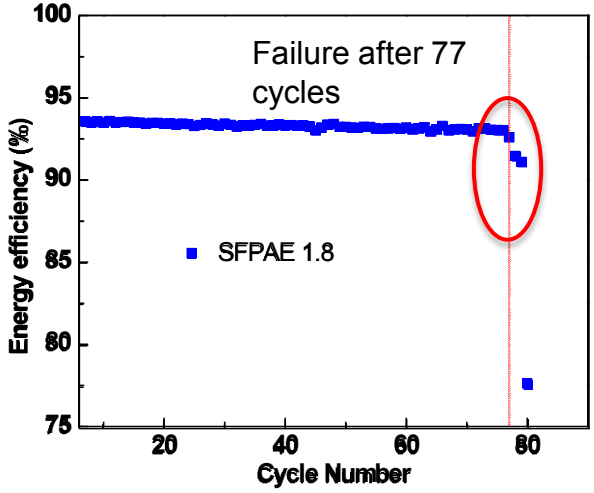


50 cycles

Film damage

SFPAE[4]



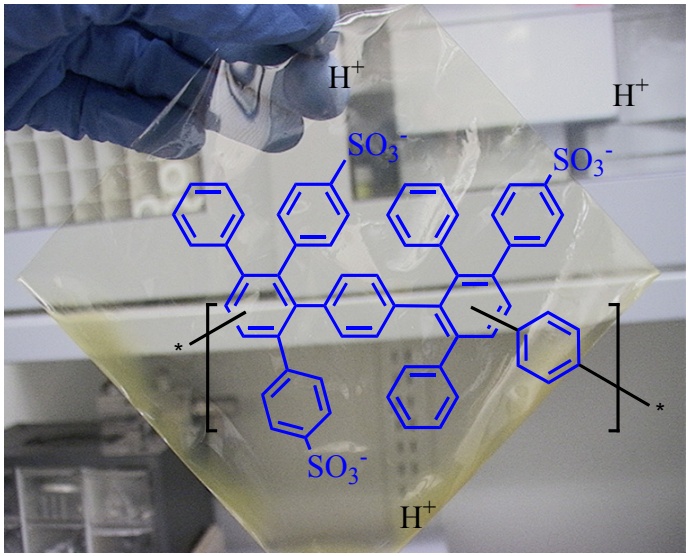


3. S. Kim, J. Yan, B. Schwenzer, J. Zhang, L. Li, J. Liu, Z. Yang, M. Hickner, Electrochemistry Communications, 13(5), 525, 2011

4. D. Chen, S. Kim, L. Li, G. Yang, M. Hickner, RSC Advances, 2(21), 8087-8094, 2012

Sulfonated arylene ether type polymers good EE, but there are durability problems; under 100 cycles

Sandia Materials – Diels Alder Polyphenylene[5]

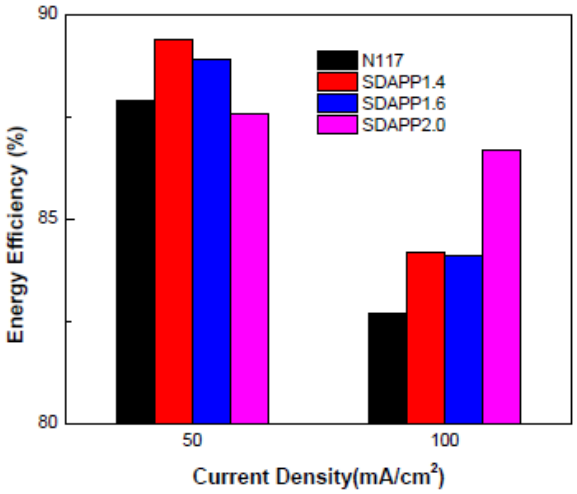


- All poly(phenylene) backbone high chemical-thermal stability
- Membranes are flexible; poly(phenylene)s [PPP] are known for being brittle
- Ease of tailoring polymer backbone [cation exchange membrane]
- Donnan Exclusion: Fixed negative charges allow positive charge to pass

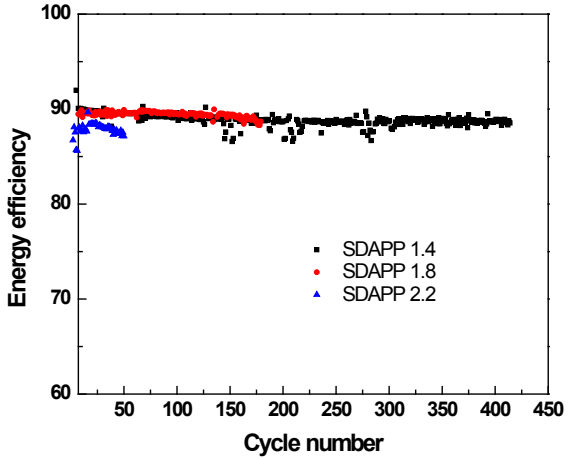
Membranes	Thickness*1 (mil)	IEC (meq/g)	Water uptake	D of V^{4+} [cm^2/min]	HFR*2 (Ωcm^2)
SDAPP 1.4	4.2	**1.4**	36%	4.4×10^{-7}	0.96
SDAPP 1.6	3.4	**1.6**	43%	8.1×10^{-7}	0.70
SDAPP 2.0	3.6	**2.0**	85%	4.3×10^{-6}	0.35
Nafion 117	7.0	0.99	35%	4.7×10^{-6}	0.84

5. C. Fujimoto, M. Hickner, C. Cornelius, D. Loy, Macromolecules, 38(12), 5010-5016, 2005

SDAPP VRFB Performance[6]



SDAPPs show slightly better EE



SDAPP1.4 shows stable EE even after +400hrs

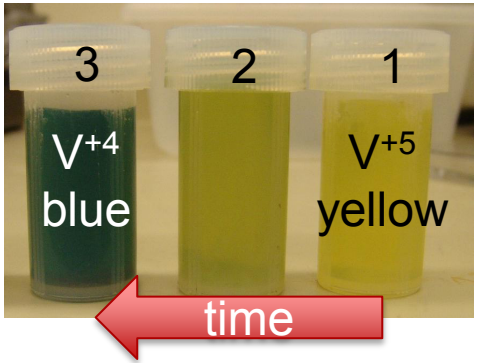
After +600 hrs SDAPP1.4 shows drop in performance

SDAPP slightly better EE than Nafion, longer cycle life than poly(arylene ether) however, +4,000 cycle lifetimes are required for VRFB

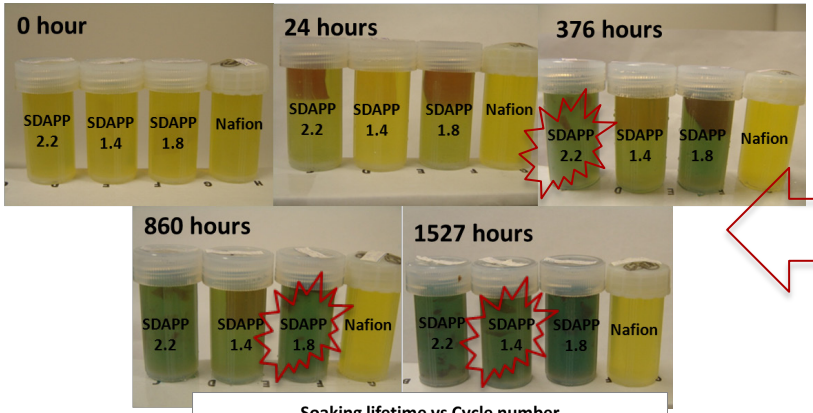
6. C. Fujimoto, S. Kim, R. Stanis, X. Wei, L. Li, Z. Yang, Electrochemistry Communications, 20, 48-51, 2012

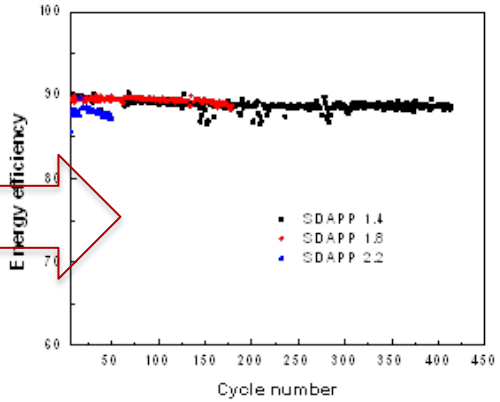
Durability Investigations

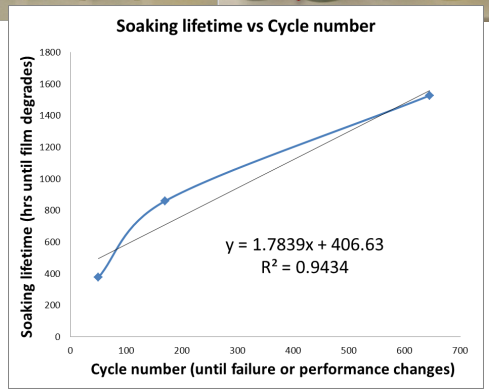
Skyllas-Kazacos used ex-situ V^{+5} soaking [0.1M] to gauge membrane lifetime



Solution: 0.1M V^{5+} + 5 M S, 40°C







Linear relationship between ex-situ in-situ data suggest that 300 days in V^{+5} may simulate 4,000 cycles; more concentrated solutions should provide shorter time windows

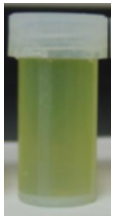
Correlations between in situ and ex situ durability studies – able to approximate soaking times that would correspond to 4,000 cycles

Conclusions:

- Collaboration between the labs has been beneficial and has helped speed up R&D
- Hydrocarbon SDAPP have shown better performances than Nafion
- Typical hydrocarbon materials have show very low cyclic lifetimes (>100 cycles), however the SDAPP have shown +400 cycles
- Improvements still need to be made to reach +4,000 cycles

Future:

- Understanding V+5 degradation mechanisms



- Mechanical
- Viscosity
- SEM

Also looking at IR and NMR, for mechanistic details

- Improving DAPP oxidative resistance for longer lasting membranes

Thank you to Dr. Imre Gyuk and the Office of Electricity for funding support.