Membranes and Electrolytes for Redox Flow Batteries

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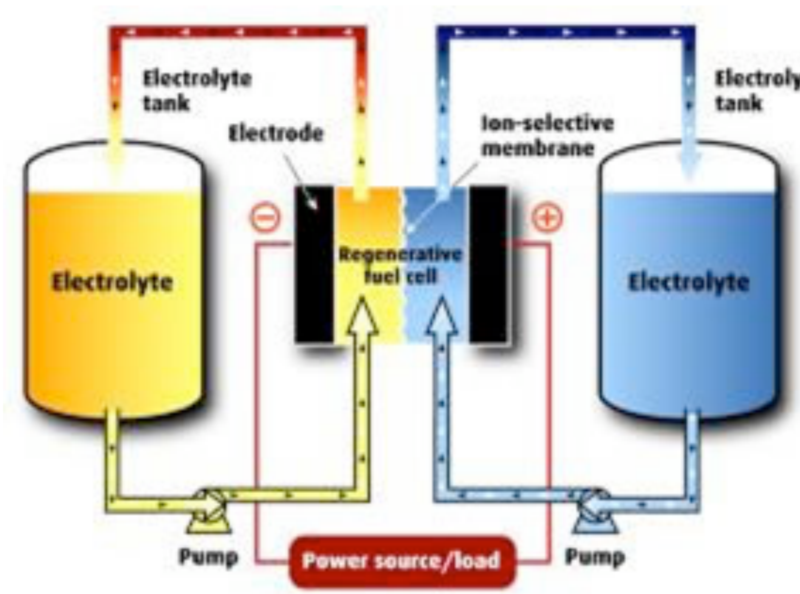
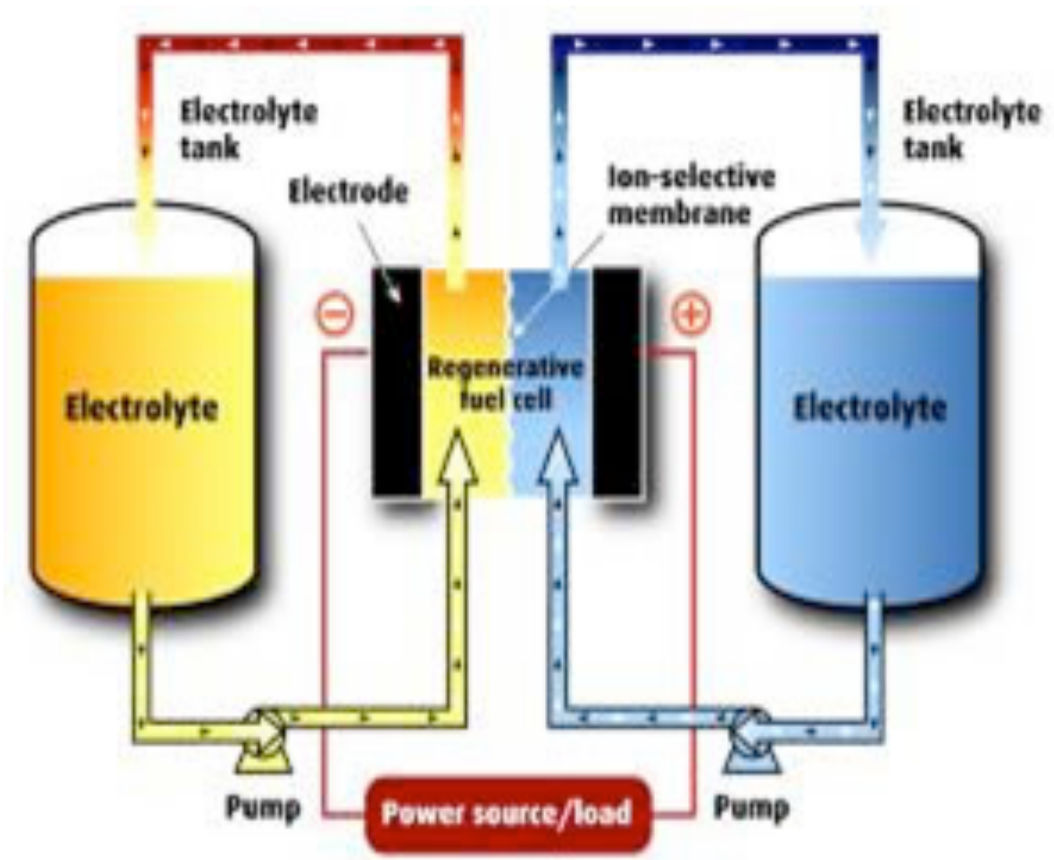


Figures Courtesy of Electrosynthesis

Redox Flow Systems



Favorable Attributes

- *Separation of Energy and Power*
- *Cost*
- *Scalability*
- *Efficiency*
- *Longevity*
- *Safety*

Conversion technology similar to PEM fuel cells

Outline

1. *Membrane and electrolyte needs for RFBs*
2. *Drawing from PEM FC Membranes: what's out there*
3. *Membrane behavior: what to expect*
   - *Composition, Transport*
   - *Stability*
4. *Prospects for electrolyte development*
   - *Trade-offs to consider*
5. *Conclusions*

Attributes required of Polymer Electrolyte Membranes

- *Low resistance under cell operating conditions.*
- *Long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments.*
- *Good mechanical strength, preferably with resistance to swelling.*
- *Low cross-over--pinhole free! Minimize water pumping!*
- *Interfacial compatibility with catalyst layers.*
- *Low cost.*

Membranes/Electrolytes for RFBs

- ✓ ***Literature shows high ASR***
  - ***Nafion 117 in a fuel cell: ~0.15 ohm-cm2***
  - ***Nafion 117 plus electrolyte solution in an RFB: as high as ~6 ohm-cm2***
- ✓ ***Improved chemical and mechanical stability***
- ✓ ***Need to ensure H-form membrane***
- ✓ ***Improved tolerance to cross-over needed***
  - ***Cross-over determines lower limit of membrane thickness***
  - ***For neutral species in aqueous solutions, it is difficult to get much 'selectivity'***
  - ***More likely for acidic solutions***

PEMs Passing Current in Contact with Electrolyte Solutions

What Happens?

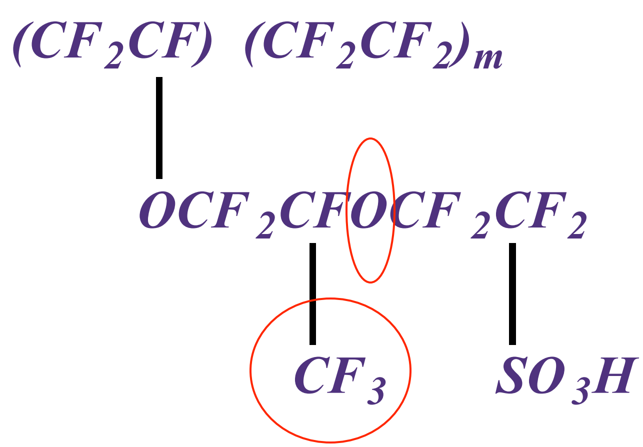
- ***Electrokinetic Phenomena***
  - ***Water pumping***
- ***Ion Exchange***
  - ***Partitioning: use acid solution***
  - ***Polyvalent ions particularly tricky***
- ***'Donnan Breakthrough'***
  - ***'Molecular' Acid or Salt Uptake***

Interplay between these…

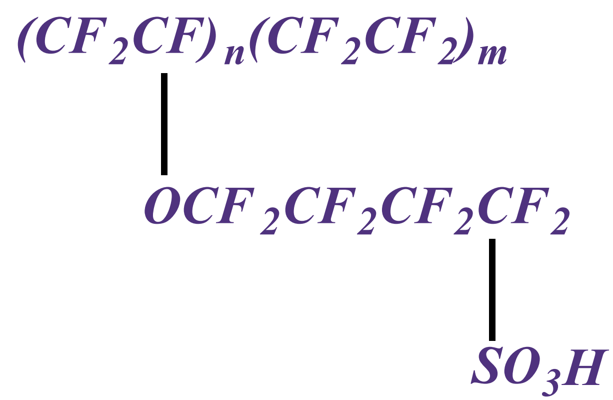
MEMBRANES FOR RFBS

We've got Options!

Membranes today: PFSAs



Nafion: The World Champion



New   3M Polymer

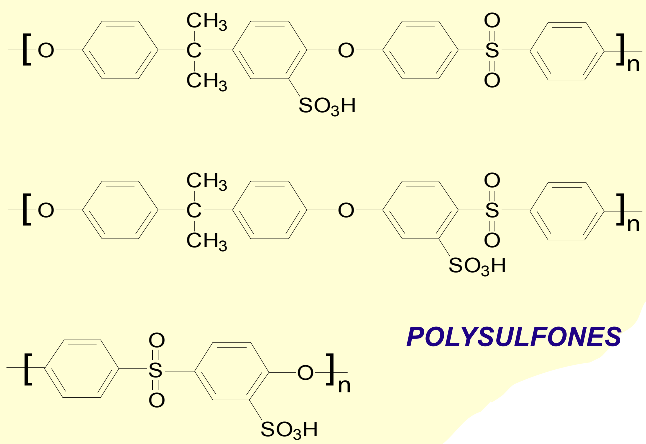
Also: Solvay-Solexis (SSC), Asahi

New variability in EW, other properties

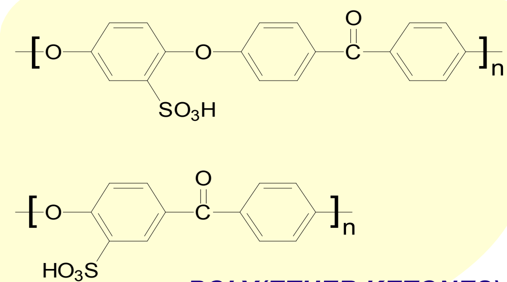
Some Proposed Approaches to Improved Membranes (ca. 1999)

- *'Synthesize and be damned'--infinite funding for synthetic organic and polymer chemists*
- *More thermally stable or less costly membranes*
  - *BUT need to keep water in or replace its function (high T)*
  - *Typically sulfonated aromatics*
- *Water 'replacements'*
  - *Imidazole (Kreuer)*
  - *Inorganic phases*
  - *Phosphoric Acid and other acids*
- *Water 'traps'*
  - *Sol-gel phase*
- *No light at end of tunnel for methanol blocking or decreased drag either*

Poly (aromatics):
If you can sulfonate it, it will be good!?

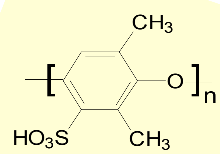


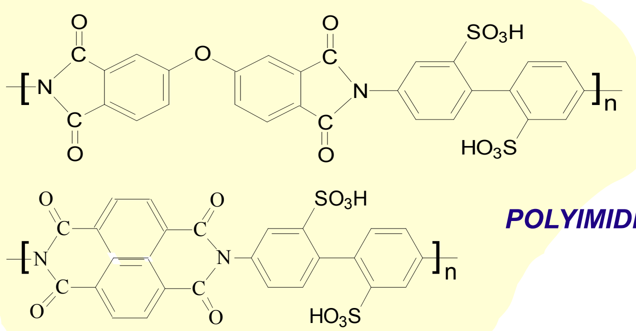
POLYSULFONES



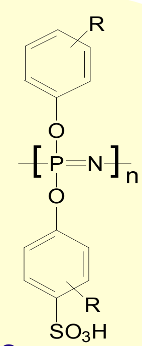
POLY(ETHER KETONES)

POLY(PHENYLENE OXIDE)





POLYIMIDES

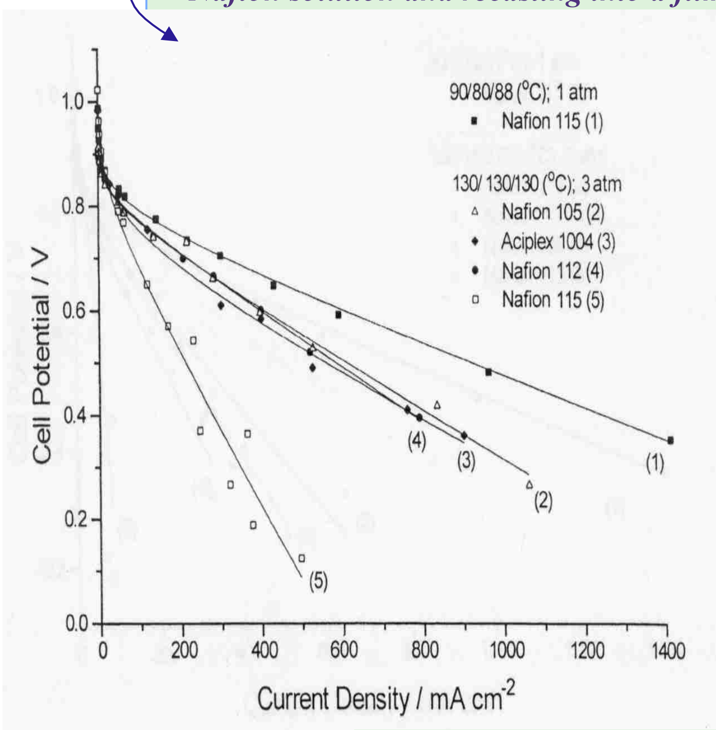


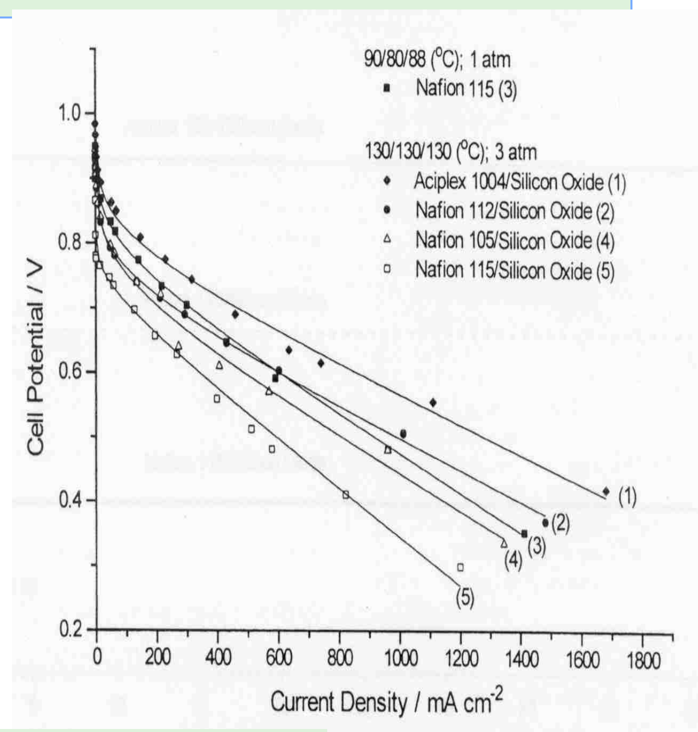
POLYPHOSPHAZENES

Improving Water Retention
'Sand' in Nafion

- ***Incorporation of highly dispersed hygroscopic metal oxide particles (SiO_2) or hydrophilic siloxane polymer to retain water (up to 10% allows operation at 130-140°C at high humidification !).***

Direct interpolymerization (precipitation) in extruded Nafion or adding silica to a Nafion solution and recasting into a film





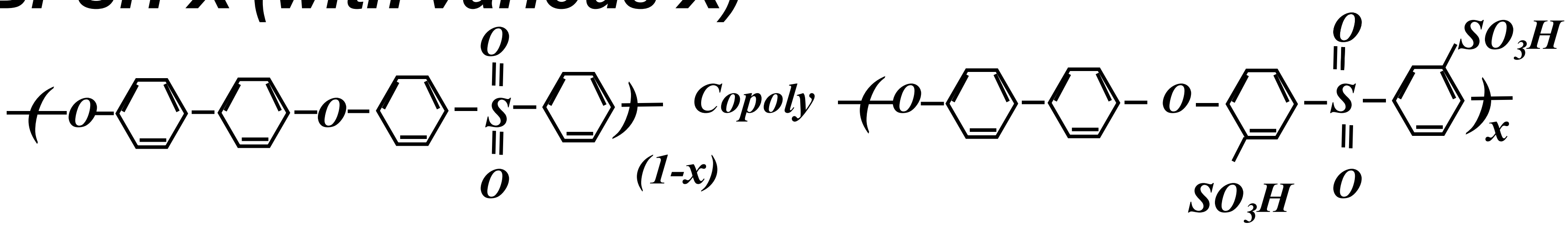
K.T. Adjemian, S. Srinivasan, J. Benziger and A.B. Bocarsly, Investigation of PEMFC operation above 100 °C employing perfluorosulfonic acid silicon oxide composite membranes, Journal of Power Sources, 109 (2002) 356-364.

Polymers: Phase 2

Smarter development: Designer Polymers

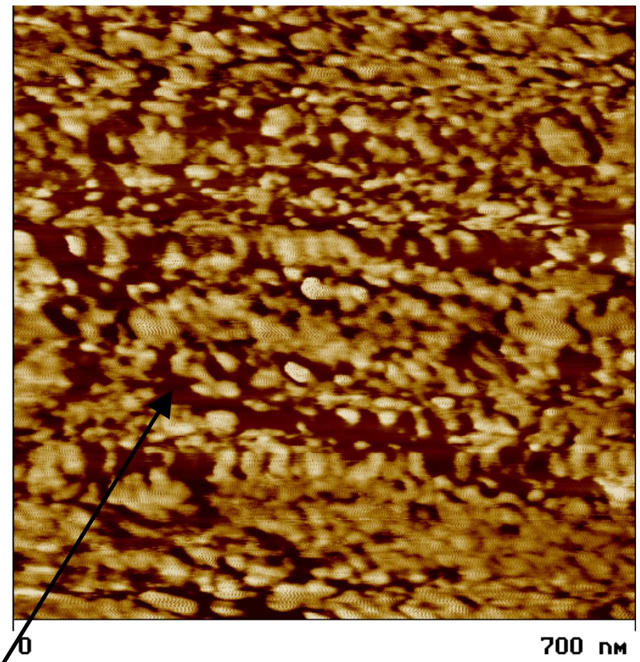
Exert control over morphology, EW etc.
A first example…

BPSH-X (with various X)



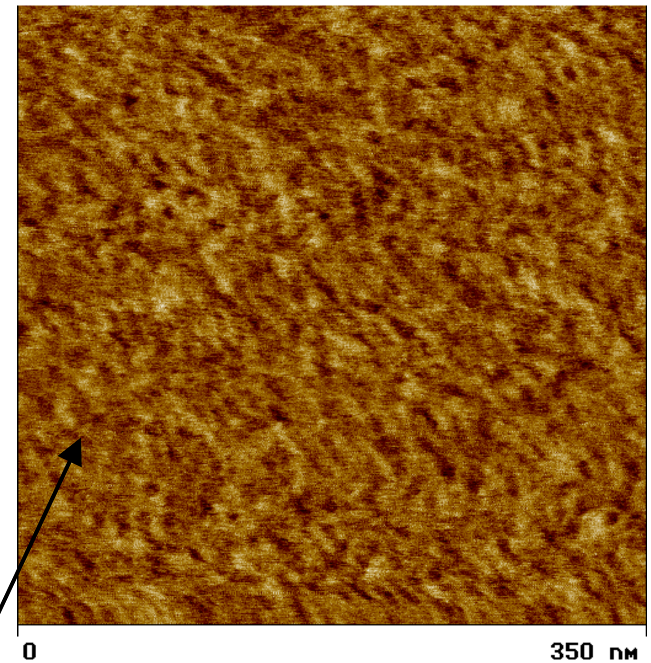
F. Wang, et al., Macromol. Symp., 175 (2001) 387-395

More AFM Images



Large, continuous ionic domains

BPSH-60

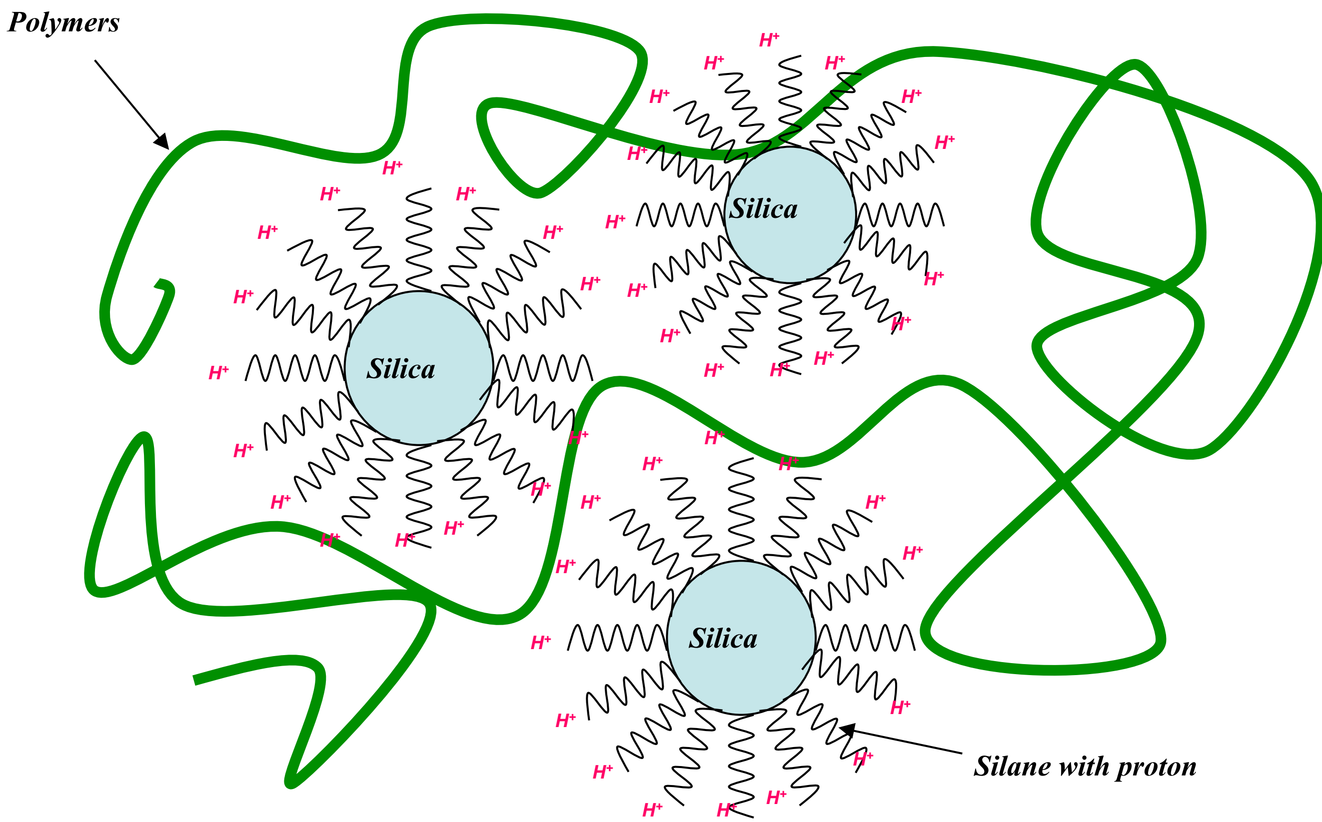


Small, well connected ionic domains

Nafion 117

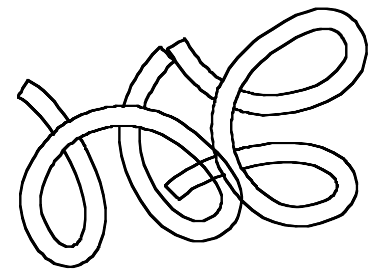
Smarter Composites

(1)Silica/Polymer composite membrane

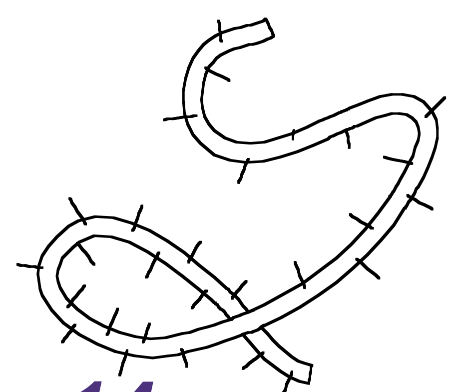


Form network in polymers

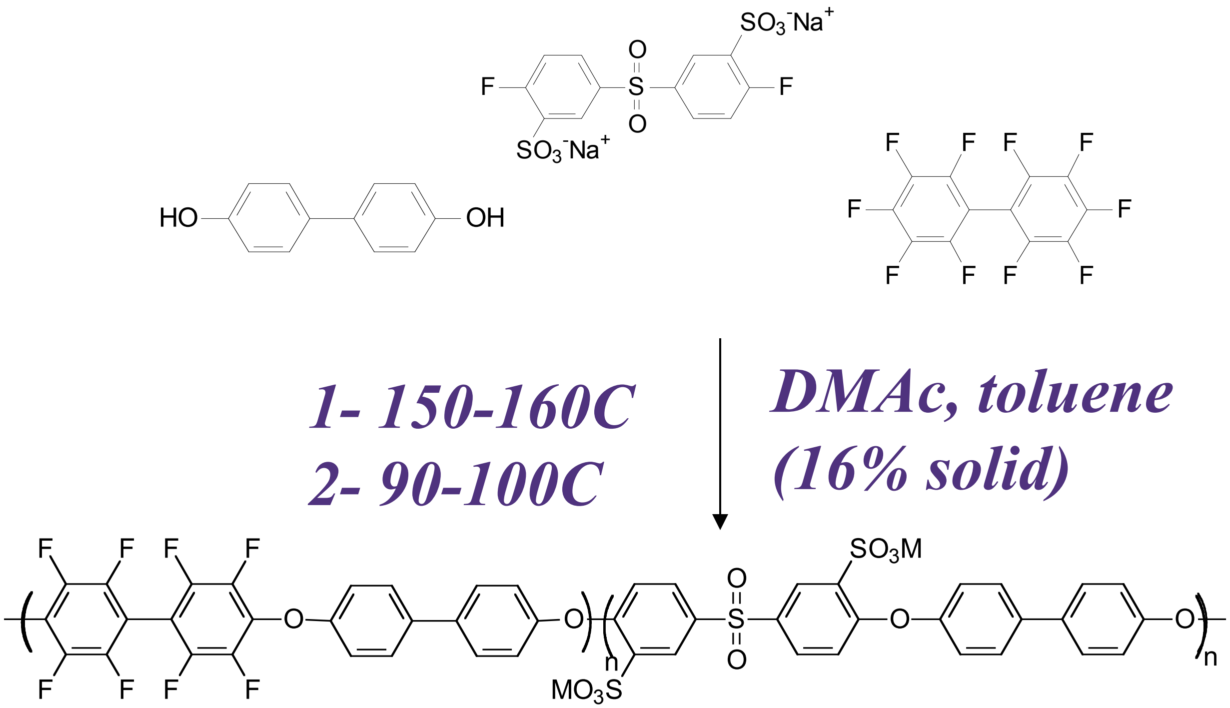
(a)Proton free polymer-PVDF

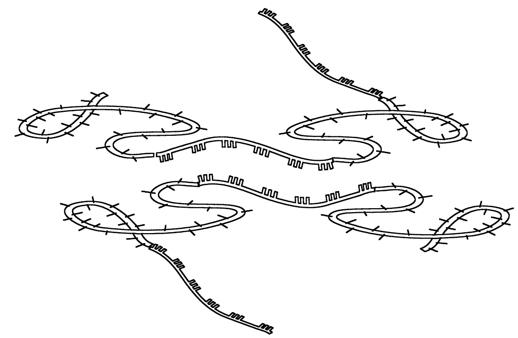


(b) Acid polymers-BPSH



Fluorinated Multiblock Copolymer





Yield: 99%, IEC (calc.): 1.29 meq/g

Toward a Description of Transport in RFB Membranes

Highly Complex: Many Species

- ***Species Diffusion, Migration***
  - ***Water pumping***
- ***Cross-terms***
  - ***Partitioning: use acid solution***
- ***Redox Active Species transport by 'Electron Hopping'***
  - ***'Molecular' Acid or Salt Uptake***

Interplay between these…

Toward a Description of Transport in RFB Membranes

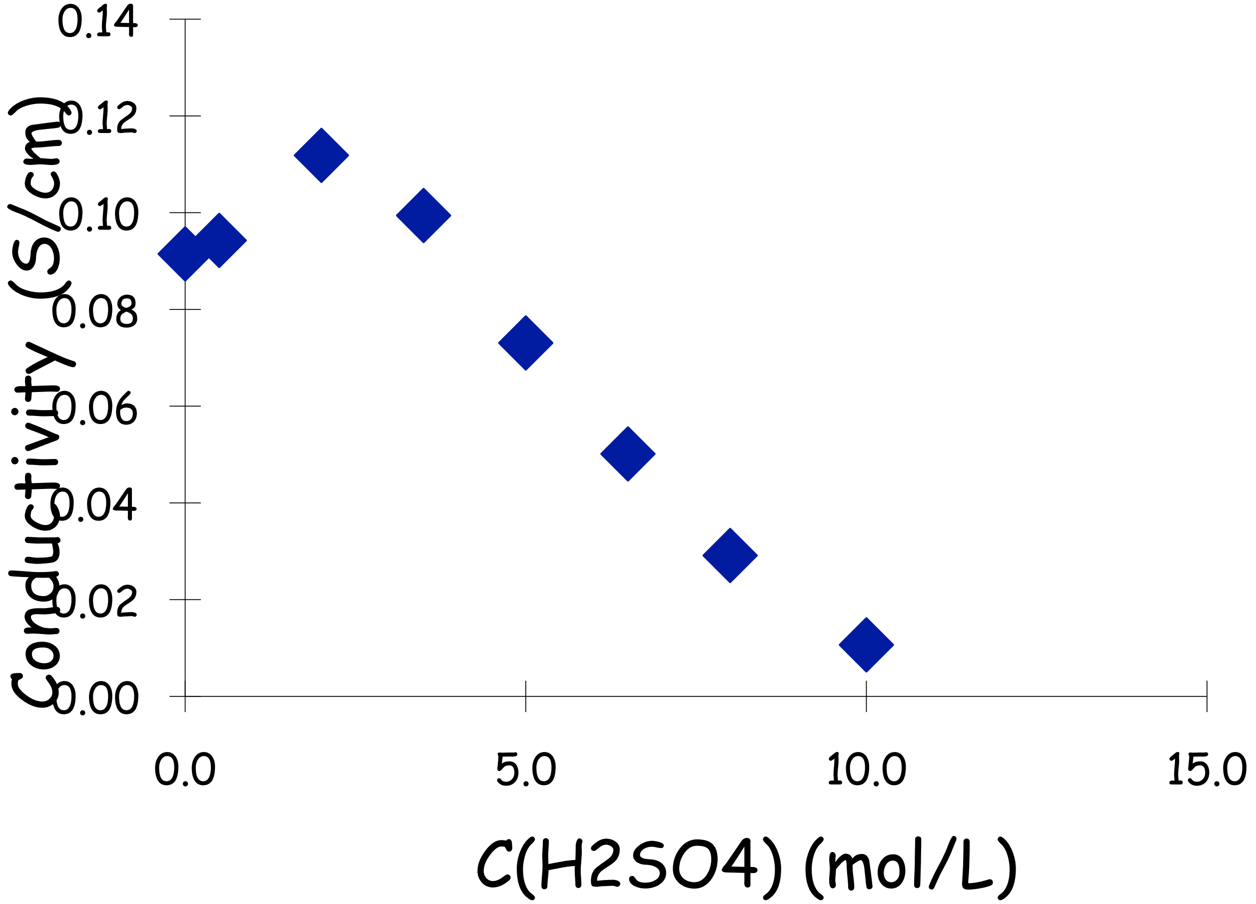
Parameters Needed

- ***Composition: water, ion uptake***
- ***Transport parameters***
  - ***Conductivity, diffusion, coupling terms***
  - ***Electron exchange rates as applicable***
  - ***'Molecular' Acid or Salt Uptake***

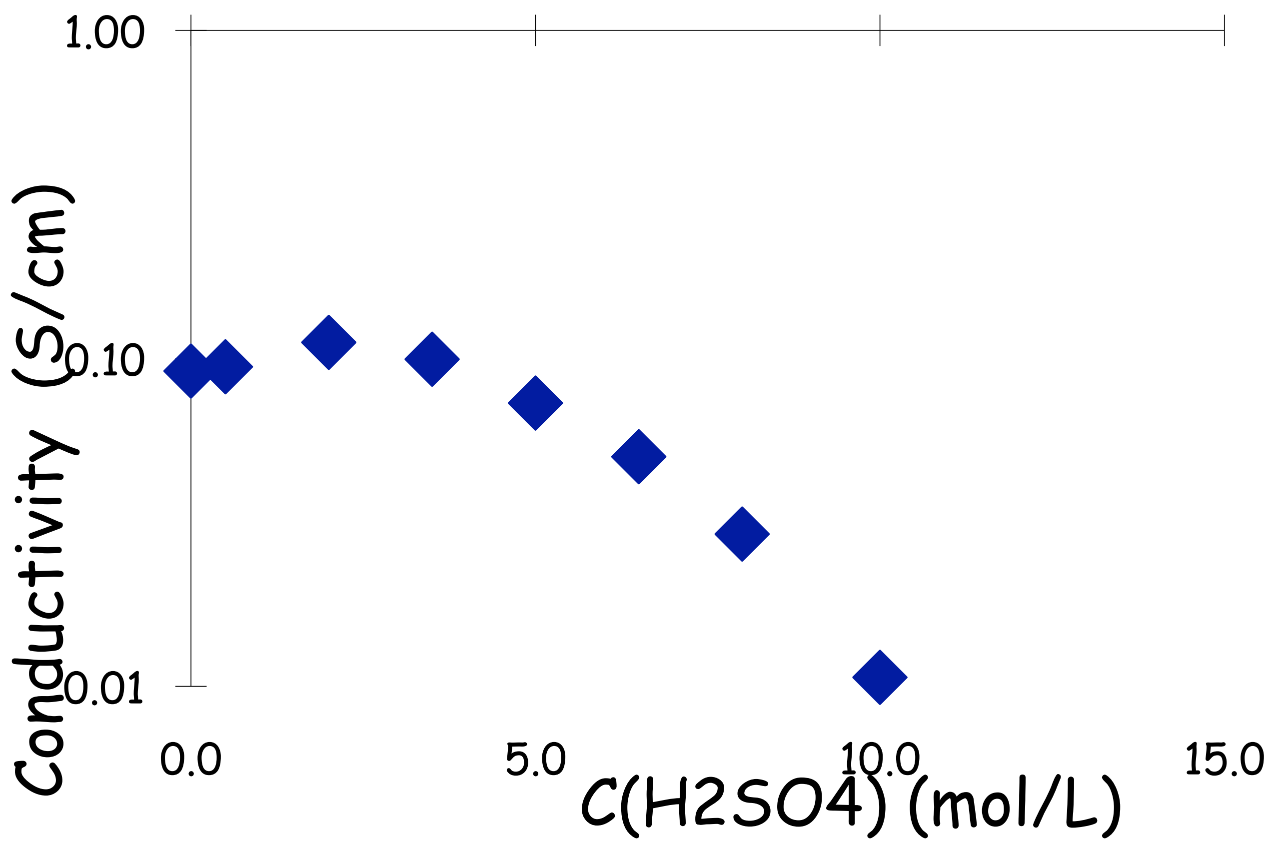
How to get all of this for every system!

Simplified models

Conductivity vs. Acid Concentration



Conductivity vs. Acid Concentration (Log Scale)

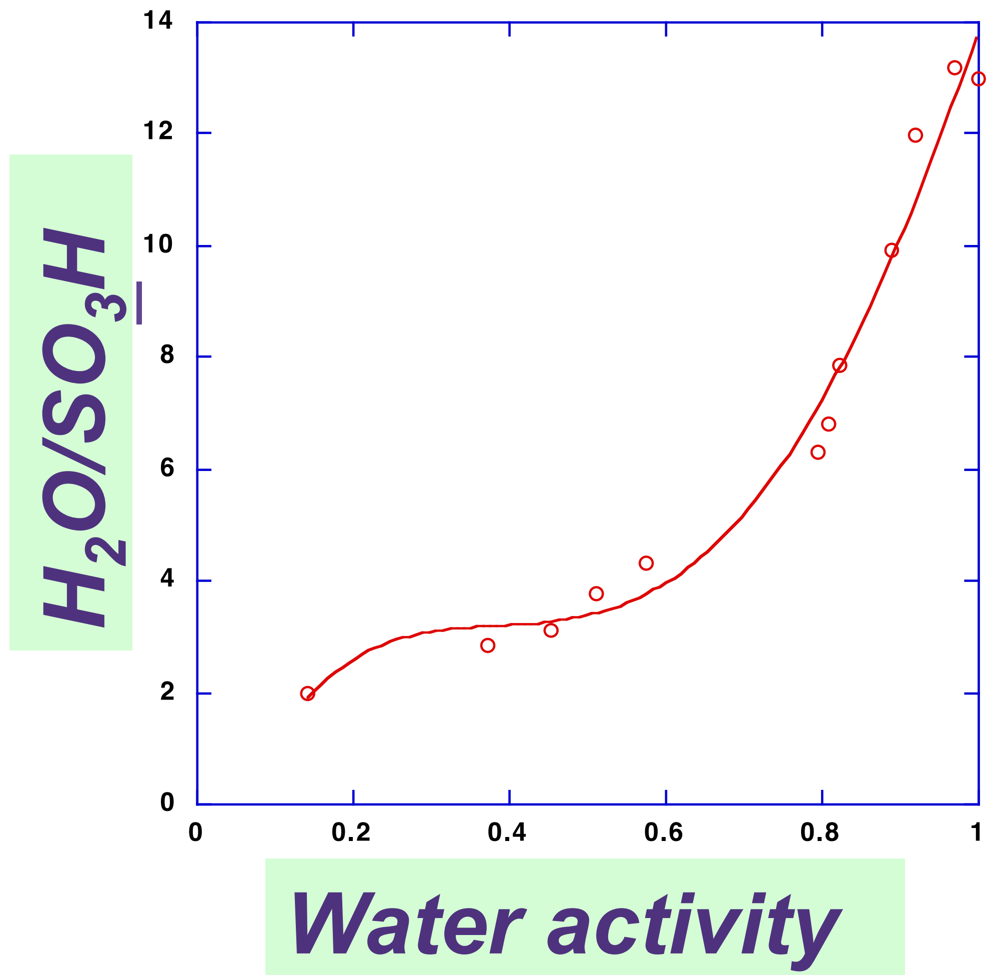


Two Effects

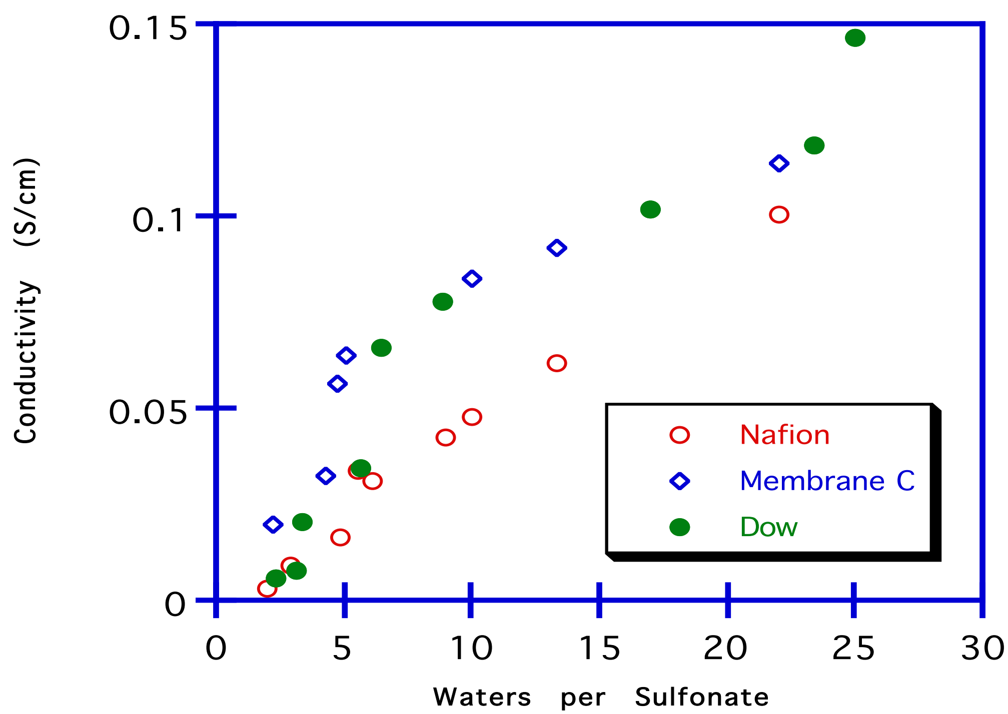
- ***Dehydration…***
  - ***Strong acid causes decrease in water content due to lowering of water activity***

Water Sorption in Nafion

- *Water uptake strongly dependent on RH even at room temperature*
- *Also strongly dependent on T*
- *At T >30, uptake is low for RH < 75%*
- *As T increases, decrease in water uptake, especially at high a_w*



Primary Fact:
H+ Conductivity is Strongly Controlled by H_2O Content



By the way, aromatic conductivity drops off much faster with lower water content

Two Effects

- ***Dehydration…***
  - ***Strong acid causes decrease in water content due to lowering of water activity***
- ***'Donnan Breakthrough'***
  - ***'Molecular' Acid or Salt Uptake causes conductivity to decrease non-linearly***

And that's w/o any ions (other than H^+) in the film!

- *All non-H+ ions decrease conductivity*

  monovalent ~5 fold

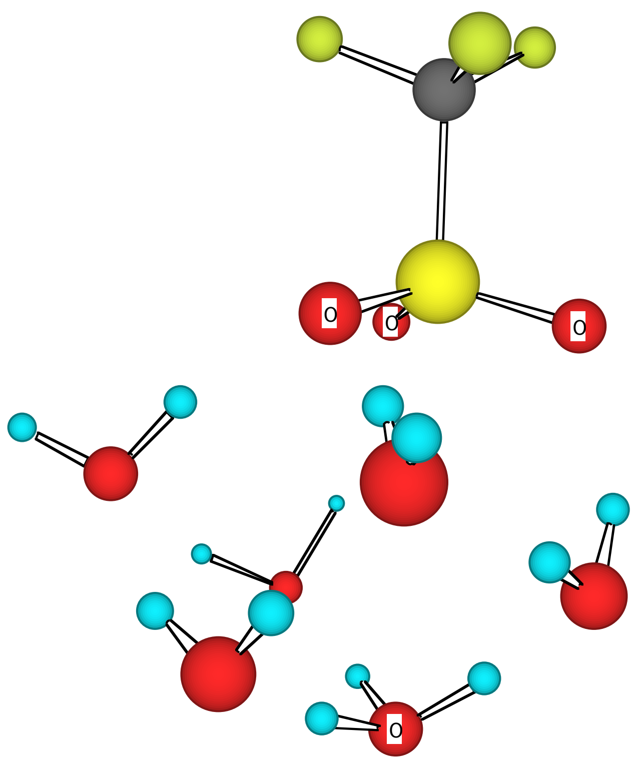
  multivalent 1 or more OM

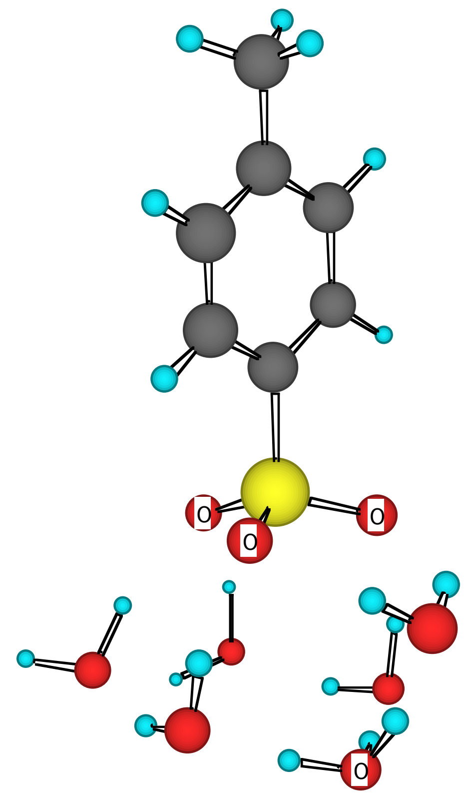
  This is even worse for aromatic sulfonates!

- *Water pumping also increased*

  Protons pull ~ 3 H_2O/H+; Na^+: 6; Sr^{3+}: 21

Conductivity Drops Even More Sharply for Ar-SO3H
Why? Acidity of Different Groups…
DFT Results





r(O–O)= ***4.235 Å*** ***3.914 Å***

Will NON-AQUEOUS electrolytes ever make sense?

- *Positive: increased voltage possible; multivalent ions*
- *Negative: even lower conductivity, COST, poor process fluids/safety*
-

Example: ionic liquid with 4 V window, multivalent : maybe 5 fold increase in ED

COST?

This might make sense for niche application that is very footprint sensitive

Summary

- *Lots of membranes, chemistries*
- *Need focused understanding of needs to guide rational tailoring of materials*
  - *Extensive studies of physical chemistry*
  - *Transport modeling*
- *Cross-over: materials vs. system*

Acknowledgements

Tang Zhigang

Alex Papandrew

Thanks!

Tom Zawodzinski

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