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Title: Ion Exchange Membranes Non-aqueous Redox Flow Batteries: Membrane Status

Author(s): Maurya, Sandipkumar
Fujimoto, Cy

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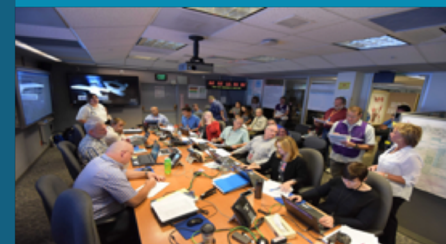
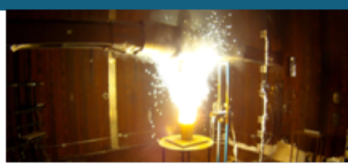
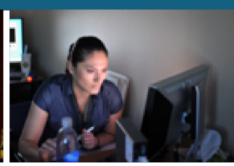
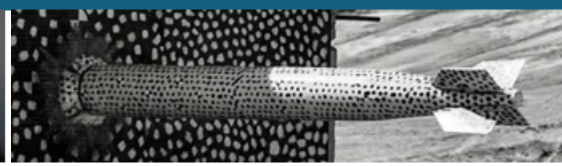
Issued: 2019-02-14

Ion Exchange Membranes









PRESENTED BY

Cy Fujimoto (SNL) and Sandip Maurya (LANL)

Sandia National Laboratories

Los Alamos NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

NNSA

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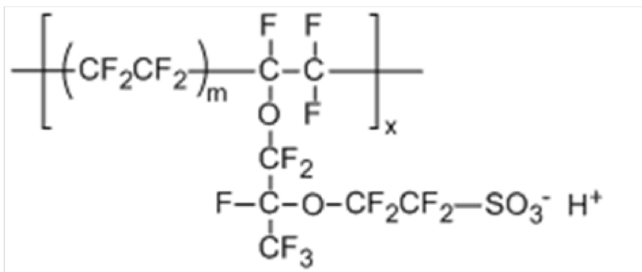
What are ion exchange membranes?

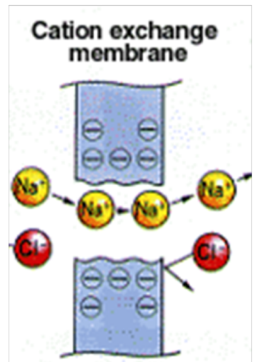
1. **Two types of fixed ions (tethered negative or positive charge)**

State of the art

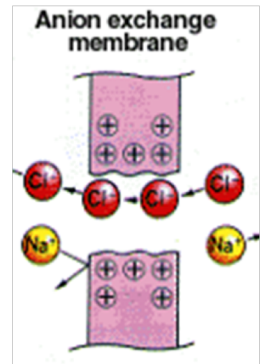


PFSA (has fixed SO_3^-)

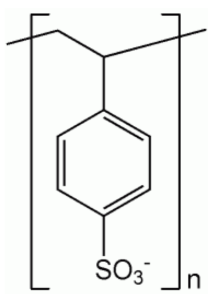
Acidic (H^+)

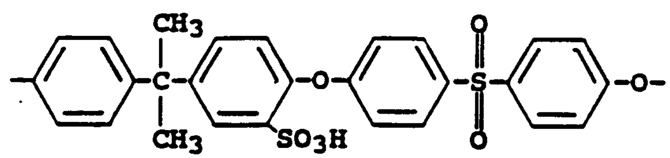


Alkaline (HO^-)



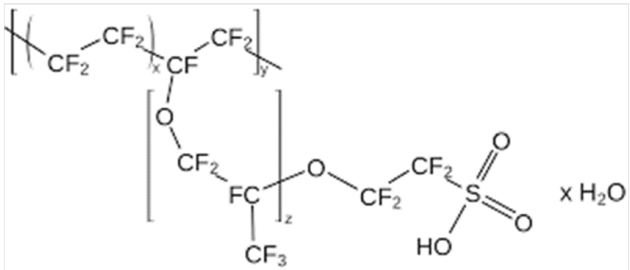
2. **Different types of polymer backbones**





Backbone stability important for electrochemical cell durability

State of the art - Cation exchange membrane



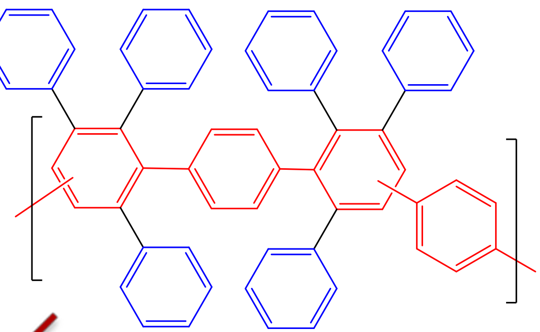
Perfluorosulfonic acid membranes (PFSA)s

Company	Product type	Trade name
DuPont now Chemours	Perfluorosulfonic acid membrane	Nafion
Asahi Chemical	Perfluorosulfonic acid membrane	Aciplex
Asahi Glass	Perfluorosulfonic acid membrane	Flemion
3M	Perfluorosulfonic acid membrane	3M MEA
Fumatech	Perfluorosulfonic acid	F-series
Gore	Reinforced perfluorosulfonic acid membrane	GoreSelect
DSM Solutech	Reinforced perfluorosulfonic acid membrane	Solupor

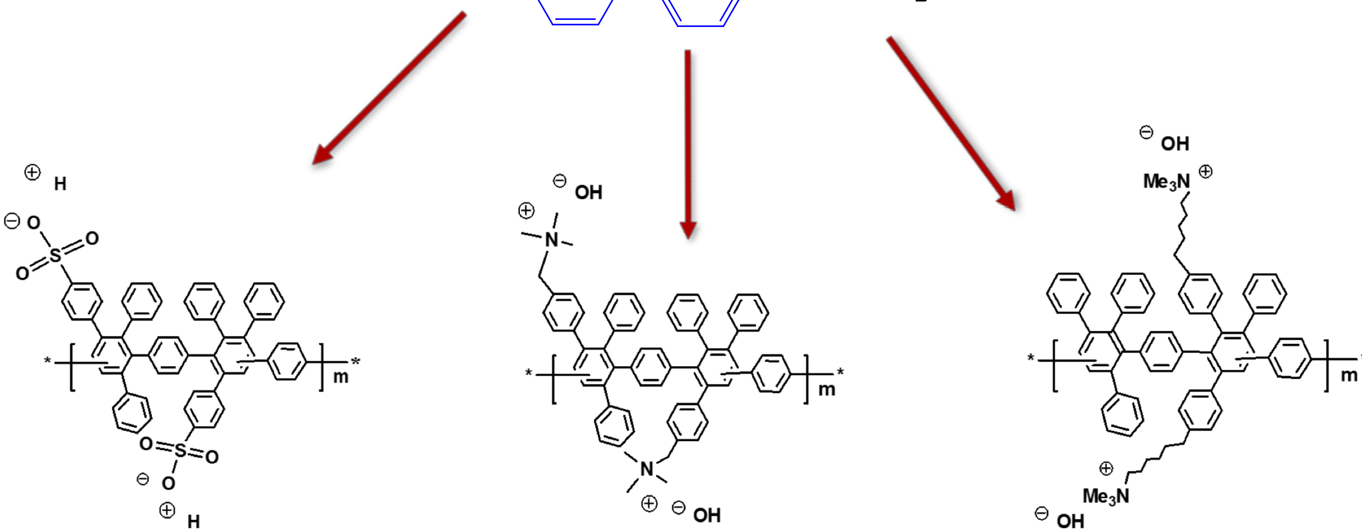
- Various suppliers for perfluorosulfonic acid membranes (PFSA)s
- Primary application chloro-alkali industry
- High cost \$250-500/m^2 associated to high capital costs

Sandia’s Ion Exchange Membranes

At SNL our platform is a poly(phenylene) backbone that can readily functionalize with various ionic groups.



DAPP = Diels Alder Poly(phenylene)



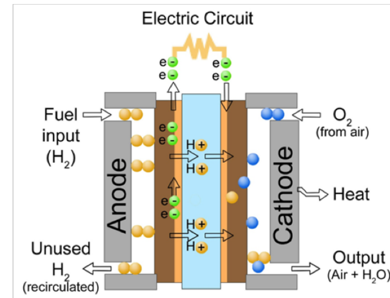
SDAPP

US Patent 7,301,002

US Patent 7,888,397

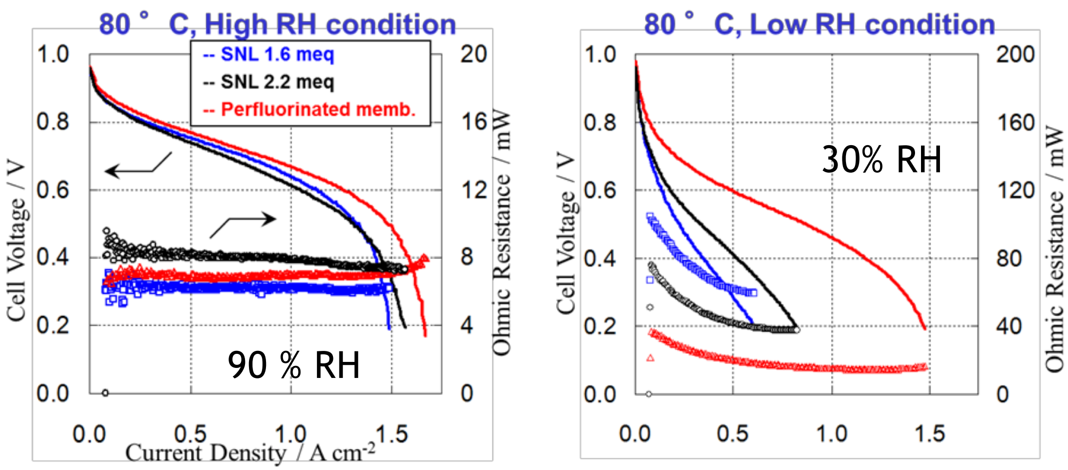
US Patent 8,809,483

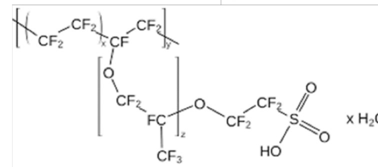
PEM Fuel Cell - Cation Exchange Membrane



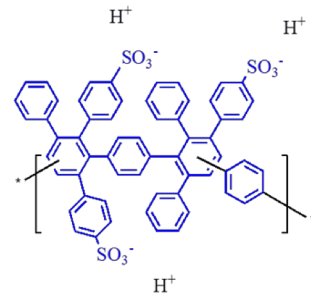
- **Challenge of membranes in PEMFC is maintaining high proton conductivities at both high and low RH.**
- **PFSAs have best performance and durability**

2004 WFO with Toyota Motor Company

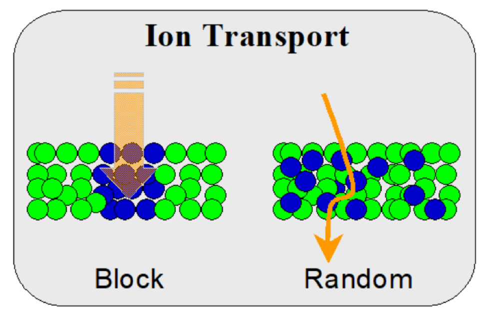




Nafion

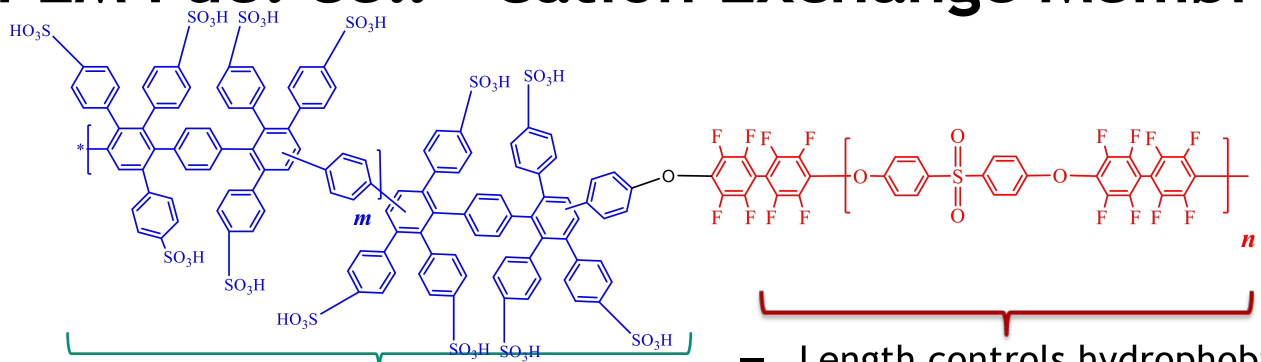


SNL



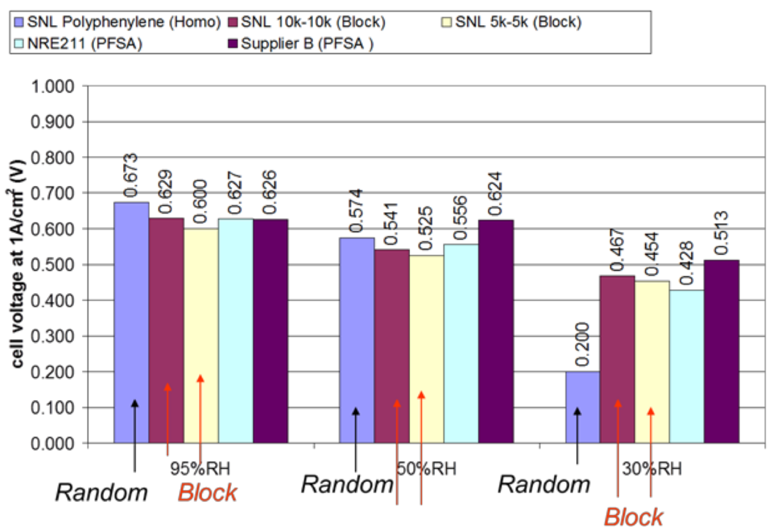
Post sulfonated polymers acid groups are distributed randomly in the polymer backbone and resulting hydrophilic domain is disorganized.
To improve performance at low RH investigate block co-polymers

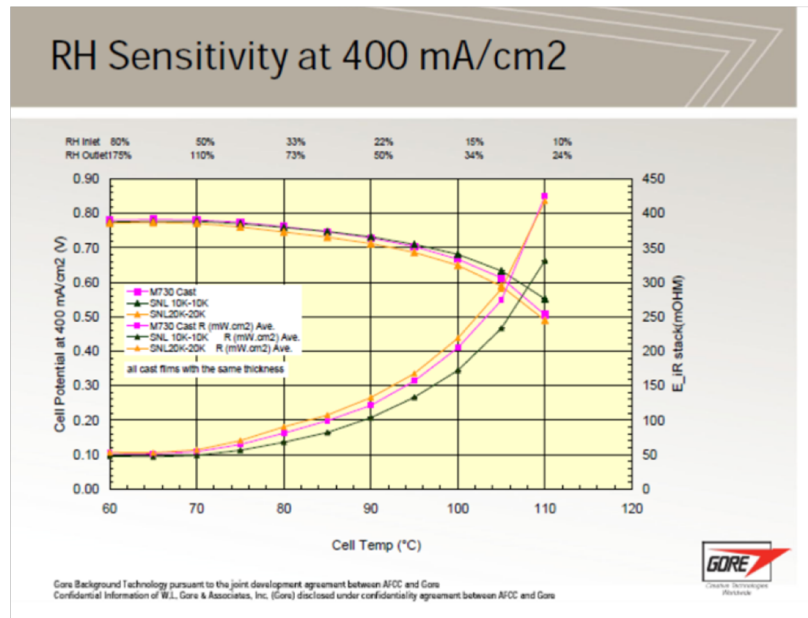
PEM Fuel Cell - Cation Exchange Membrane



Length controls hydrophilic domain size = Length controls hydrophobic domain size

Hydrophilic / Hydrophobic segments length the same

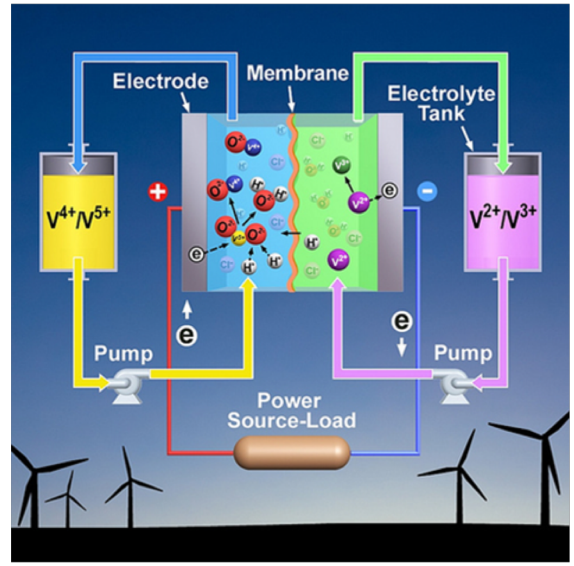




Industrial testing showed SNL block performance equivalent to PFSA

Vanadium Redox Flow Batteries (VRFB)

- Separation of energy and power.
- Several US companies looking to commercialize this technology.
- Multiple demonstration projects in the US and abroad.



UniEnergy Technologies

WattJoule

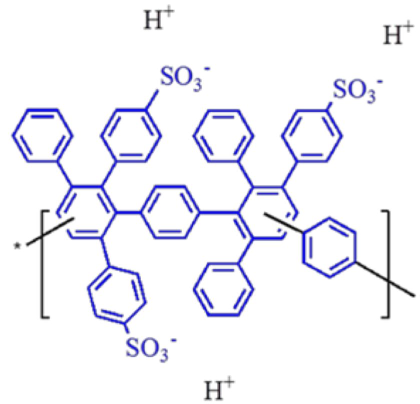
VIONX ENERGY

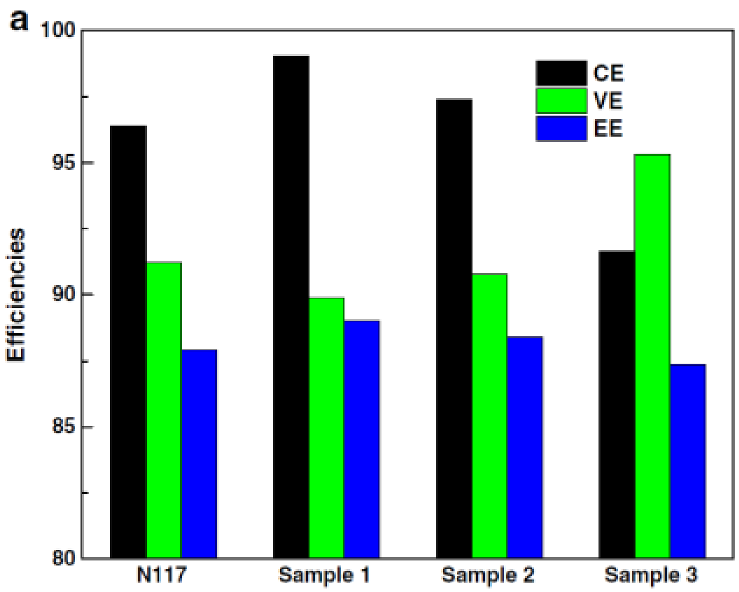
According to a CEO of a VRFB company, membranes account for 1/3 of the overall system cost

VRFB - Cation Exchange Membrane

Post sulfonated polymer:

- Performance equivalent to PFSAs
- Capacity fade equivalent to PFSAs
- Durability, after 179 cycles oxidation of film



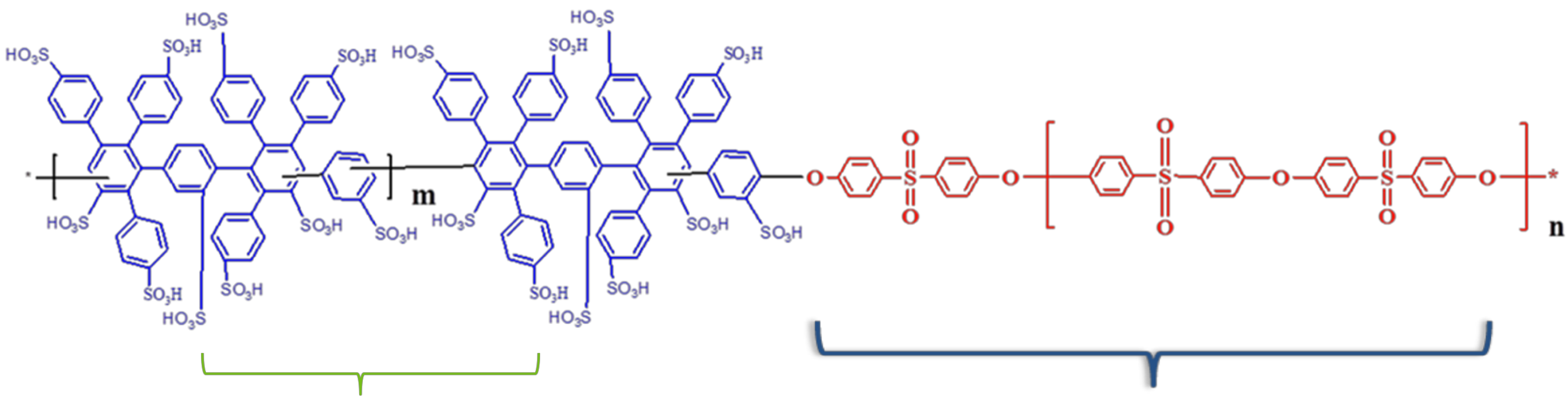


SDAPP1.6
179 cycles (27d)

Very brittle

Post sulfonated poly(phenylene) had capacity fade and durability issues

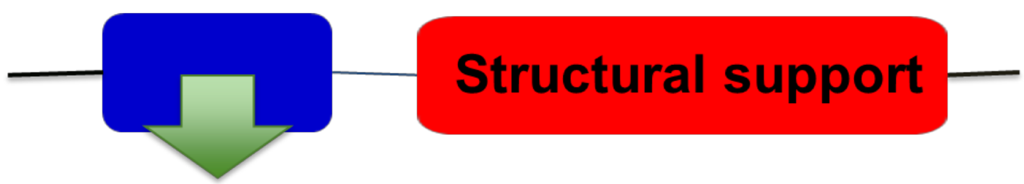
VRFB - Cation Exchange Membrane



Hydrophilic segment
Controls ions and water flow

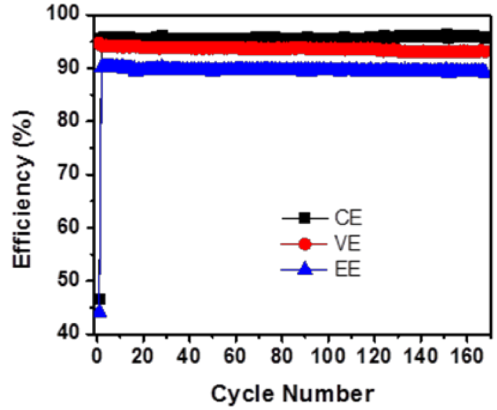
<

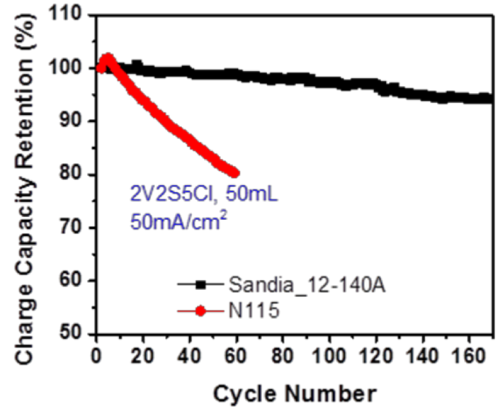
Hydrophobic segment
Mechanical support



Ions and water transport

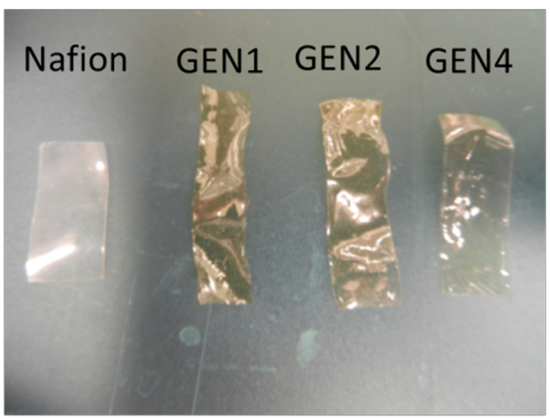
VRFB – Cation Exchange Membrane



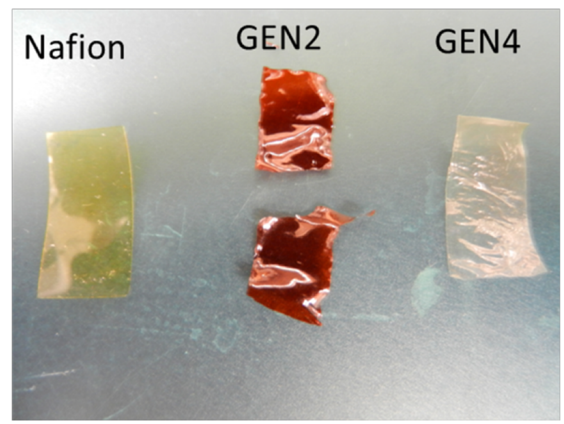


Data by PNNL, SNL membrane has high efficiencies (90% EE, PFSA 75%) and high capacity retention; PFSA 75% EE

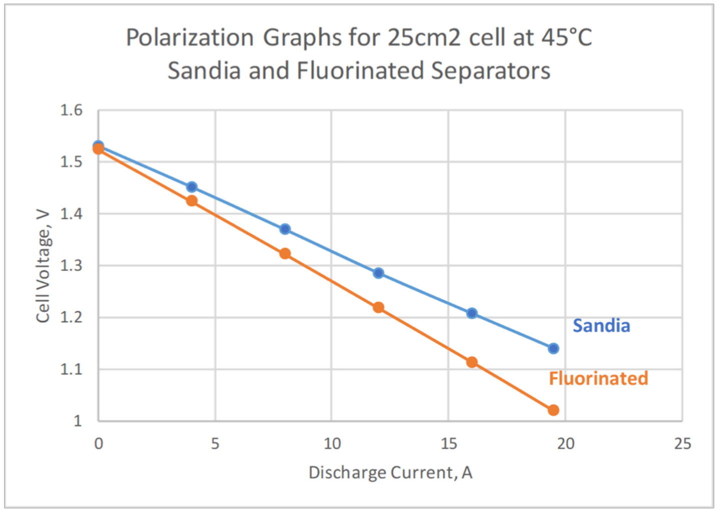
Block also had much better durability in contact with V^{+5}!



One week in 1.5 M V^{+5}



VRFB - Cation Exchange Membrane



Membrane	Efficiency, Round Trip	Efficiency, Coulombic	Efficiency, Voltaic
Sandia	82.2%	96.2%	85.4%
Fluorinated	72.3%	92.5%	78.2%

Cycling Performance Comparison in 25-cm^2 cell at 45°C
Sandia and Fluorinated Membranes
WattJoule Electrolyte (2M Vanadium)

	Pmax, mW/cm^2	Specific Resistance, Ωcm^2
Sandia	1159	0.505
Fluorinated	946	0.610

Data from WattJoule shows block has higher energy efficiency (+10%).
High coulombic efficiency.

Anion Exchange Membrane

- Unlike cation exchange membranes, which has an established SOA (PFSAs) there is no agreement on a alkaline stable, anion exchange membrane.
- There is a large interest in alkaline electrochemical systems (non precious metal catalysts, faster redox reaction kinetics).

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-[illegible]					
Poly(propylene)	[illegible]						

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

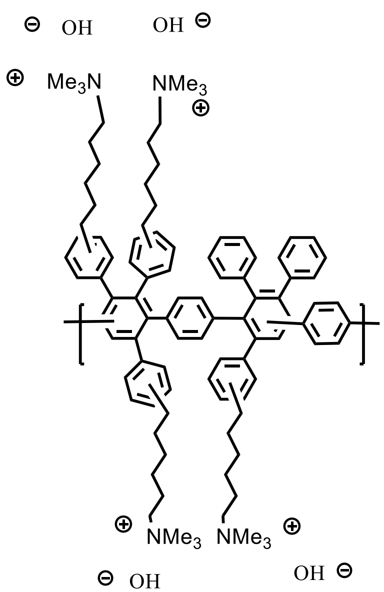
J. Mater. Chem. A, **6**, 15456-15477 (2018)

Recent publication surveyed several anion exchange membrane and found SNL has the highest alkaline stability.

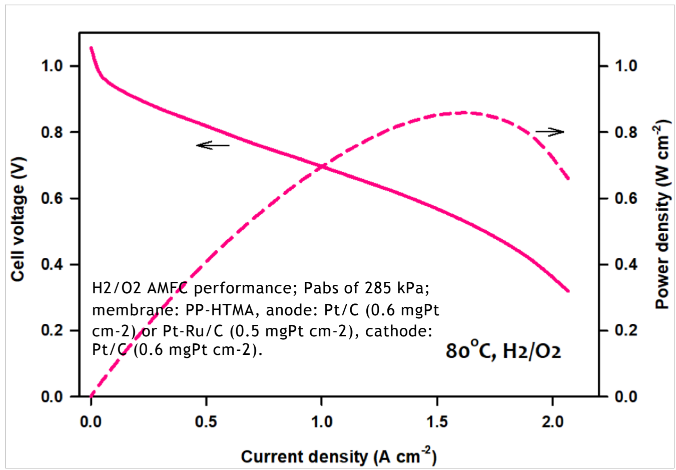
Potential application areas

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

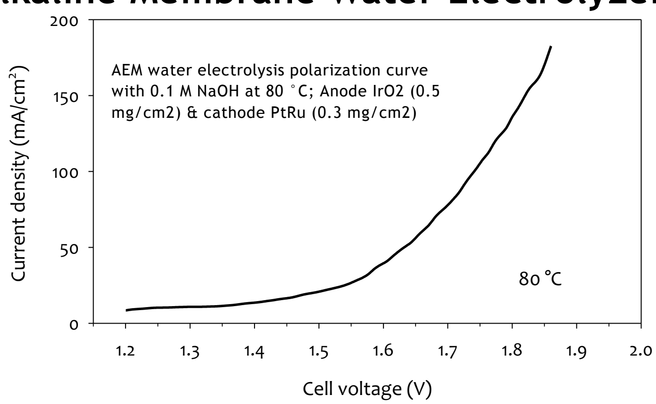
Anion Exchange Membrane



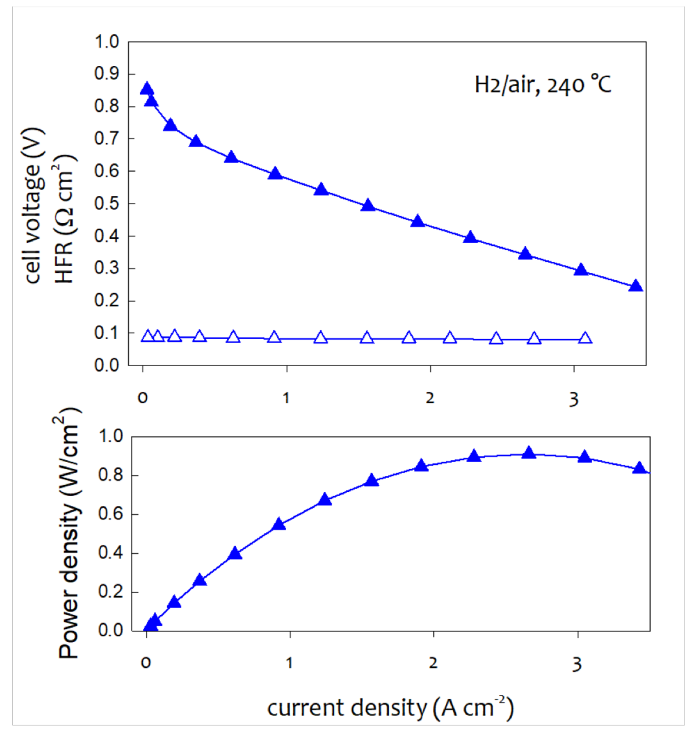
Alkaline Membrane Fuel Cells



Alkaline Membrane Water Electrolyzer



High Temperature Membrane Fuel Cells



H2/air High temperature proton exchange membrane fuel cell performance; anode catalyst: PtRu/C (0.5 mgPt cm-2), cathode catalyst: Pt/C (0.6 mgPt cm-2). Tested under 147.2 kPaabs backpressure.

Los Alamos
NATIONAL LABORATORY

Non-aqueous Redox Flow Batteries

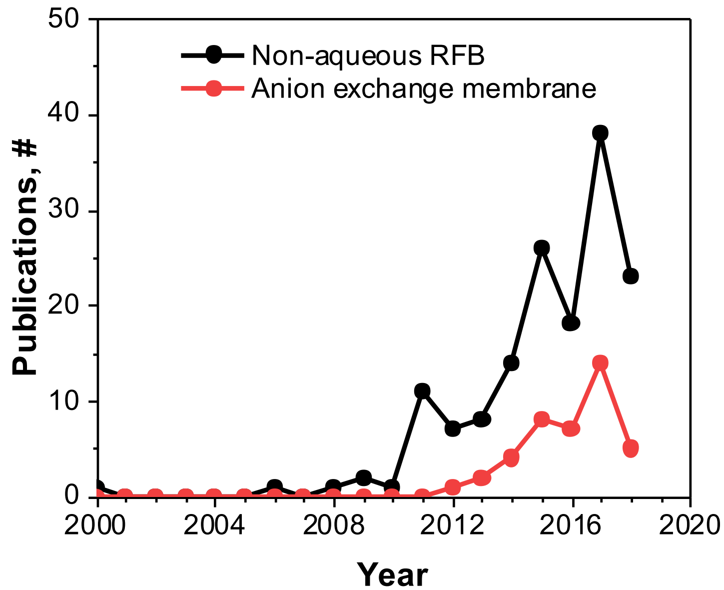
Membrane Status

Sandip Maurya

Los Alamos National Laboratory

Workshop on Non-Aqueous Flow Batteries
Santa Fe, NM
January 30-31, 2019

Non-aqueous redox flow batteries – an emerging field



Scopus search:
["non aqueous redox flow batteries" (black) and anion exchange membrane] (red)
accessed on 1/24/2019

Most of the research focused on the development of organic or metal based redox couples.

Early days of non-aqueous redox flow battery

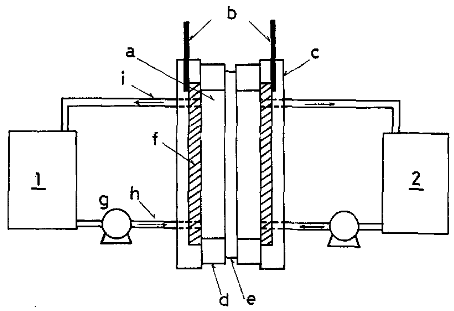


Fig. 2. Schematic diagram of the flow-type cell system, (a) carbon fibre cloth, (b) terminal leads, (c) cell case, (d) Teflon spacer, (e) diaphragm (AEM), (f) current-collector, (g) pump, (h) electrolyte inlet, (i) electrolyte outlet, *1* anolyte tank, *2* catholyte tank.

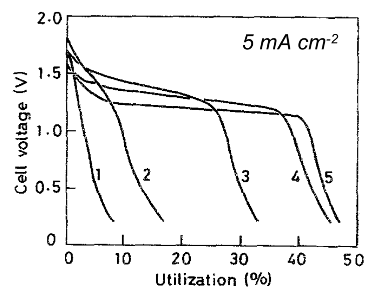
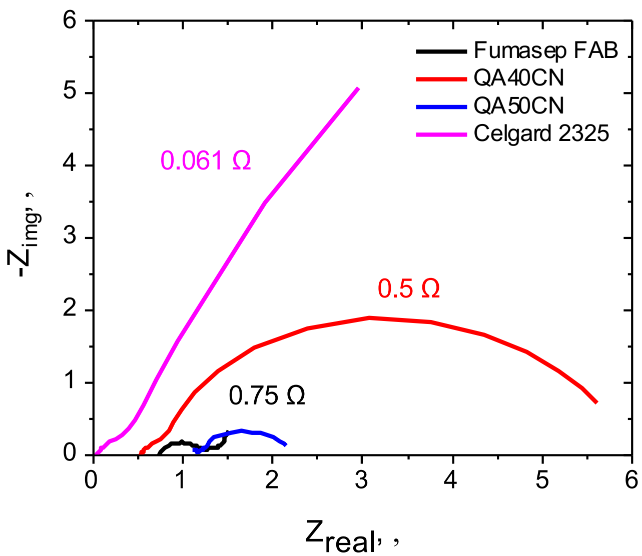


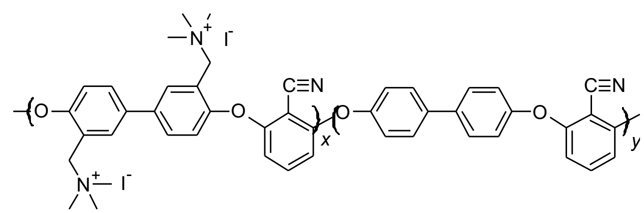
Fig. 12. Discharge curves of the flow-type cell with the AEM after 50% charge at constant voltage (3.0 V). Electrolyte is Et_4NBF_4 (0.1 mol dm^{-3})/CH_3CN containing 2×10^{-2} mol dm^{-3} [Ru(bpy)$_3$](BF$_4$)$_2$, flow rate = 0.18 cm^3 s^{-1}, pre-immersion time of the AEM in CH_3CN = 20 min.

- Sintered glass and anion exchange membrane were used as a separator.
- A discharge current density of *5 mA cm^{-2}* was achieved.

Matsuda et al. J. applied electrochem. 18 (1988) 909-914

Non-aqueous RFB performance – Polynitrile membranes

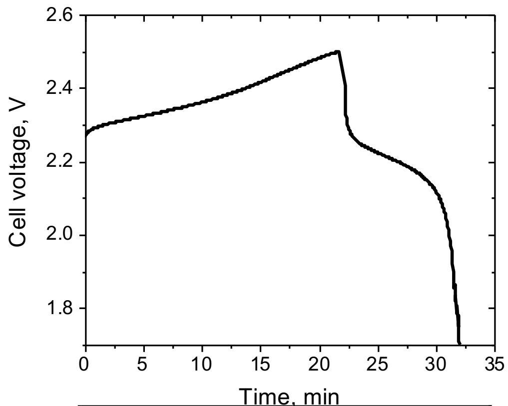


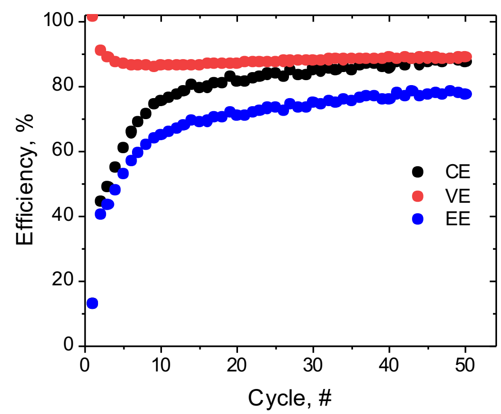


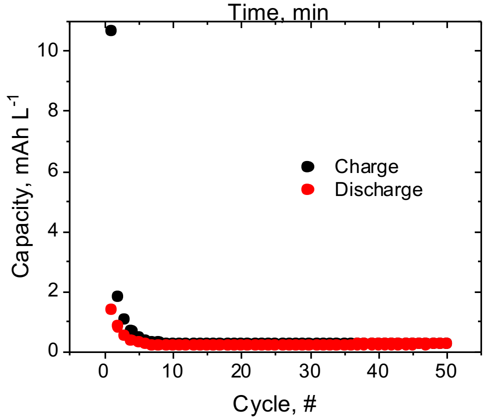
Conditions:
Electrolyte: 0.1 M $V(acac)_3$ + 1 M $TEABF_4$ / CH_3CN
Volume: 40 ml each side
Flow rate: 20 ml/min

- Polynitrile membrane (QA40CN) has lower resistance compare to Fumasep FAB.
- Still, polynitrile membranes do not undergo charge/discharge cycling.

Non-aqueous RFB performance – Fumasep FAB







Conditions:

Electrolyte: 0.1 M V(acac)$_3$ + 1 M TEABF$_4$ / CH_3CN

Volume: 40 ml each side

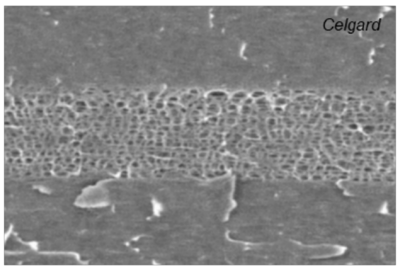
Flow rate: 20 ml/min

Cut-off voltage: 1.8 – 2.5 V

Operating current density: 2 mA/cm^2

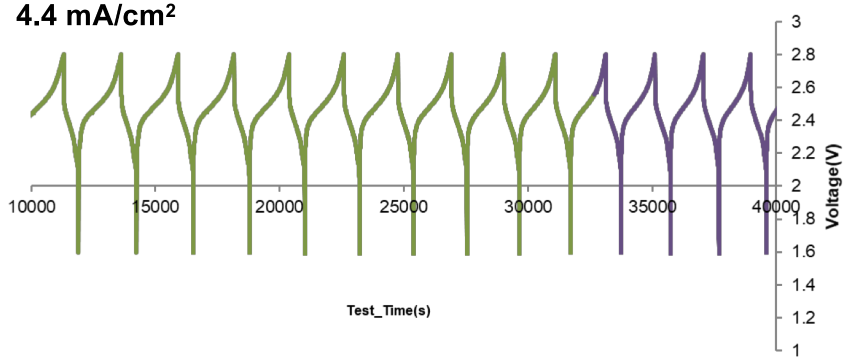
Fast capacity decay

Non-aqueous RFB performance – Celgard 2325



Trilayer PP/PE/PP separator Celgard 2325

4.4 mA/cm²

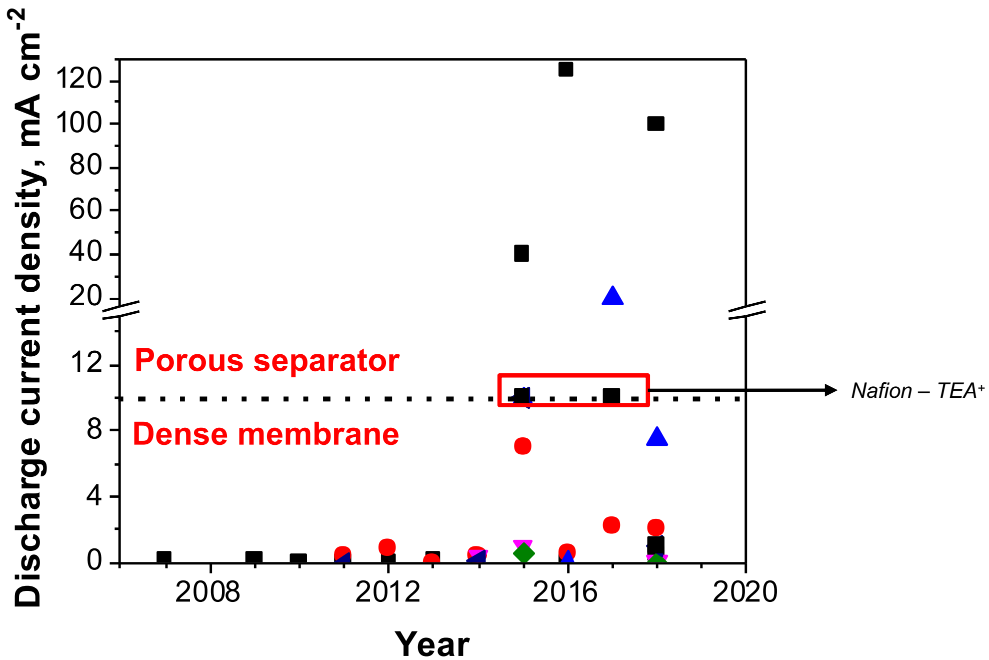


Cycle, #	Discharge Capacity, Ah L^{-1}
5	0.23
15	0.24
50	0.30
110	0.25
Average / cycle	0.27
Reference	~ 0.13

Journal of Power Sources, 296 (2015) 245-254

- Commercial Fumasep and lab-made polynitirle membranes showed almost no or poor cyclability.
- On the other hand, porous Celgard separator showed good cyclability with stable discharge capacity.

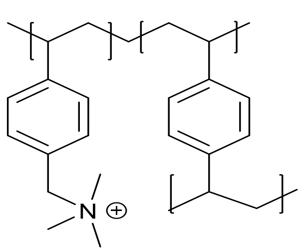
Is membrane a barrier for high current operations ?



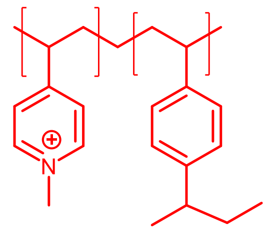
- Most of the AEMs showed abnormally low discharge current densities (< 7 mA cm^{-2}).
- On the other hand, porous separators can achieve discharge current densities up to 125 mA cm^{-2}.

Anion exchange membrane chemistry

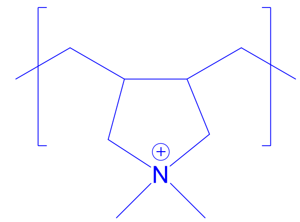
QA Poly(vinyl benzyl)



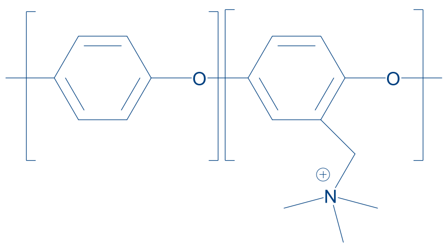
Poly(vinylpyridinium)



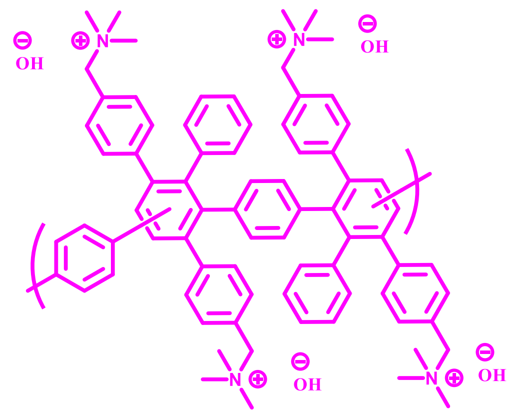
Poly(diallyldimethylammonium)



QA poly(phenylene oxide)



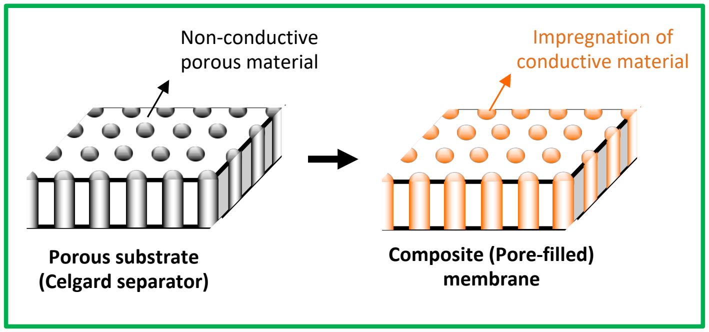
QA poly(phenylene)



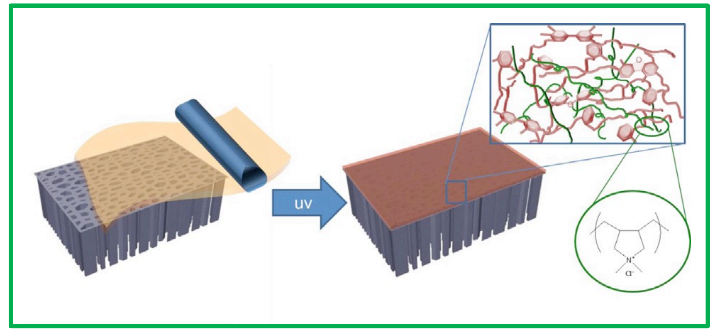
Summary of AEMs used for non-aqueous RFBs

Membrane	Type	Redox chemistry	Reference
Chitosan/Urushi	Interpenetrating polymer network (IPN) - composite	$V(acac)_3$	Gong et al., ChemistrySelect, 2 (2017) 1843-1849
QA poly(phenylene oxide) (PPO)	Crosslinked film	$Cu(MeCN)_4][Tf_2N]$	Li et al., J. Power Sources, 378 (2018) 338-344
poly(diallyldimethylammonium chloride) (PDDA)/urushi	Composite (pore-filled)	$[Ni(bpy)_3(BF_4)_2]$ and $Fe(bpy)_3(BF_4)_2$	Kim et al., J. Memb. Sci., 564 (2018) 523-531
Neosepta AHA (commercial)	**Composite AEM**	**$V(acac)_3$**	**Maurya et al., J. Power Sources, 255 (2014) 325-334**
FAP-PK (commercial)	Composite AEM	$V(acac)_3$	Hudak et al., J. Electrochem.Soc., 162 (2015) A2188-A2194
Porous Separators (Celgard, Daramic, etc)	porous	Various Chemistries	
QA Poly(vinyl benzyl)	Composite (pore-filled)	Fe & Ni	Kim et al., J. Memb. Sci., 454 (2014) 44-50
QA Poly(vinyl benzyl)	Composite (pore-filled)	$V(acac)_3$	Maurya et al., J. Memb. Sci., 443 (2013) 28-35
N212 (commercial)	Perfluorinated - sulfonated	$V(acac)_3$	Escalante-García et al., J. Electrochem.Soc., 162 (2015) A363-A372

Composite membranes



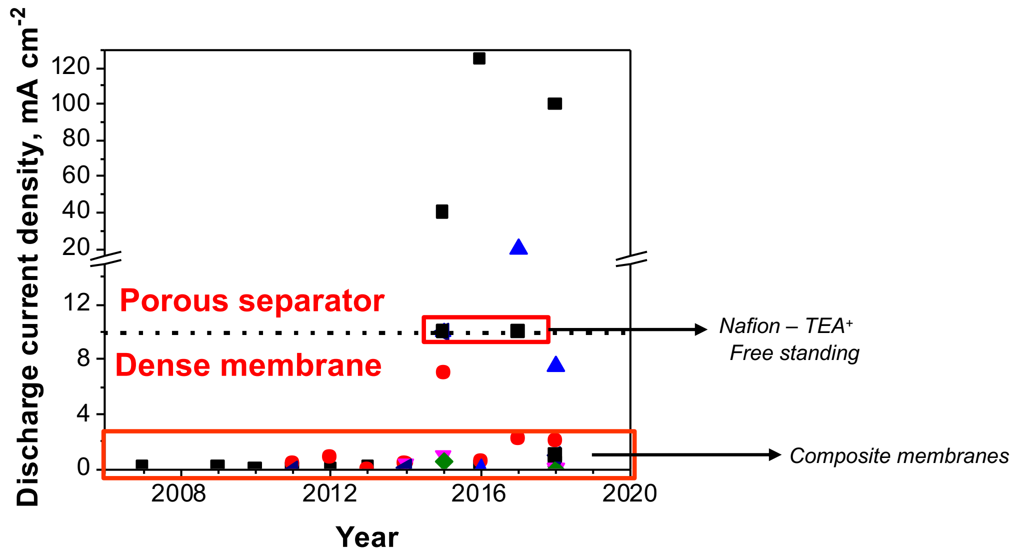
Maurya et al., J. Memb. Sci., 443 (2013) 28-35



Kim et al., J. Memb. Sci., 564 (2018) 523-531

- Most of the composite membranes consist of ion conductive polymer and inert/non-conducting support.
- Non-conducting support provides mechanical stability however it also disrupts ionic channels needed for fast transport of ions.

Yes, membrane is a barrier for high current operations.



- More efforts are needed to develop suitable membranes which can support a large volume of ions' transport.
- Further discussion on strategies to develop membranes for non-aqueous RFBs is welcome.

THANK YOU !