This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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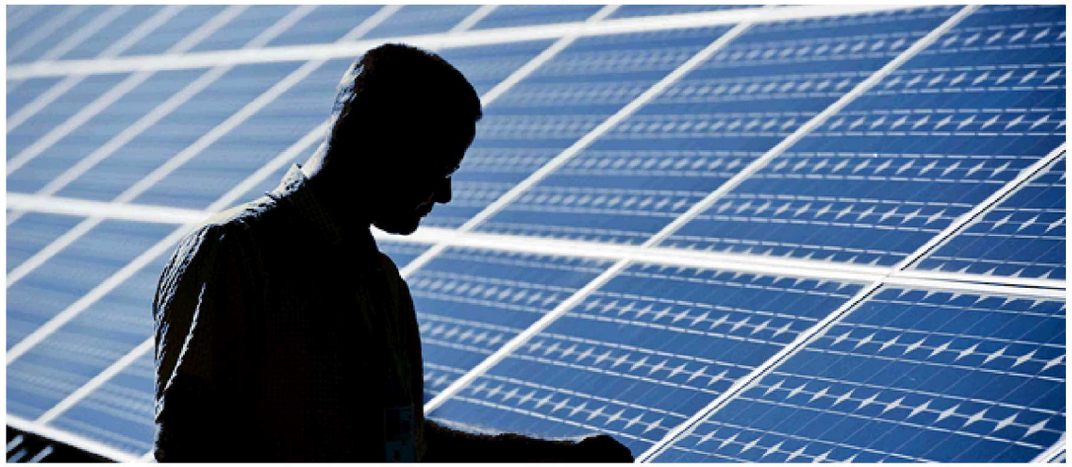

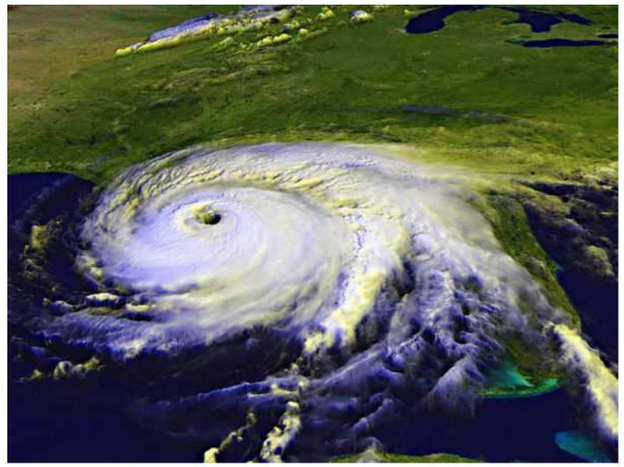

Advanced Membranes for Flow Batteries

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

Proceeding through a start up incubator within Albuquerque company

- Nearly 2 years trying to get a materials start-up running (Energy Enablers)
- Energy Enablers negotiated licenses of two membrane products, an cation and anion exchange membranes.
- In all, 10 formal meetings with VCs.
- VC concerns are:
    1. Difficult to compete with large industry
    2. Materials company profit margins typically small
    3. Small changes in demand of product may lead to dramatic consequences

Membrane Commercialization

Pacific Northwest NATIONAL LABORATORY

Mixed acid to increase vanadium solubility

UniEnergy Technologies

- PNNL developed chemistries to increase vanadium concentration, but UET is producing systems
- 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 suggests SNL anion exchange membrane 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)	Test condition 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)	
	DMBA	QPAF-DMBA	1	80	500	<5 (σ)	45
	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)**

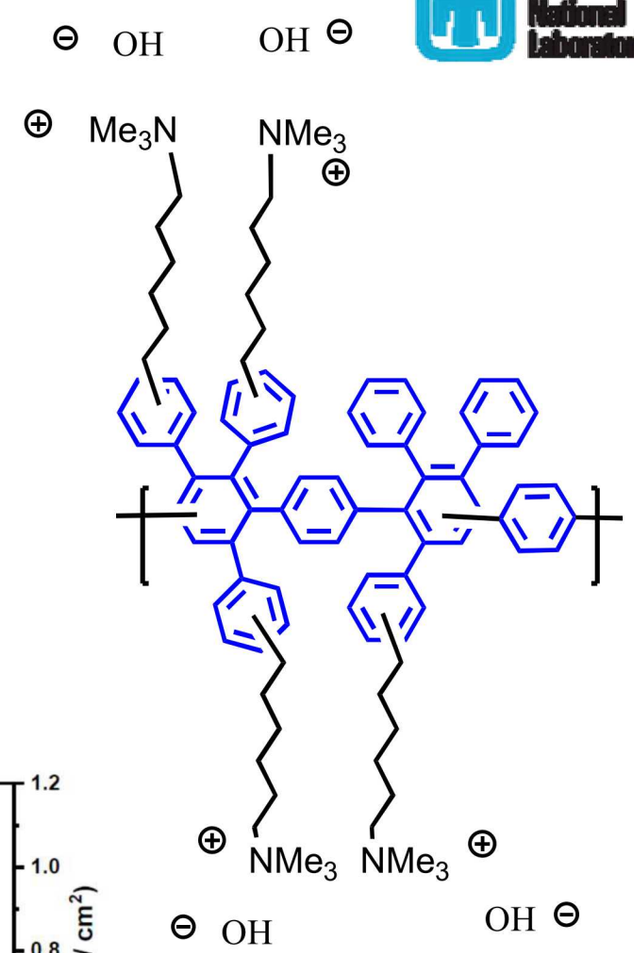
That means we can make alkaline electrochemical devices can now be further explored.

Possible application area

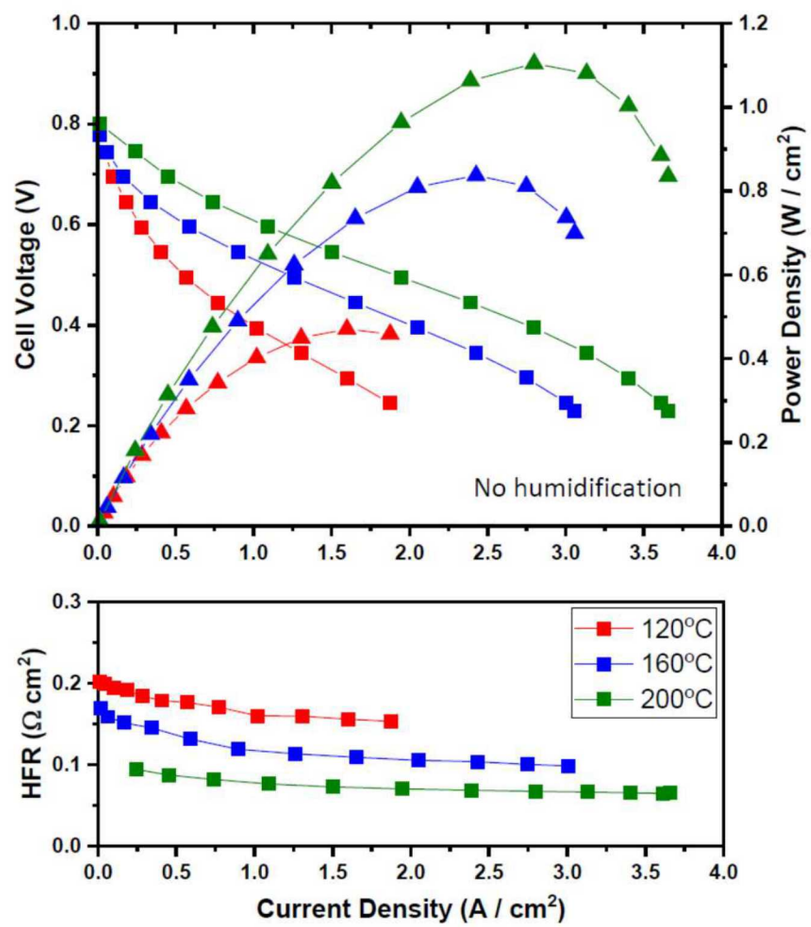
1) Bipolar membrane dialysis* – Waste water treatment
2) Alkaline redox flow battery – Energy storage
3) Alkaline membrane fuel cells – Energy conversion
4) High-temperature membrane fuel cells – Energy conversion
5) Alkaline based water electrolyzers – Energy production
6) Metal-air batteries – Energy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

Membrane Commercialization

- High conductivity, durable and high Tg
- "Game changing" application may have been developed by LANL with high temperature FC employing SNL anion exchange membrane
- High temperature FC performance no water

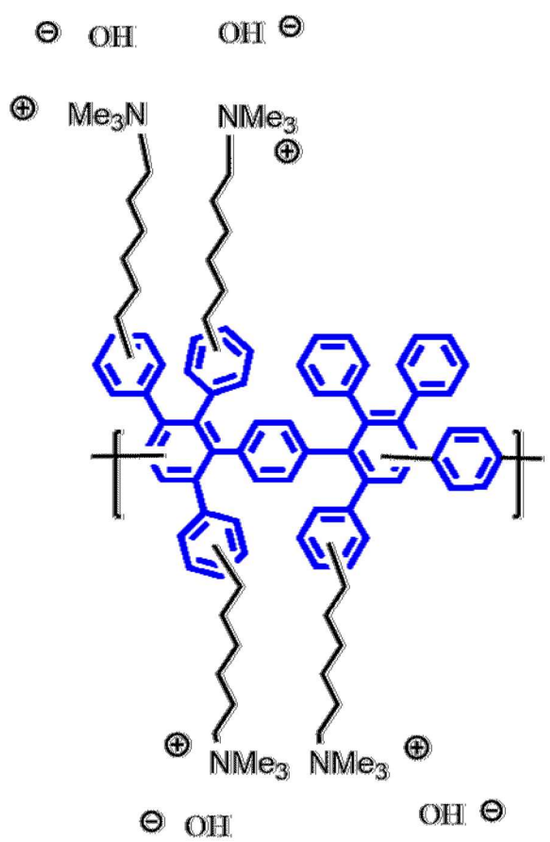


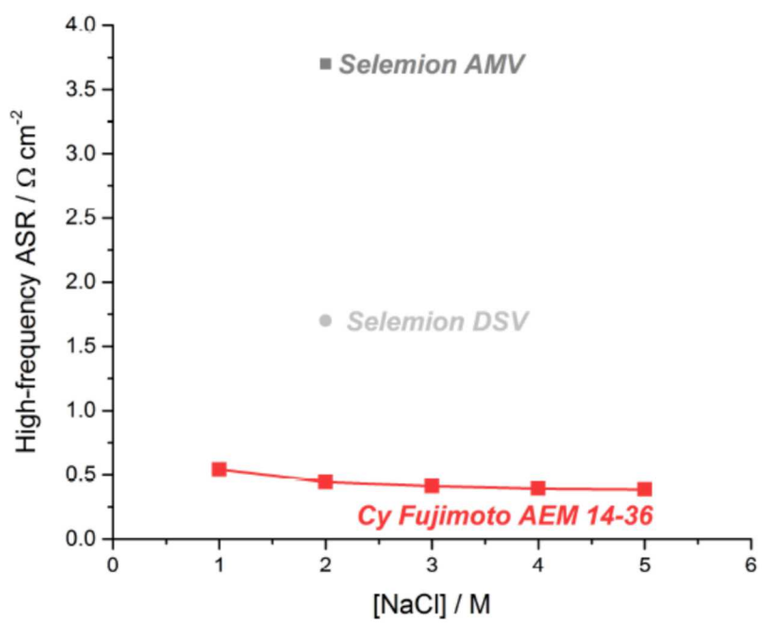
LANL and SNL is currently discussing a path forward to package lab IP



Aqueous Soluble Organic FB

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

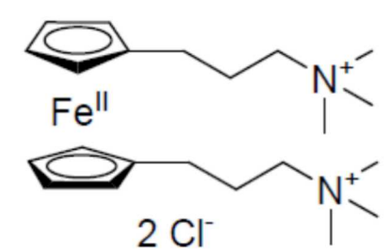




SNL 3.5 x lower resistance than Selemion DSV

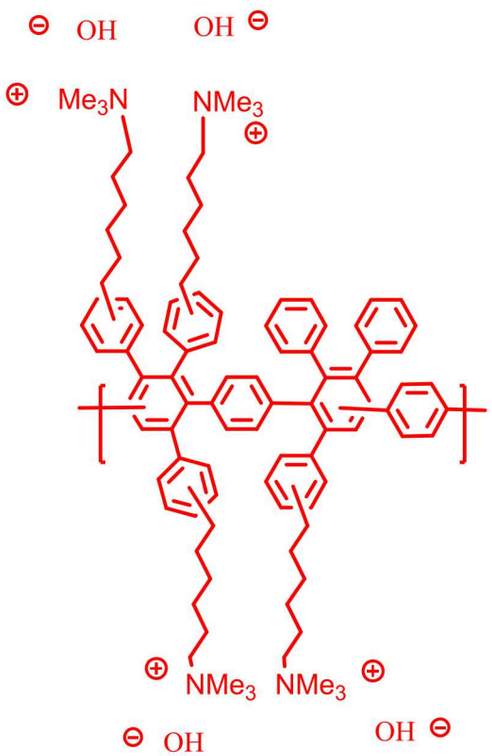
But….

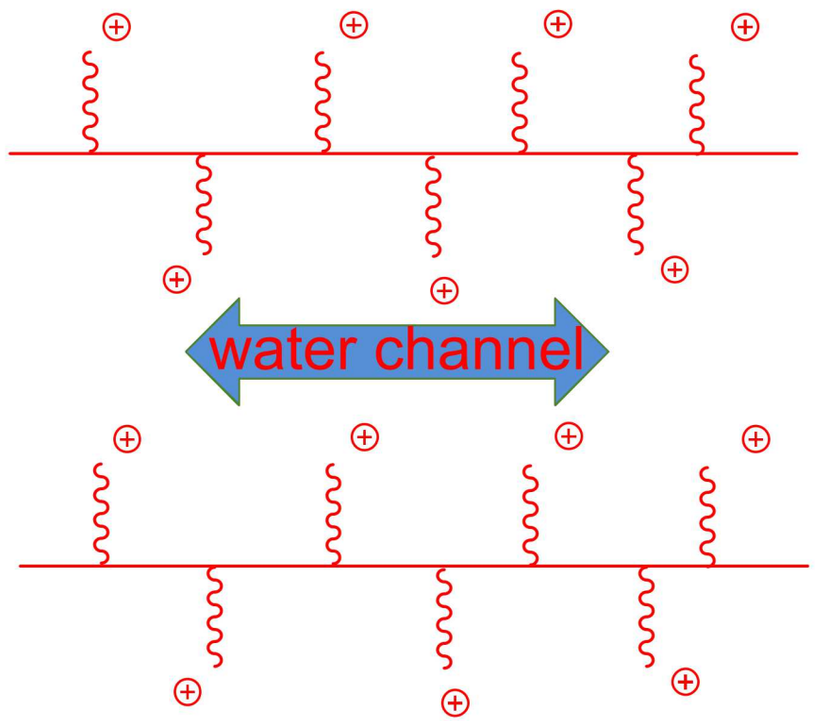
Cross-over issues



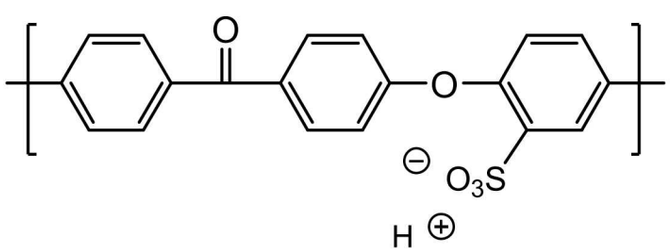
Target 1×10^{-10} cm^2/s
SNL 6×10^{-9} cm^2/s
Selemion DVS 1×10^{-12} cm^2/s

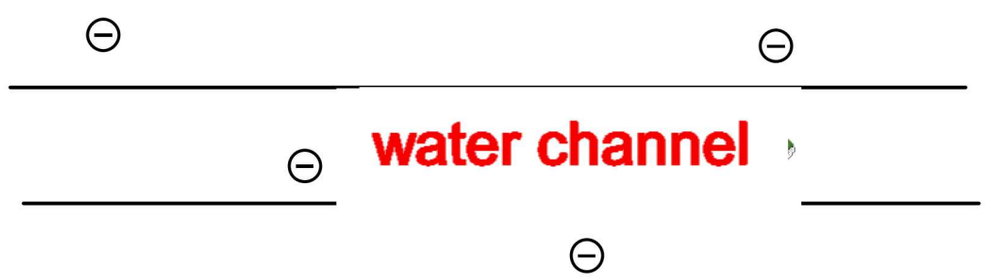
Aqueous Soluble Organic FB Concept





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





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

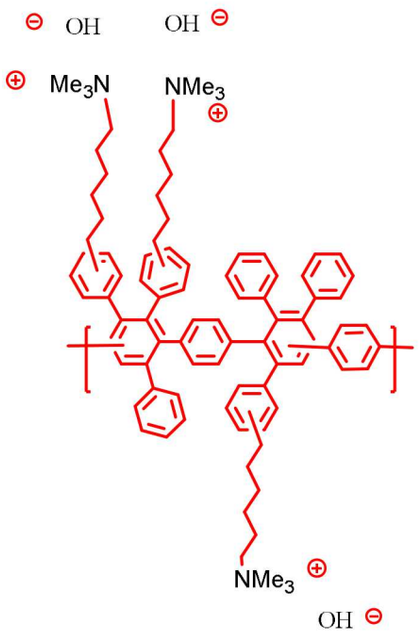
SPEEK

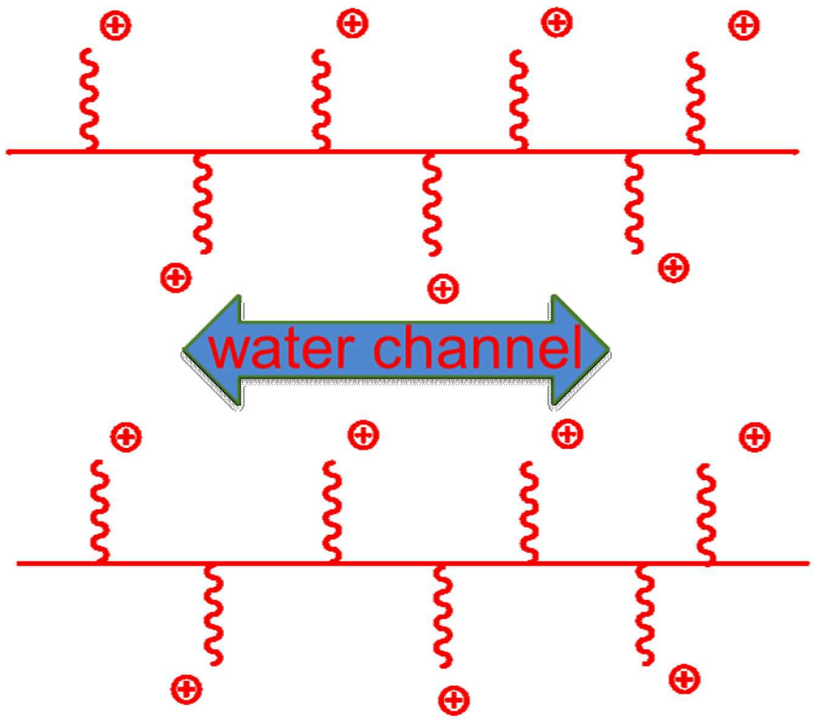
Aziz, M., et al. J. Electrochem. Soc., 165 (5), **2018**, A1137-A1139

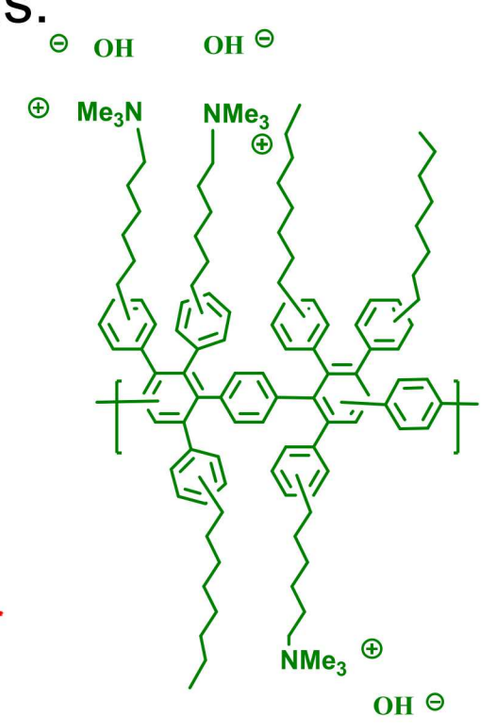
Membrane	ASR (Ω cm^2)	Permeability Fe(CN)6 cm^2/s
SPEEK	0.51	5.3×10^{-12}
Nafion	0.75	4.5×10^{-9}

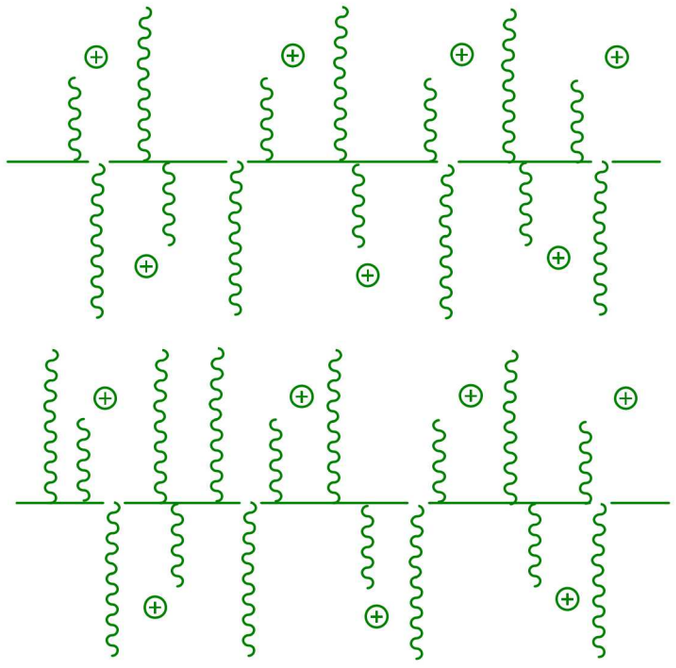
Aqueous Soluble Organic FB Concept

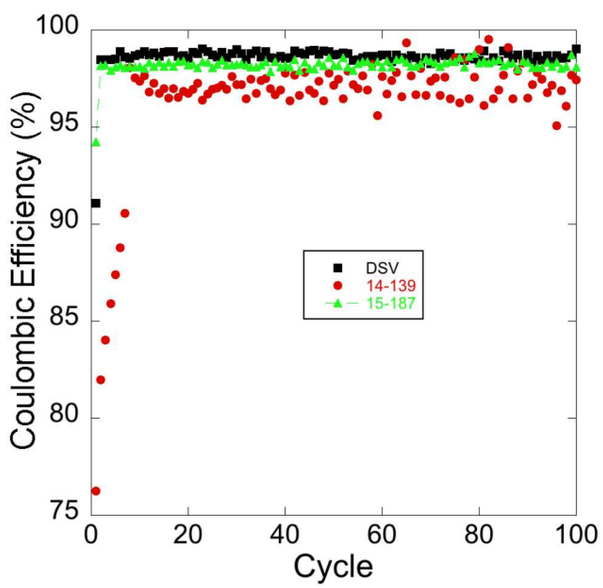
To improve membrane selectivity goal: Crowd the ionic units with non conducting groups that will sterically block transport of larger ions.

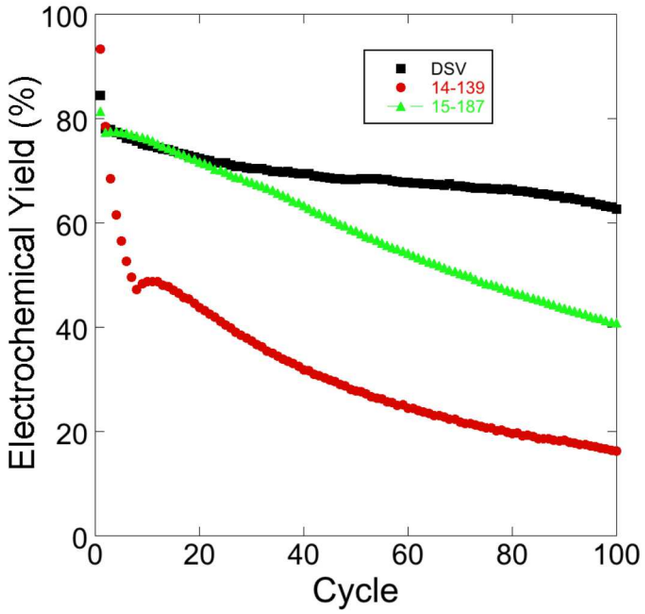










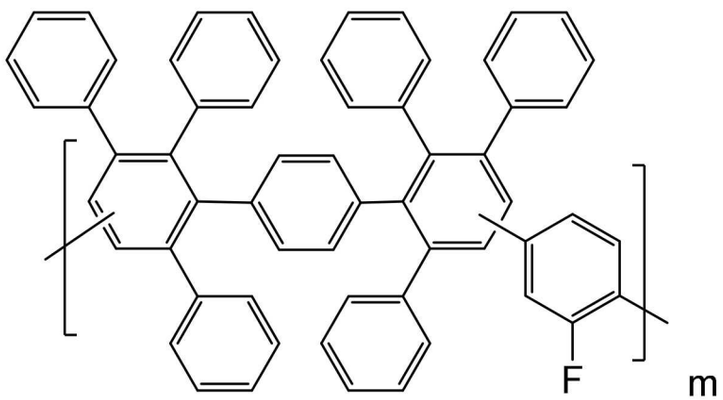


This concept of crowding substituents around ionic group show promising results thus far.

- US Patent: 10,053,534 Functionalization of Diels Alder Poly(phenylene) polymers
- US Patent: 15/911,641 Halo-Containing Anion Exchange Membranes and Methods Thereof

VRFB Membranes – Membrane Development

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



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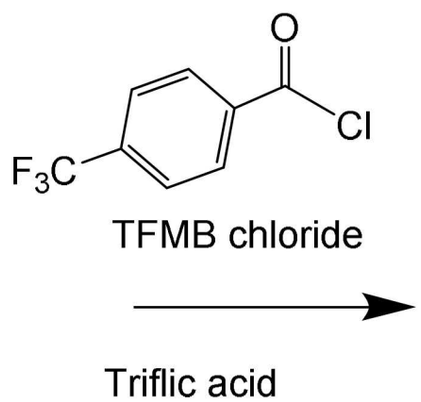

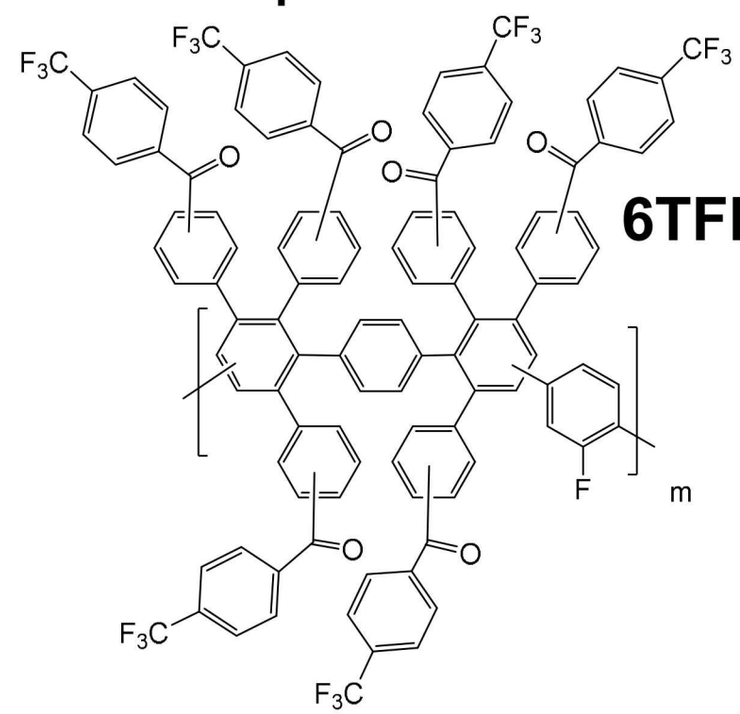

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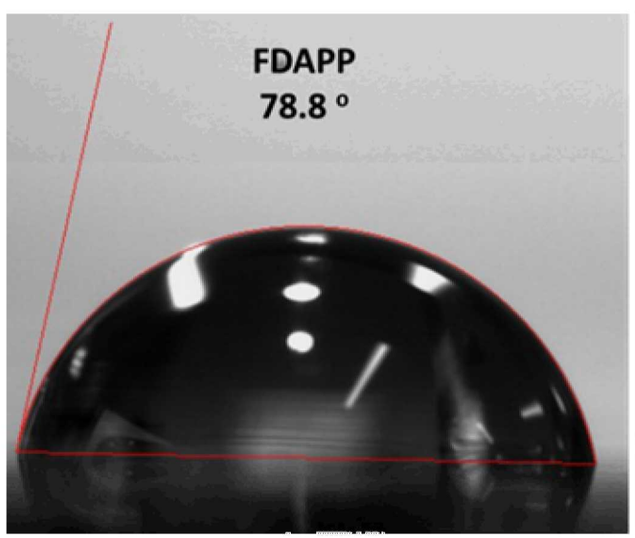

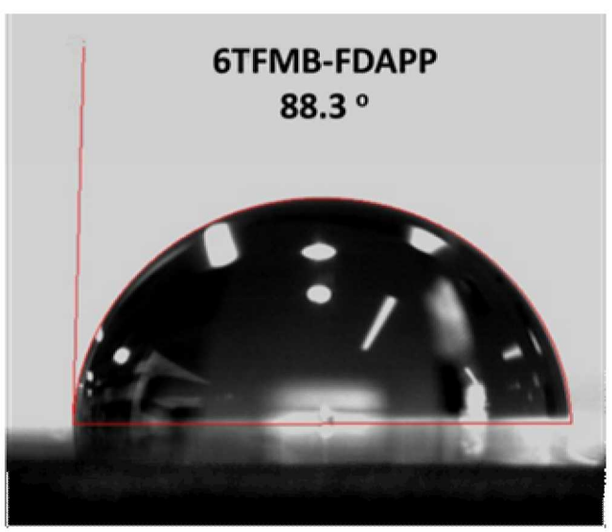

Submitted paper

Summary/Conclusions

- Anion exchange membranes have been getting attention due to good performance and durability.
- Commercialization efforts - partner with LANL to push system rather than solely materials.
- Anion exchange membranes need to be modified for improved flow battery performance – have concept show promise.
- Developing fluorinated poly(phenylene)s for VRFB

Future Tasks

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

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?

chfujim@sandia.gov