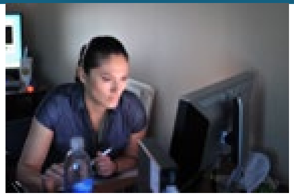
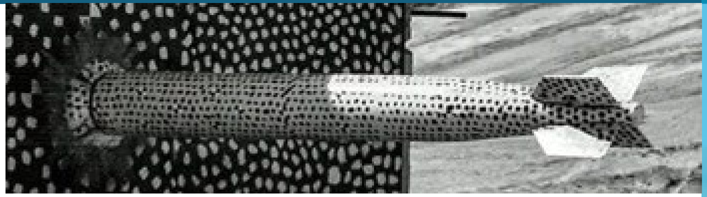
Advanced Membranes for Flow Batteries





PRESENTED BY

Cy Fujimoto

Travis Anderson and Harry Pratt @ SNL; Tom Zawodzinski @ ORNL; Vince Sprenkle and Wei Wang @ PNNL; Michael Aziz @ Harvard

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Membrane Commercialization

A start up incubator company (Energy Enablers, EE) within established Albuquerque tech firm.

SolAero TECHNOLOGIES

- SolAero looking to expand businesses portfolio / Allow EE small lab space to help facilitate pilot scale runs.
- In all, 10 formal meetings with VCs.
- VC concerns are:

    1. Difficult to compete with large industry.
    2. Material company profit margins typically small.
    3. If demand of product is lower than projected, short fuse.

Membrane Commercialization

Pacific Northwest
NATIONAL LABORATORY

Mixed acid to double vanadium concentration

UET UniEnergy Technologies

- PNNL developed chemistry/material to increase vanadium concentration, but integrated materials into a system = UET.
- Looking to couple membrane technology to a system.

Material + Integrated System = Promising start up

Membrane Commercialization

- Most popular material is our anion exchange membrane
- Recent publication surveyed several anion exchange membrane and found SNL has the highest alkaline stability

Table 3 Alkaline stability of different backbone AEMs.

Sandia membrane

Polymer backbone	Cationic group	Sample name	Test condition Conc. (M)	Temp. (°C)	Duration (h)	% σ or IEC loss	ref
Aryl ether-free polyaromatics							
DAPP	BTMA	ATMPP	4	80	1800	30 (σ)	94
	TMHA	TMAC6PP	4	80	2200	<5 (IEC)	
Poly(fluorene)	TMHA	PFBFF	1	80	720	<5 (IEC)	41
Ni-catalyzed poly(phenylene)	BTMA	QPAF-TMA	1	80	1000	95 (σ)	45
	DMBA	QPAF-DMBA	1	80	500	<5 (σ)	
	TMHA	QPAF-4	1	80	1000	<5 (σ)	47
	Imidazolium	PPMB	2	80	168	5 (IEC)	48
Acid-catalyzed poly(phenylene)	TMPA	BPN1-100	1	95	1440	8 (IEC)	95
	TMPA	*m*-TPN1	1	95	1440	<5 (IEC)	
	Piperidinium	PTPipQ1	2	90	700	5 (IEC)	58
	Piperidinium	PTPipQ8	2	90	700	70 (IEC)	
	Piperidinium	QAPPT	1	80	210	5 (IEC)	59
			10	80	240	33 (IEC)	
Spiro-ionene	*N*-spirocyclic QA	Spiro-ionene **2**	1	80	1896	<5 (IEC)	68
Poly(arylene imidazolium)	Imidazolium	HMT-PMPI	10	100	168	<5 (IEC)	76
Aryl ether-containing polyaromatics							
Partially fluorinated poly(arylene ether)	BTMA	QPE-bl-9	1	80	500	97 (σ)	61
Poly(arylene ether ketone)	BTMA	QPAEK-x	4	rt	168	17 (σ)	96
Poly(arylene ether sulfone ketone)	BTMA	QPE-bl-11	1	60	1000	66 (IEC)	97
Poly(ether sulfone)	BTMA	B-110-PSU-NMe$_3$-OH	1	50	6	39 (IEC)	64
	TMHA	PES-6-QA	1	60	720	12 (σ)	23
Poly(fluorene sulfone)	Imidazolium	AEM	1	60	400	6 (σ)	98
Poly(arylene ether sulfone nitrile)	Imidazolium	ImPESN-19-22	2	60	600	67 (σ)	84
Poly(phenylene oxide)	Multication	T20NC6NC5N	1	80	500	10 (σ)	99
	TMHA	50PPOC6NC6	1	80	1000	7 (σ)	85
	Piperidinium	PPO-7bisQPi-1.7	1	90	192	9 (σ)	100
Polyolefins							
Poly(ethylene)	Imidazolium	AAEM-2					
Poly(propylene)							

Ranked No#1 in stability among all alkaline membrane developed from a recent review paper

J. Mater. Chem. A, 6, 15456-15477 (2018)

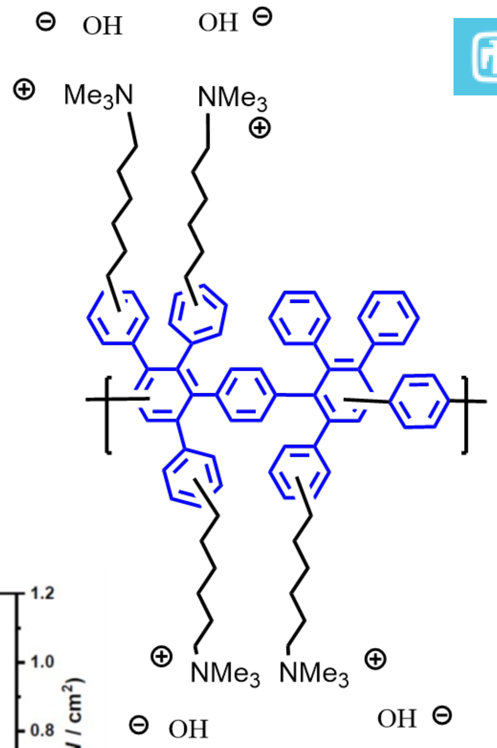
Alkaline electrochemical devices can now be further explored:

Potential application areas

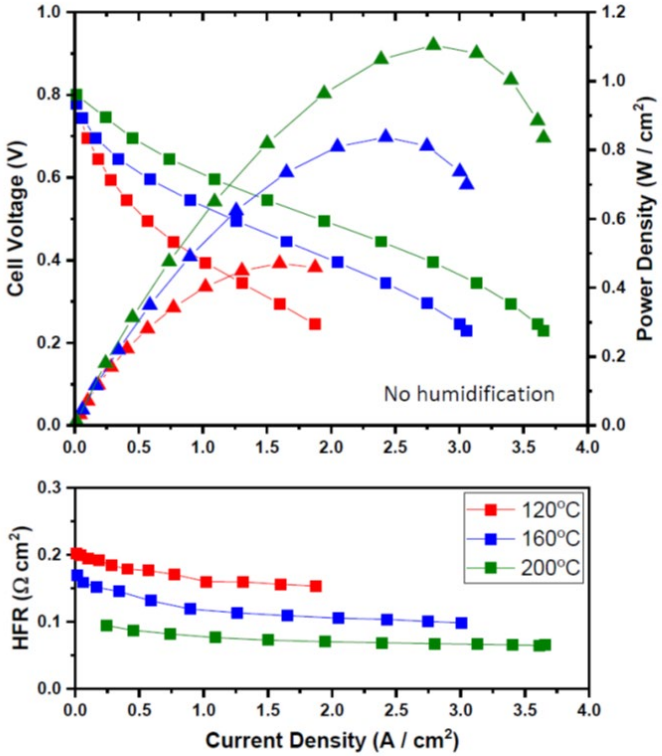
1. Bipolar membrane dialysis* – Waste water treatment
2. Alkaline redox flow battery – Energy storage
3. Alkaline membrane fuel cells – Energy conversion
4. High-temperature membrane fuel cells – Energy conversion
5. Alkaline based water electrolyzers – Energy production
6. Metal-air batteries – Energy storage
7. Super capacitors – Energy storage
8. Electrochemical ammonia synthesis – Energy production

Membrane Commercialization

- High conductivity and durable.
- Would be BIG win if could couple anion exchange membrane/ASOFB…..
- "Game changing" application may have been developed by LANL with intermediate temperature FC employing SNL anion exchange membrane.
- FC operates with no water.

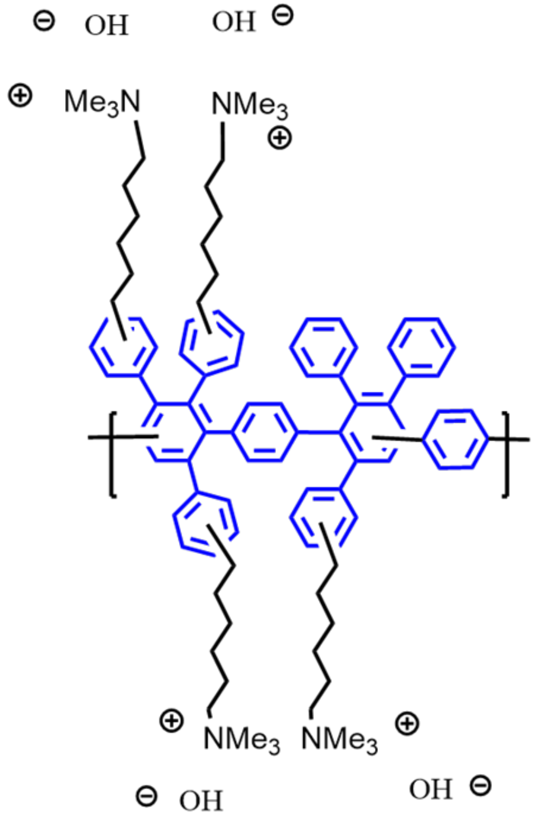


LANL and SNL is currently discussing a path forward to package lab IP

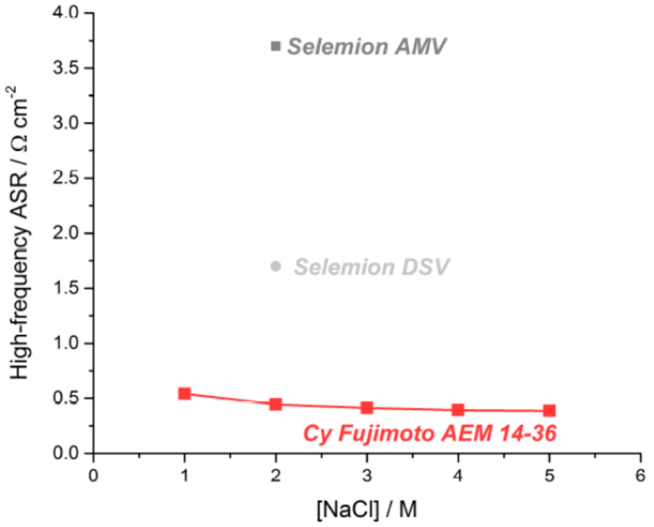


Aqueous Soluble Organic FB

- Slight pivot this year to focus on membranes for ASOFB than VRFB.
- ASOFB there is a need for new materials (electrolyte, membrane, electrochemical species, etc.).
- Capture multiple applications employing our anion exchange membrane.

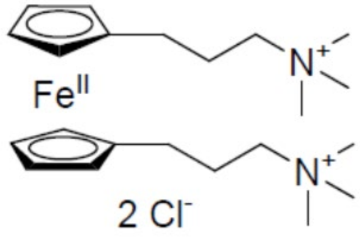


SNL = Low resistance



SNL 3.5 x lower resistance than Selemion DSV

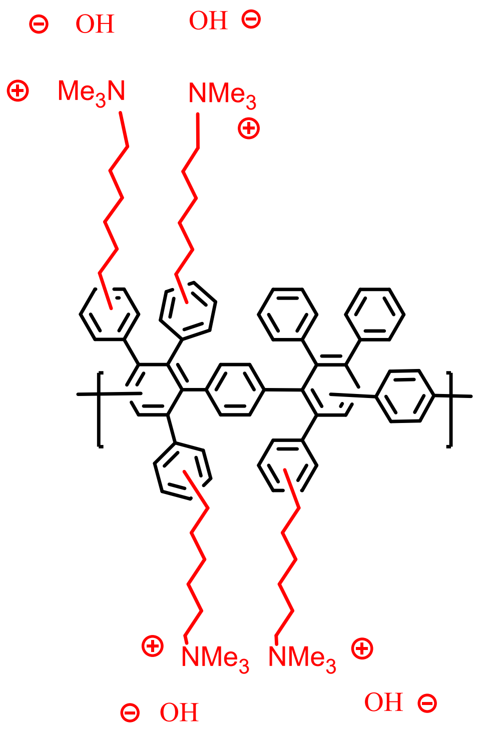
SNL = Low selectivity



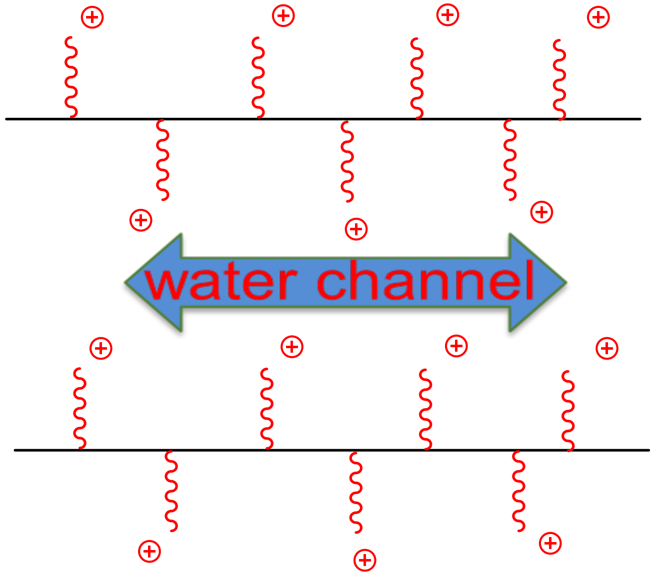
Target $1x10^{-10}$ cm^2/s
SNL 6 x 10^{-9} cm^2/s
Selemion DVS $1x10^{-12}$ cm^2/s

Unpublished work from Dr. Aziz labs

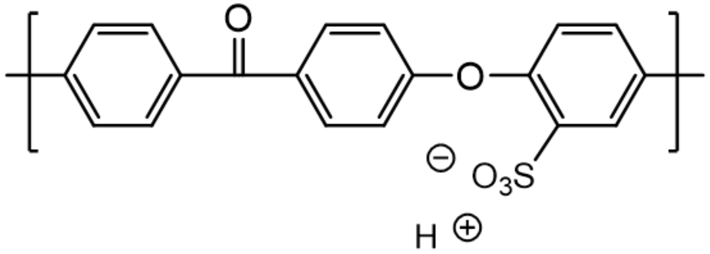
Aqueous Soluble Organic FB Concept



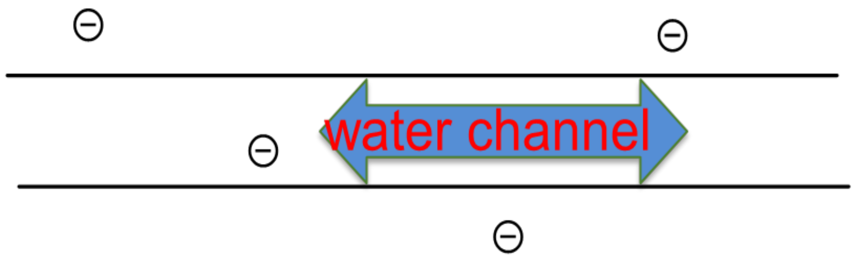
In membrane polymer chains will stack



Due to bulky backbone/substituents, large chain to chain distance = larger hydrophilic domain high ion cross over



SPEEK



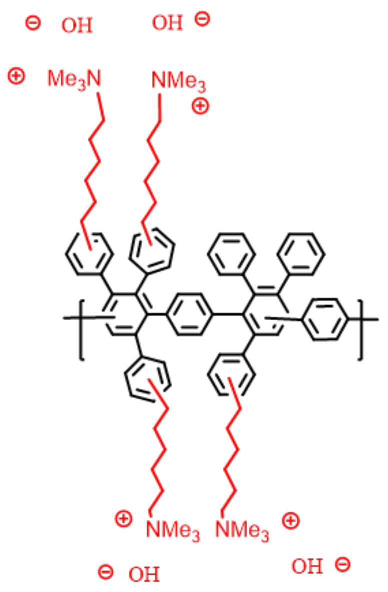
Less bulky backbone and backbone attached ionic group = smaller hydrophilic domain low ion cross over

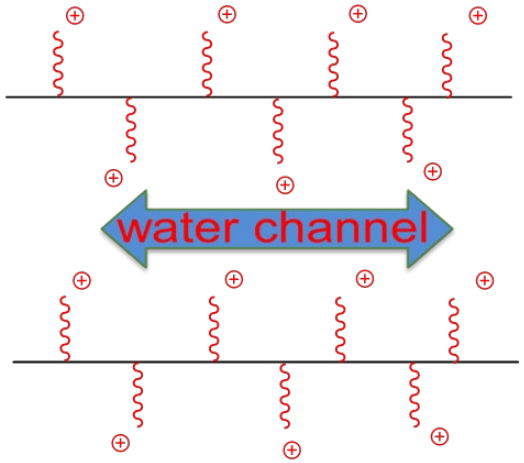
Aziz, M., et al. J. Electrochem. Soc., 165 (5), 2018, A1137-A1139

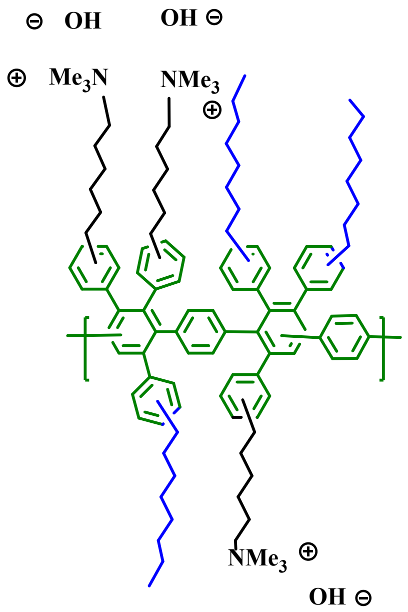
Membrane	ASR (Ω cm^2)	Permeability Fe(CN)6 cm^2/s
SPEEK	0.51	5.3×10^{-12}
Nafion	0.75	4.5×10^{-9}

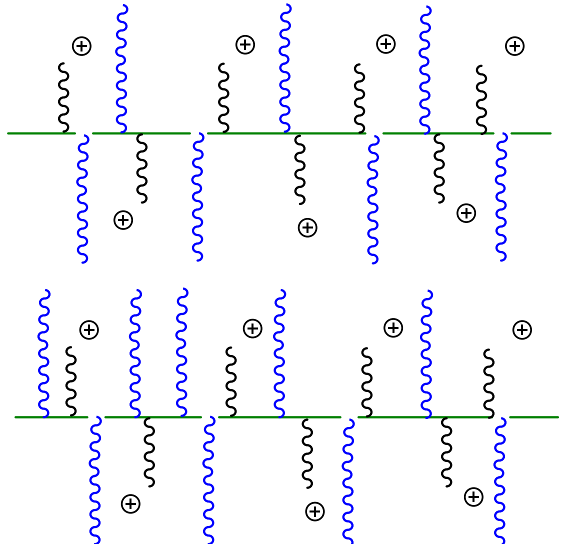
Aqueous Soluble Organic FB Concept

To improve membrane selectivity goal: Incorporate non conducting functional groups around ionic moieties to control water channel size.

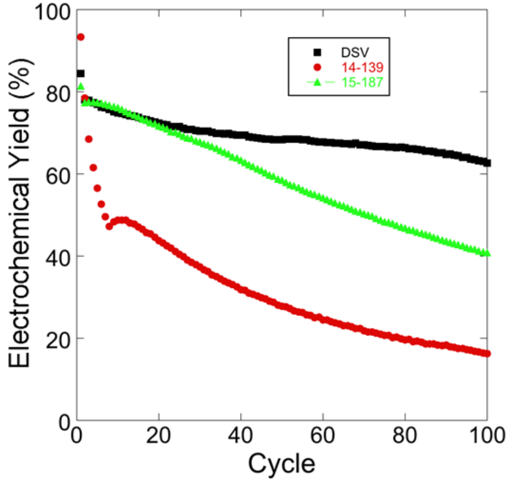






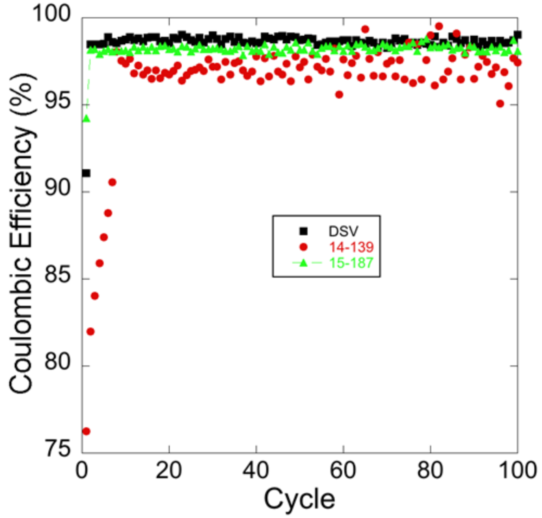


0.5 M methyl viologen
0.5 M HO-TEMPO
1.5 M NaCl



ASR in 1.5 M NaCl

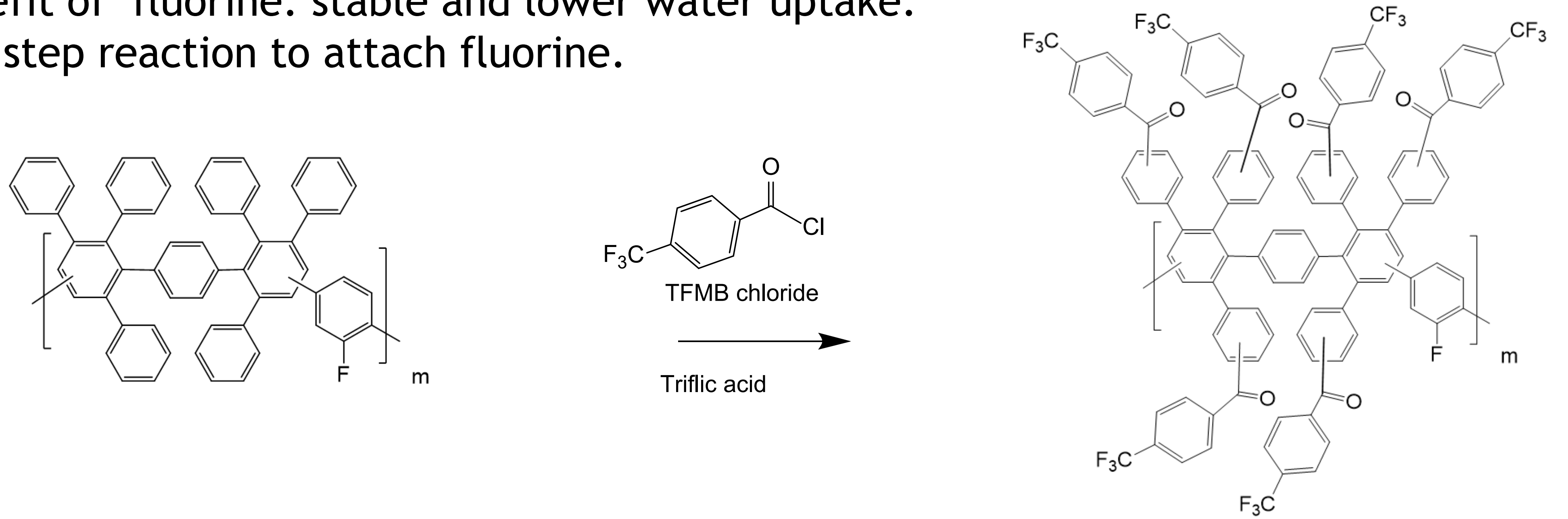
0.6 Ω cm^2
1.1 Ω cm^2
1.7 Ω cm^2



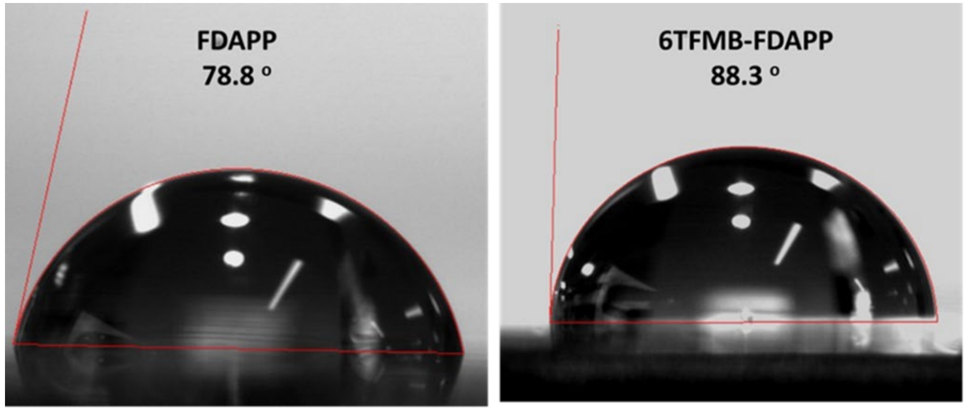
Concept works, now looking at varying length of ion containing tether

VRFB Membranes – Membrane Development

- Developing Nafion-like materials by attaching fluorine containing groups.
- Benefit of fluorine: stable and lower water uptake.
- One step reaction to attach fluorine.



Water contact angle measurements of substituted CF_3 polymer has reduced surface energy and increased water contact angles = higher degree of hydrophobicity.



Submitted publication to Polymer journal.

Summary/Conclusions

- Commercialization efforts – Materials or System?
- Anion exchange membranes need to be modified for improved flow battery performance – have concept shows promise.
- Developing fluorinated poly(phenylene)s for VRFB
- Three issued patents and one patent application

Future Tasks

- Membrane commercialization
- Battery testing of new polymer architectures (Travis/Harry), send to collaborators.

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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