

# Anion Exchange Membranes for Fuel Cells

Andrew M. Herring

CSM

Bryan Pivovar

NREL



# Anion Exchange Membranes

## (Presented to Parallel Breakout Sessions)

- Stability Challenges
  - Chemical (OH attack)
  - Other (Mechanical, RH, peroxide?)
- Transport/Conductivity Challenges
  - Conductivity
  - Water Uptake
  - Permeability

Plenty of places where these two issues overlap  
Comparisons to PEMs a common theme of this presentation.

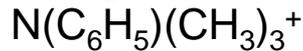


# Covalently Tetherable Cations

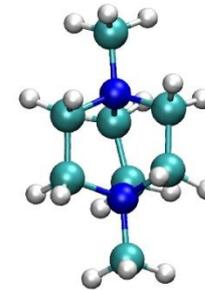
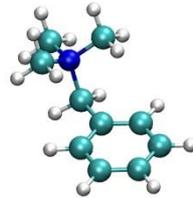
TMA



PTMA

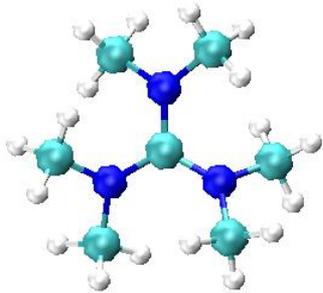


BTMA

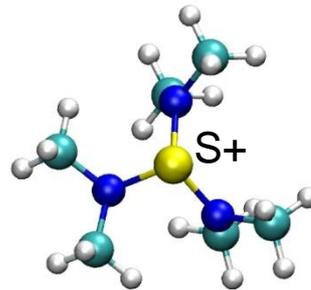


DABCO(2+)

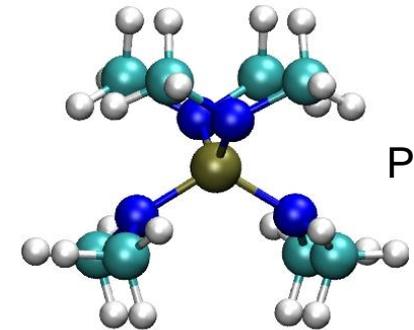
1,4-diazabicyclo[2.2.2]octane



Methyl  
Guanidinium<sup>+</sup>



(TAS)<sup>+</sup>  
trimethyl amino sulfonium



Phosphazanium<sup>+</sup>  
Tetrakis[dimethylamino]phosponium

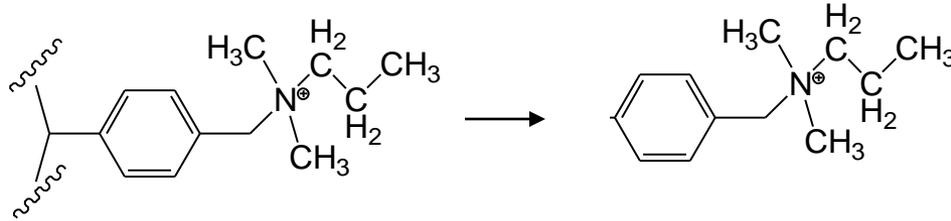
Membranes require covalently tetherable cations. These have seen various levels of investigation.



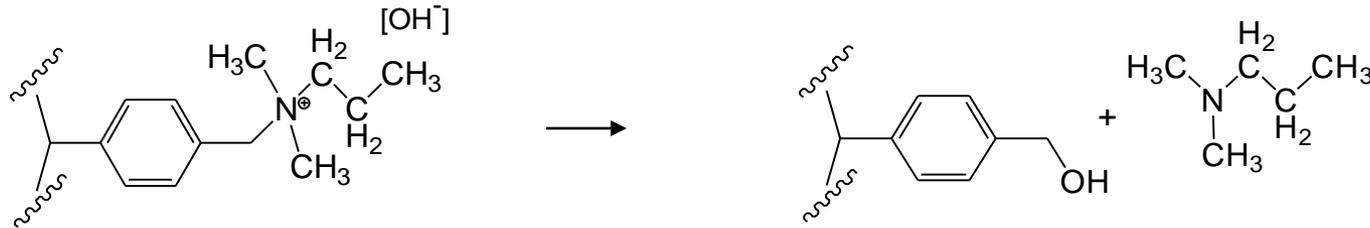
# Chemical Stability of AEMs

## 3 Potential Sources of Chemical (Hydroxide) Degradation

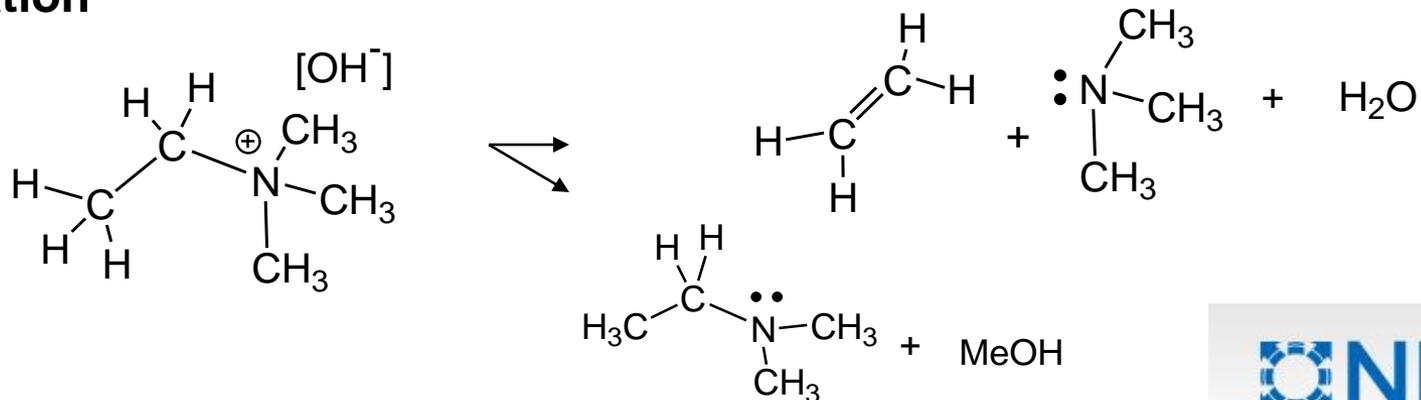
### – Polymer backbone



### – Tether

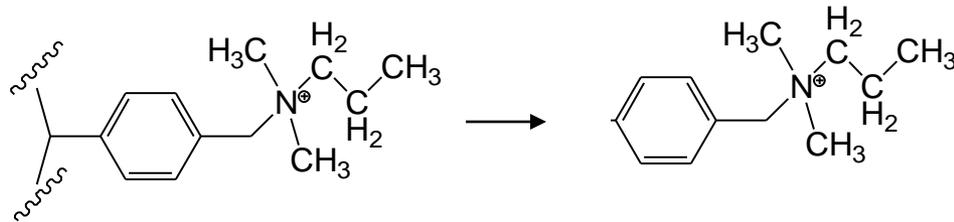


### – Cation



# Polymer Backbone

- **Degradation**
  - (unzipping analogous to PFSA, chain scission)



- **Most current AEMs based on wholly aromatic backbones.**
- **Relatively minor concern – multiple backbones possible including perfluoro and wholly aromatic – good stability as PEMs or in base.**
- **Initial membranes based on ion exchange materials (Polystyrene) may have been significantly limited by backbone stability.**
- **Current materials show dramatic improvement, but still far short of ideal.**



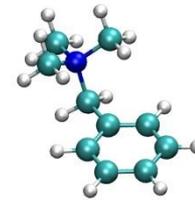
# Tether

- Tether
  - In most cases cations will be tethered to a backbone and the tether can also be the weak link (exception cations incorporated into backbone)
- Non-tethered cation (TMA simplest analogue of covalently tetherable cation)
- Tether containing cation (BTMA most commonly used cation in AEMs)
- In some cases like amination of sulfonyl fluoride form PFSA (Tosflex), a sulfonamide linkage results and can only be avoided with additional steps.
- Alkyl linkages are convenient but susceptible to Hoffman elimination.

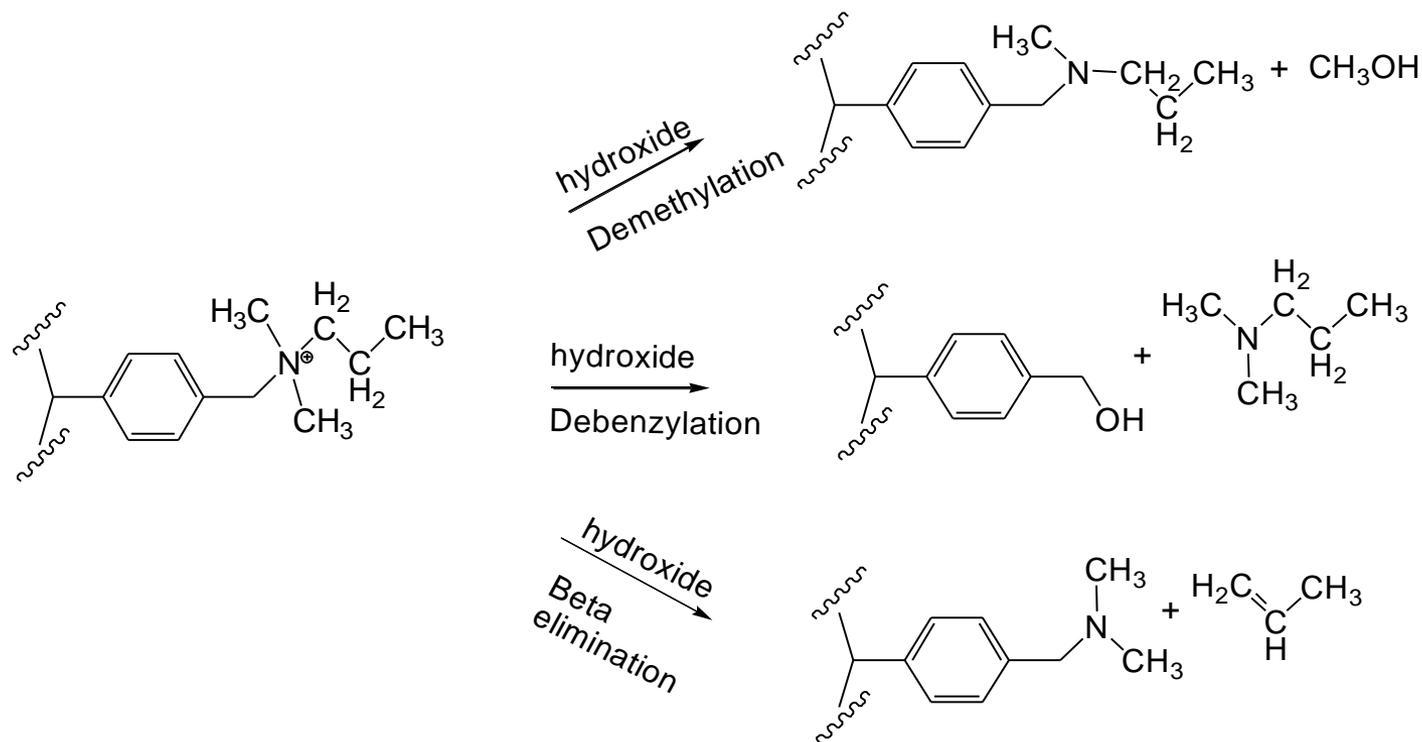
TMA



BTMA



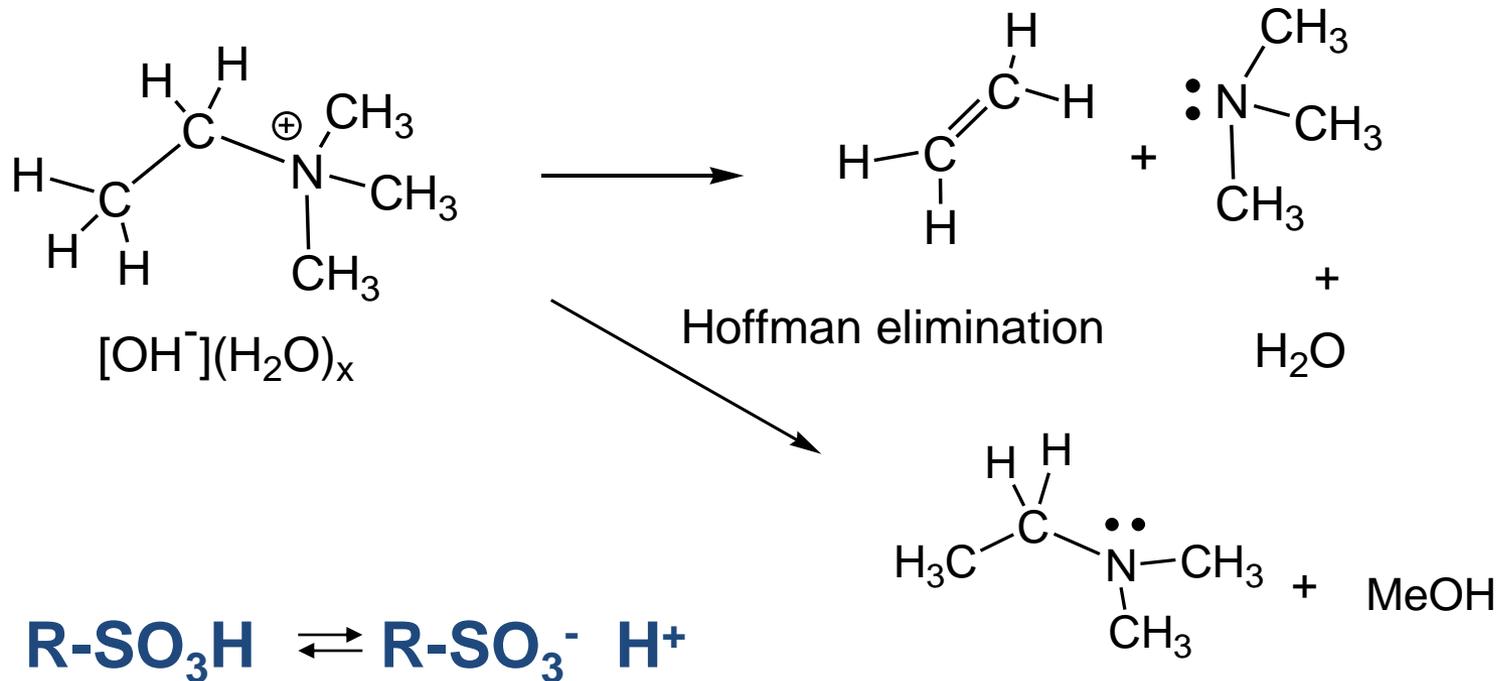
# Cation Degradation Routes



Traditional anion exchange membrane cations degrade by these routes. Has been suggested that lifetimes of  $\sim 1000$  hours at  $50\text{-}60^\circ\text{C}$  could be achieved, early reports did not approach this stability.



# Reversibility of Reaction



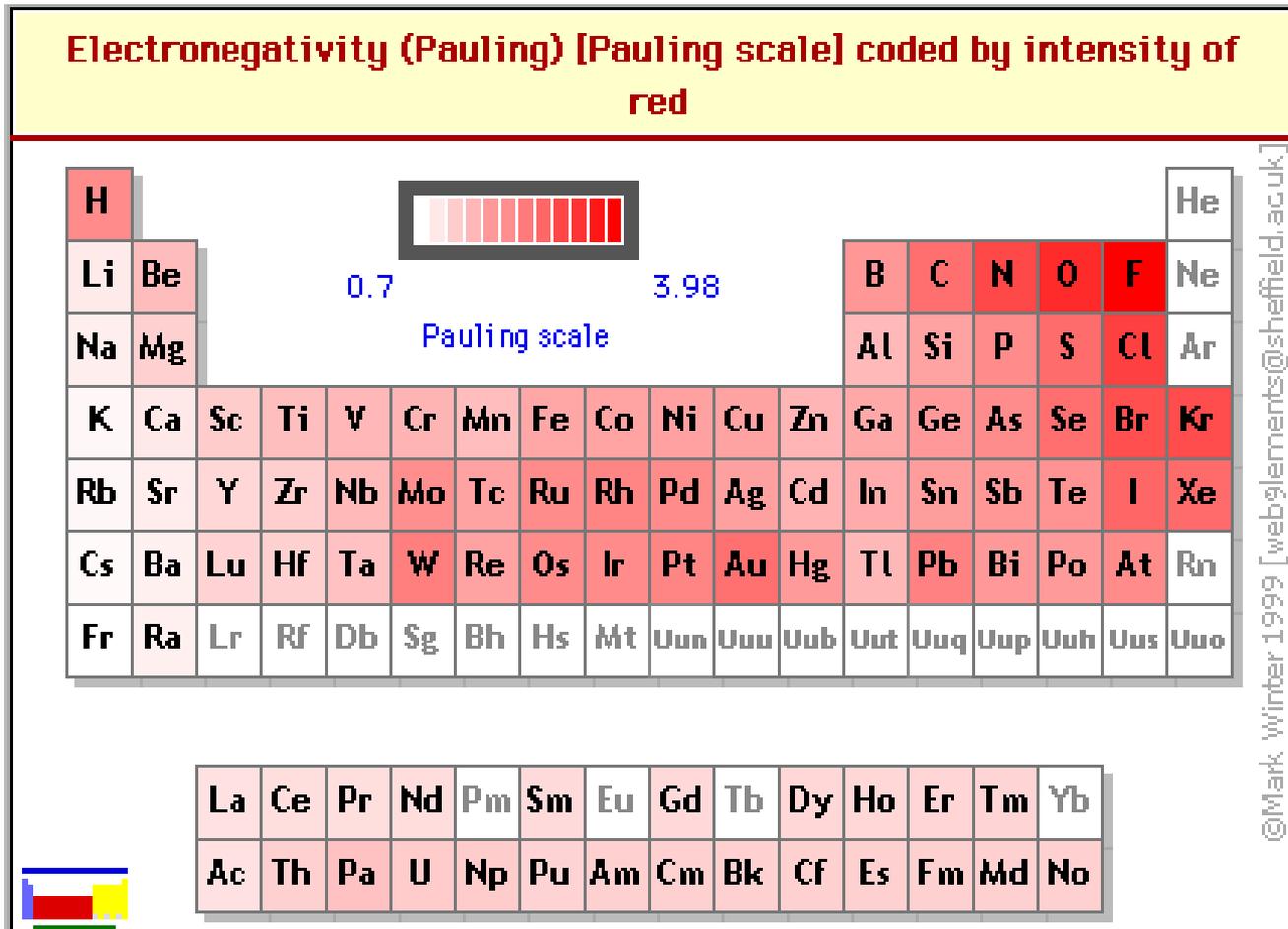
In general, cationic species do not have a reversible analogue to that of acidic groups, and formation of a neutral species results in an irreversible reaction.

Most anion exchange materials are used for anions other than hydroxide, where this reactivity is not an issue. Anions more acidic than cations are basic.



# Covalently Tetherable Ionic Groups (Cations v. Anions)

Electronegative species can be covalently incorporated much more easily than electropositive.



# Cations – Bulky and Hydrophobic

Compact cations have not shown necessary stability and basicity.

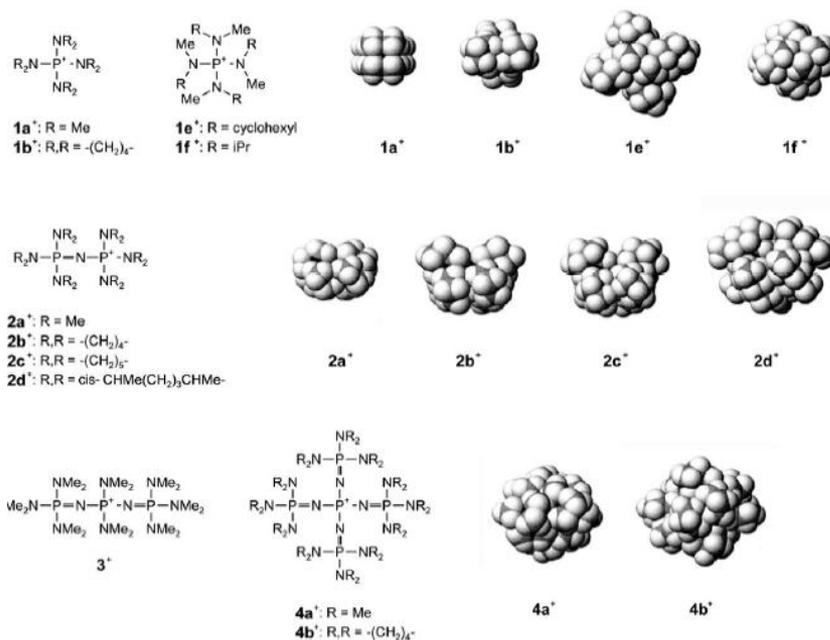
Table 1. Half lives of phase transfer catalysts in 50% NaOH/chlorobenzene at 100°C.

Entry	Compound	$t_{1/2}$ [h]
1	Bu <sub>4</sub> P <sup>+</sup> Cl <sup>-</sup>	0.08/20 °C <sup>[4]</sup>
2	Ph <sub>4</sub> As <sup>+</sup> Cl <sup>-</sup>	2/20 °C <sup>[a]</sup>
3	Ph <sub>3</sub> PNPPPh <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	1.1/20 °C <sup>[a]</sup>
4	Bu <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	0.33
5	1a-Cl	0.33
6	1b-Cl	0.9
7	1c-Cl	67
8	1f-Cl	6
9	2a-Cl	8 (9 <sup>[4]</sup> )
10	2b-Cl	21
11	2c-Cl	7
12	2d-Cl	8
13	3-Cl	3.7
14	4a-Cl	33/110 °C
15	4b-Cl	477/110 °C

[a] CH<sub>2</sub>Cl<sub>2</sub> as solvent.<sup>[4]</sup>

Schwesinger et al., *Chem. Eur. J.*, 2006, 12, 429 – 437.

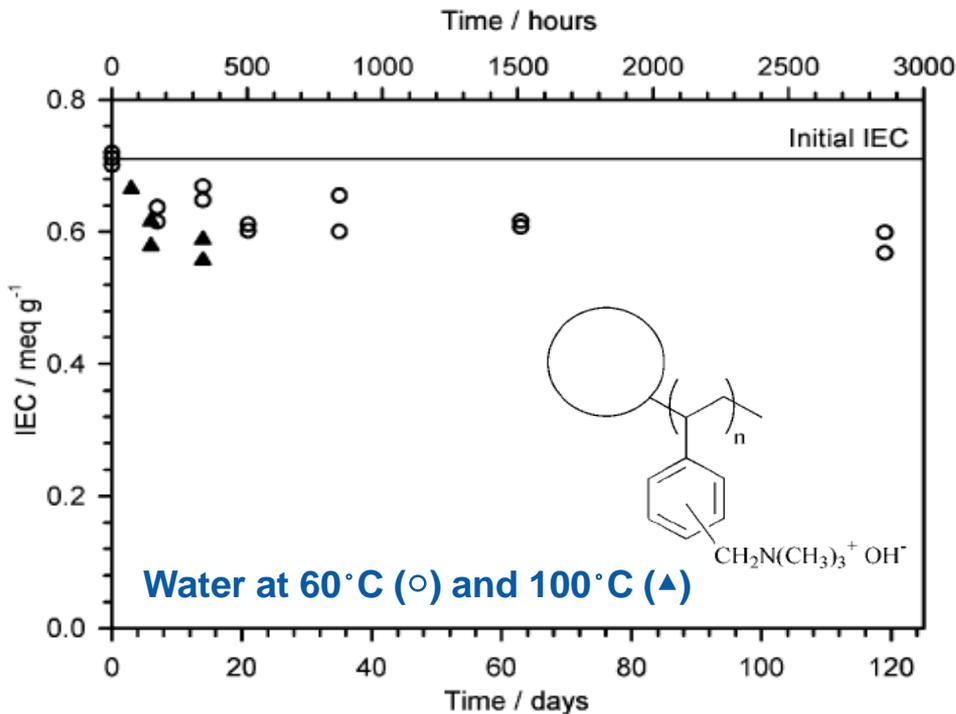
**Increased base strength and stability come at cost of size/hydrophobicity.**



Ion	# of atoms
triflate	8
TMA	17
4b	165

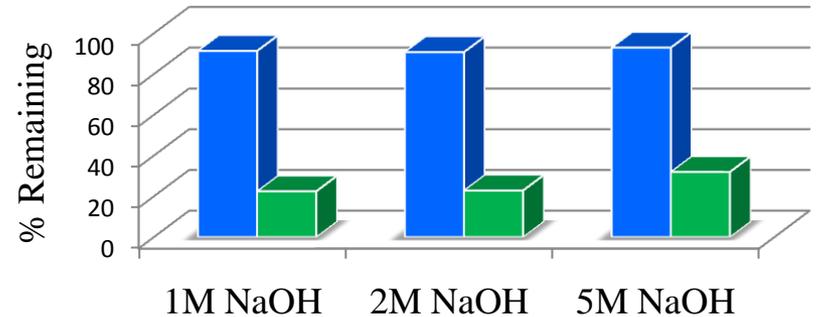


# Stability of ammonium cations

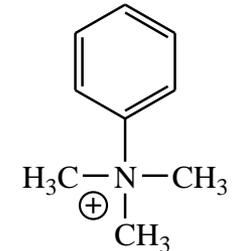
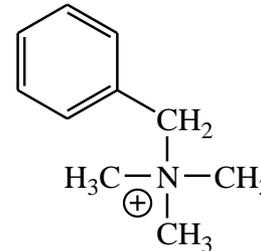


T.N. Danks, R.C.T Slade, J.R Varcoe, J Mater. Chem., 2003, 13, 712.

## NMR Study - 0.1 M cation conc. 80 °C



■ benzyltrimethylammonium ■ phenyltrimethylammonium

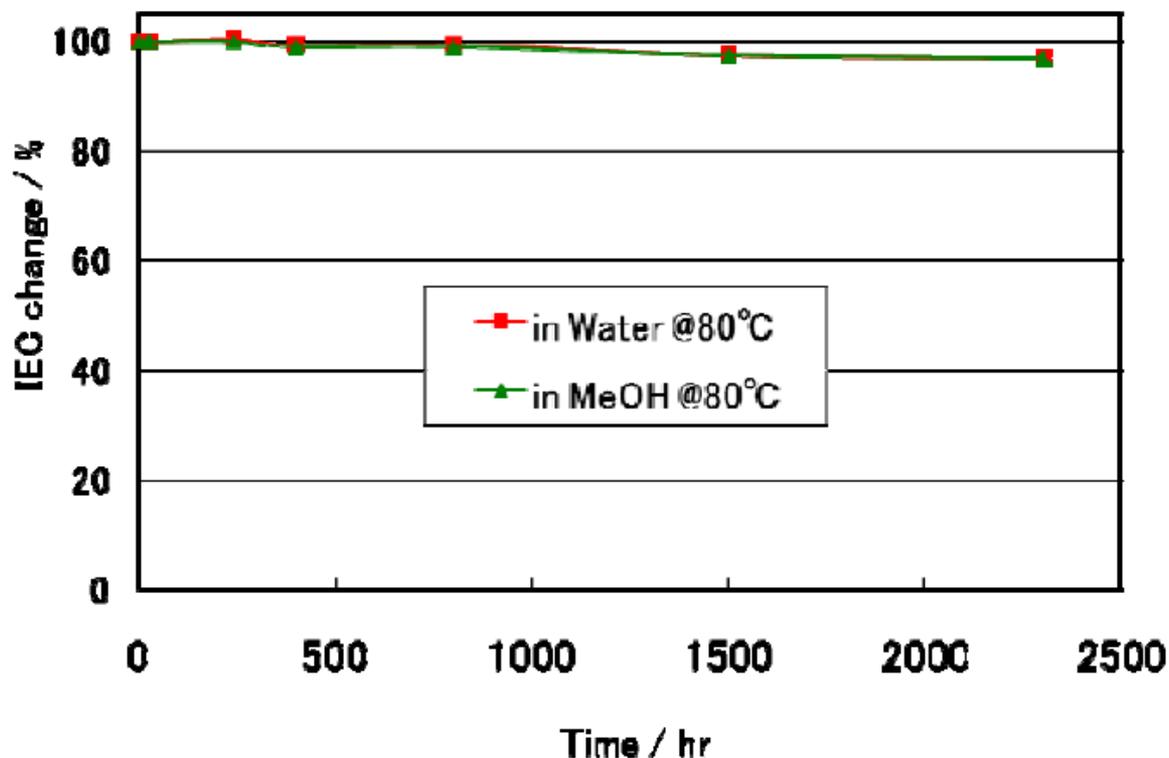


B.R. Einsla, S. Chempath, L.R. Pratt, J.M. Boncella, J. Rau, C. Macomber and B.S. Pivovar, *ECS Transactions*, 2007; v.11, no.1, p.1173-1180.

While high T durability is less than ideal it is still potentially acceptable for some applications and better than expected several years ago. Due to high dependence of rates on T, specific temperatures are very important.



# Tokuyama Membranes



Role of carbonate unclear.

Follow up in Tokuyama presentation

Further suggests that stability may be adequate for a number of applications.

**Fig. 1 Thermal durability of AEMs at 80 °C**

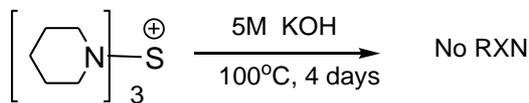
Membrane was ion-exchanged to OH<sup>-</sup> form before durability test. □ is kept in water, △ is kept in Methanol

Yanagi and Fukuta, *ECS Trans.*, 16 (2), 257-262 (2008).

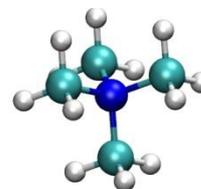
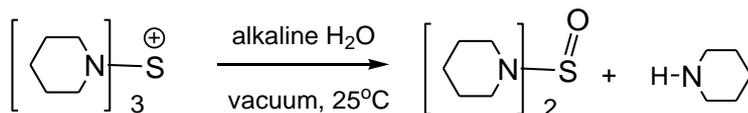


# Effect of Water Concentration, Dielectric Constant, and OH<sup>-</sup> Solvation

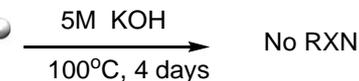
## NMR Study (unpublished D. Thorn, LANL)



but!



TMA

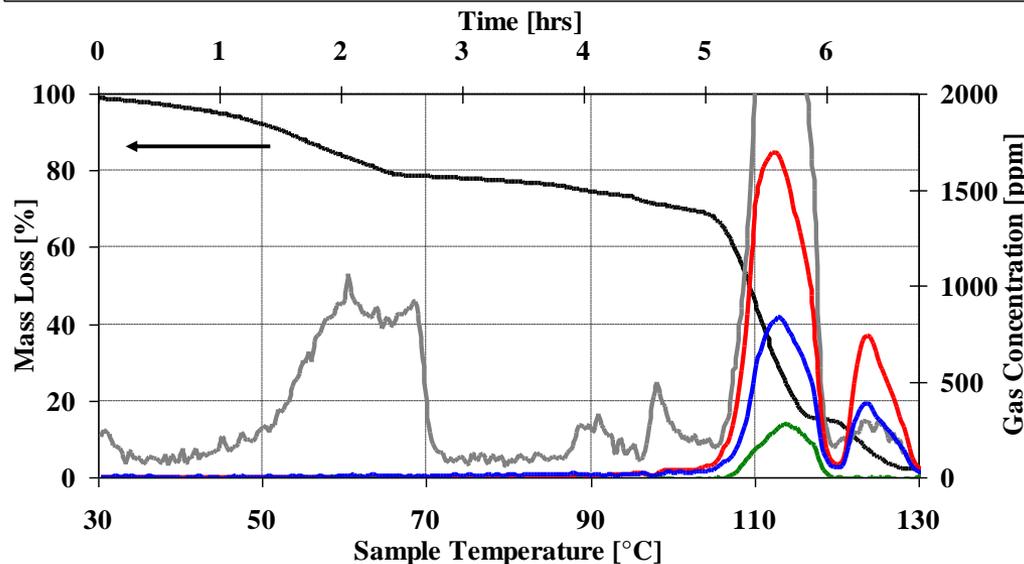


but!

## EGA Study

C. Macomber, J. Boncella, B. Pivovar, J. Rau, *J. Therm. Anal. And Cal.*, 93(1), 225-229 (2008).

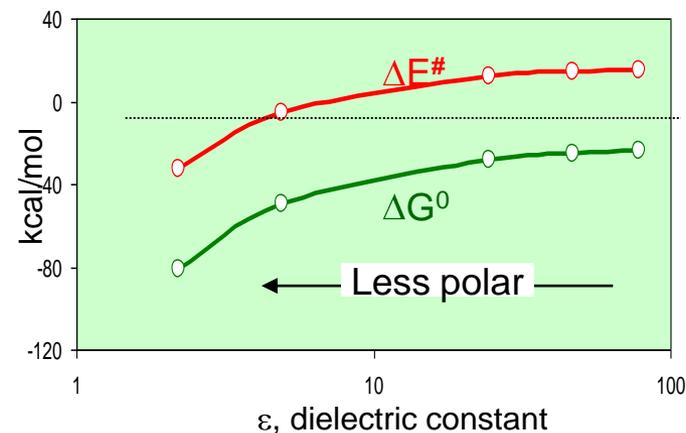
— Mass Loss — Water — Trimethylamine — Methanol — Dimethyl Ether



## Computational study

S. Chempath, B. Einsla, L. Pratt, C. Macomber, J. Boncella, J. Rau, B. Pivovar, *J. Phys. Chem. C*, 112(9), 3179-3182 (2008).

## B3LYP/6-311++g(2d,p) & PCM

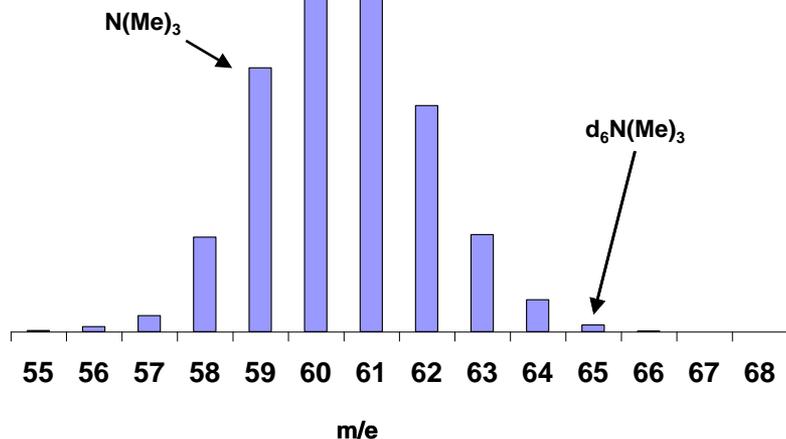


Water stabilizes hydroxide lessening S<sub>N</sub>2 attack



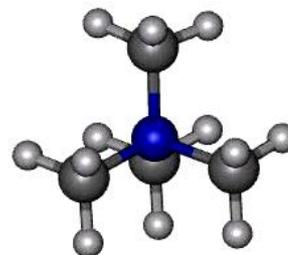
# Ylide Formation

C. Macomber, J. Boncella,  
B. Pivovar, J. Rau, *J.*  
*Therm. Anal. And Cal.*,  
93(1), 225-229 (2008).

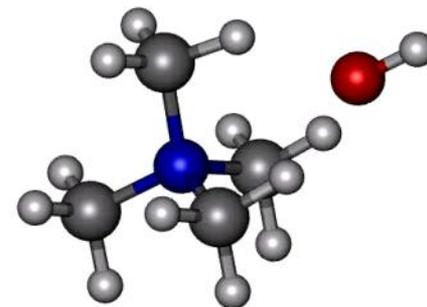


Isotopic labeling yields scrambled samples.  
Confirms presence of ylide species.

$S_N2$



**YLIDE**



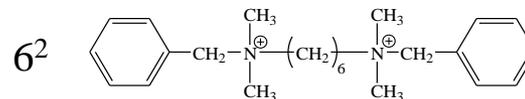
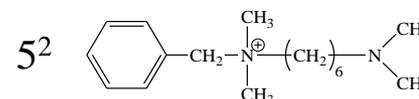
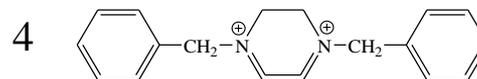
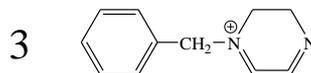
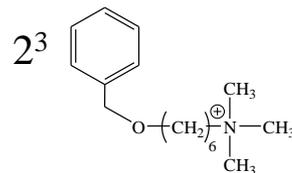
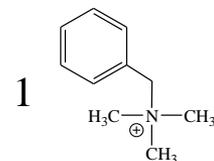
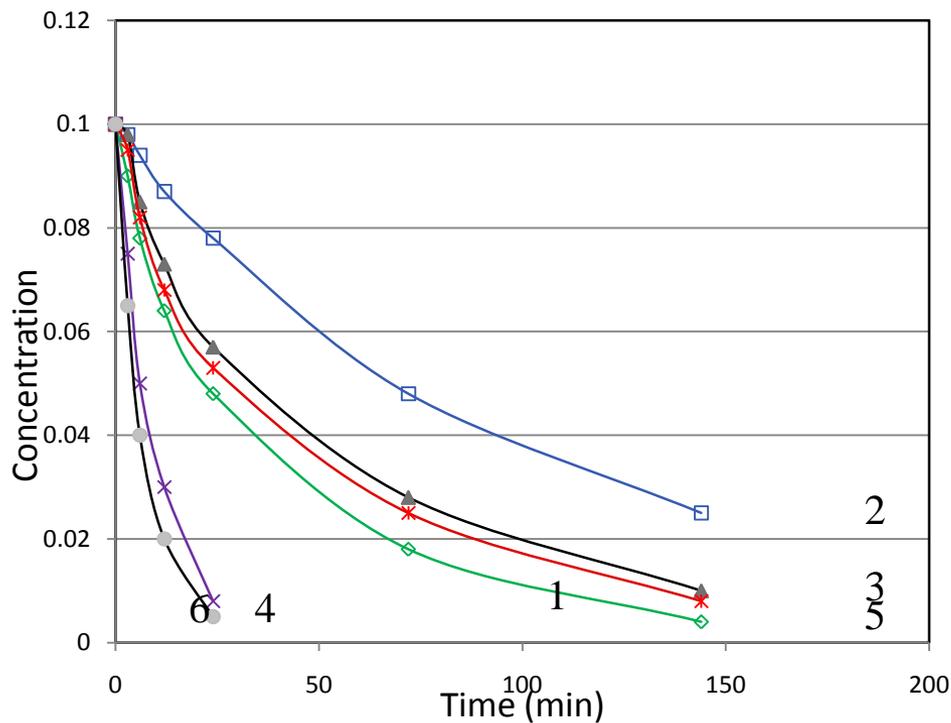
$S_N2$  attack results in MeOH and  
trimethyl amine.

Ylide attack results in H<sub>2</sub>O and  
(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>CH<sub>2</sub><sup>-</sup>

Ylide attack can result in  
degradation reactions



# NMR Degradation of Cations (0.1M) in 2M NaOH at 160°C



Half-life (min)	Literature <sup>1</sup> (min)
23	29.1
73	
36	42
8	2.3
29	
7	

<sup>1</sup>Bauer, B.; Strathmann, H.; Effenberger, F. *Desalination* 1990, 79, 125.

<sup>2</sup>J.R. Varcoe, R.C.T. Slade, G.L. Wright and Y. Chen, *J. Phys. Chem. B*, 110, 21041 (2006).

<sup>3</sup>Tomoi, M.; Yamaguchi, K.; Ando, R.; Kantake, Y.; Aosaki, Y.; Kubota, H. *J. Appl. Polym. Sci.* 1997, 64, 1161.

3 cations with improved stability compared to BTMA.

3x improvement in stability quantified.

160°C compromise between time and physical factors.



# Membrane Stability beyond OH<sup>-</sup> attack

- Most of the effort to date has focused on chemical degradation
- PEM systems have been investigated extensively for degradation by additional mechanisms (Mechanical, RH, peroxide)
- As most current AEMs are based on HCs, lessons learned from PEMs suggest
  - Higher water uptakes and higher modulus leads to poorer durability to RH cycling and mechanical issues (exacerbated by reduced conductivity of AEMs and tendency to go to even higher water uptakes)
  - HC membranes also show lower stability in peroxide, but this may be less of an issue in base.



# Transport/Conductivity

- Relatively little exists regarding transport properties of AEMs, most of the focus has been on conductivity often as a function of water uptake and/or ion exchange capacity (IEC)
- PEM systems have been investigated extensively for properties such as permeability, water self diffusion coefficient, electro-osmotic drag and the dependence of these properties on chemistry and morphology.
- As most current AEMs are based on HCs, speculation can be made using PEM results as guides.



# Conductivity – Protons vs. Cations

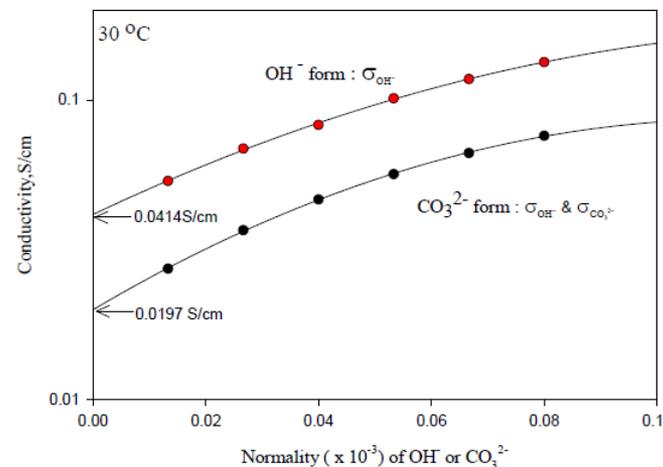
## Protons vs. Anions

\*Cussler, Diffusion, 1997.

Infinite Diffusion Coefficient\* ( $10^{-5}$

<u>Ion</u>	<u>cm<sup>2</sup>/s</u>
H <sup>+</sup>	9.3
OH <sup>-</sup>	5.3
CO <sub>3</sub> <sup>2-</sup>	0.9

Yu Seung Kim, 2010 DOE AMR presentation, available at [http://www.hydrogen.energy.gov/pdfs/review10/fc043\\_kim\\_2010\\_o\\_web.pdf](http://www.hydrogen.energy.gov/pdfs/review10/fc043_kim_2010_o_web.pdf)



**At similar concentrations/mobilities, significantly increased ohmic losses should be expected.**

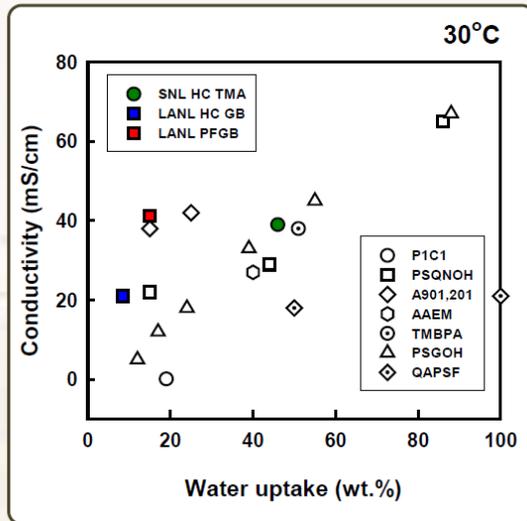
**Findings in membranes have reasonably reflected what might be expected (data at right, plus Tokuyama data shown in later presentation ).**



# Conductivity vs Water Uptake

Yu Seung Kim, 2010 DOE AMR presentation, available at [http://www.hydrogen.energy.gov/pdfs/review10/fc043\\_kim\\_2010\\_o\\_web.pdf](http://www.hydrogen.energy.gov/pdfs/review10/fc043_kim_2010_o_web.pdf)

## Hydroxyl Conductivity Comparison at RT



Sample	Water uptake (wt.%)	IEC (meq./g)	$\sigma$ (mS/cm)
P1C1 <sup>a</sup>	19	0.5	0.13
PSQNOH50 <sup>b</sup>	15	1.9	22
PSQNOH80 <sup>b</sup>	86	2.8	65
A901 <sup>c</sup>	15	2.6	38
A201 <sup>c</sup>	25	1.7	42
AAEM <sup>d</sup>	40	-	27
TMBPA <sup>e</sup>	51	0.7	38
PSGOH <sup>f</sup>	17	1.2	12
PSGOH <sup>f</sup>	55	1.9	45
QAPSF1 <sup>g</sup>	50	-	18
QAPSF2 <sup>g</sup>	100	-	21
SNL HC TMA	46	1.32	39
LANL HC GB	8.5	1.2	21
LANL PFGB	15	0.9	41

- Poly(CTFE-*alt*-VE) - Bruno Ameduri
- Poly(arylene ether sulfone) - Suobo Zhang group
- Hydrocarbon polymer - Tokuyama Corporation
- Poly(ethylene-co-tetrafluoroethylene) - John R. Varcoe
- Poly(arylene ether sulfone) - Michael Hipps
- Poly(arylene ether sulfone) - Suobo Zhang group
- Poly(arylene ether sulfone) - Paul A. Kohl group

## PEM conductivity at RT

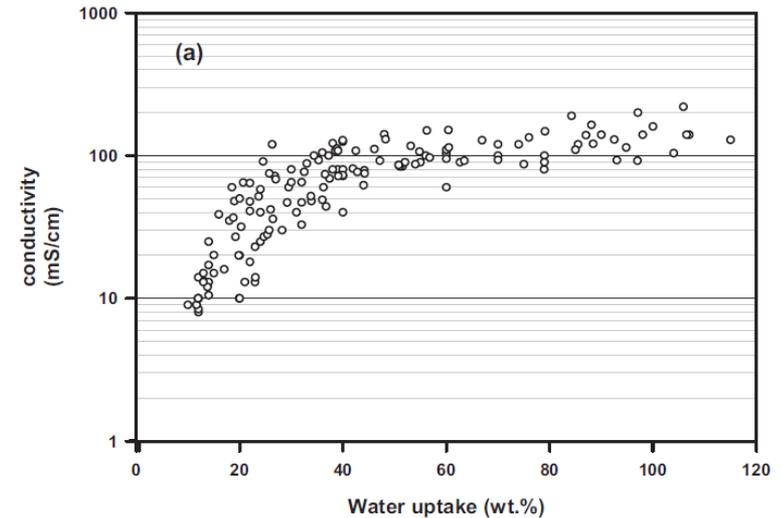


Figure 2

Proton conductivity as a function of (a) water uptake and (b) weight-based ion exchange capacity (IEC) of 32 sulfonated polymers. Proton conductivity under fully hydrated conditions at ambient temperature was taken from the literature (10–41).

Kim and Pivovar, Annu. Rev. Chem. Biomol. Eng. 2010. 1:123–48.

- Conductivities of AEMs tend to be less than that of PEMs, both systems have trends for increasing conductivity with increasing IEC/water uptake.
- Key issues revolve around how important are ohmic loss and permeability, how thin can membranes be made, and what is the impact of increasing water uptake as a method to address IEC.



# Water Transport (NMR)

M Hibbs, M Hickner, T Alam, S McIntyre, C Fujimoto, and C Cornelius; Chemistry of Materials, 2008. **20**(7): p. 2566-2573.

Klaus-Dieter Kreuer, S Paddison, ESpoehr, and M Schuster; Chemical Reviews, 2004. **104**(10): p. 4637-4678.

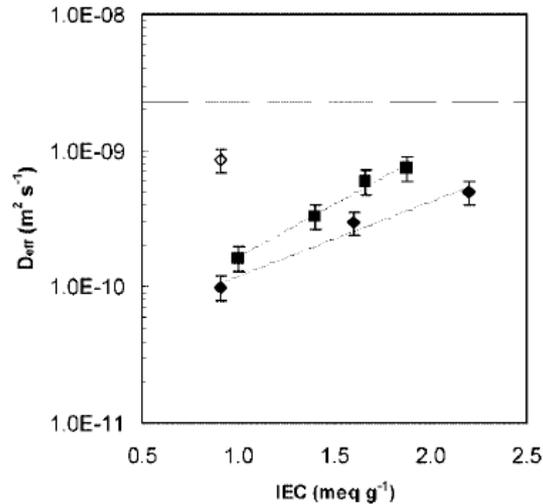
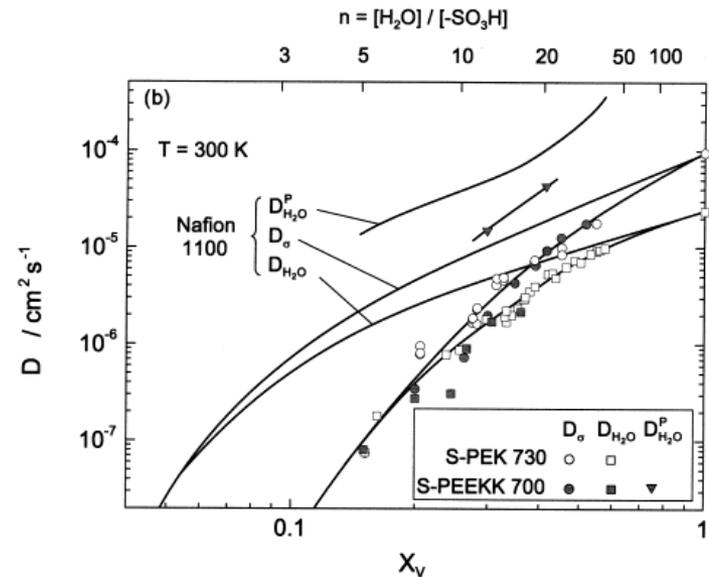


Figure 5. Effective water self-diffusion coefficient at 25 °C ( $\Delta = 50$  ms) in the membrane as a function of ion exchange capacity: ( $\diamond$ ) Nafion, ( $\blacksquare$ ) PS-AEM, ( $\blacklozenge$ ) SDAPP, and (dashed line) liquid bulk water.



- A single example exists in the literature comparing PFG NMR water self diffusion values of an AEM to PEMs (left).
- While reasonably consistent with the HC PEM and other reported studies (highlighted right), additional studies of this type are necessary.
- Water permeability as well as electro-osmotic drag and reactant permeabilities are also often reported for PEMs. These values critical for modeling systems.



# Chemistry and Morphology (PEM)

32

K.D. Kreuer / Journal of Membrane Science 185 (2001) 29–39

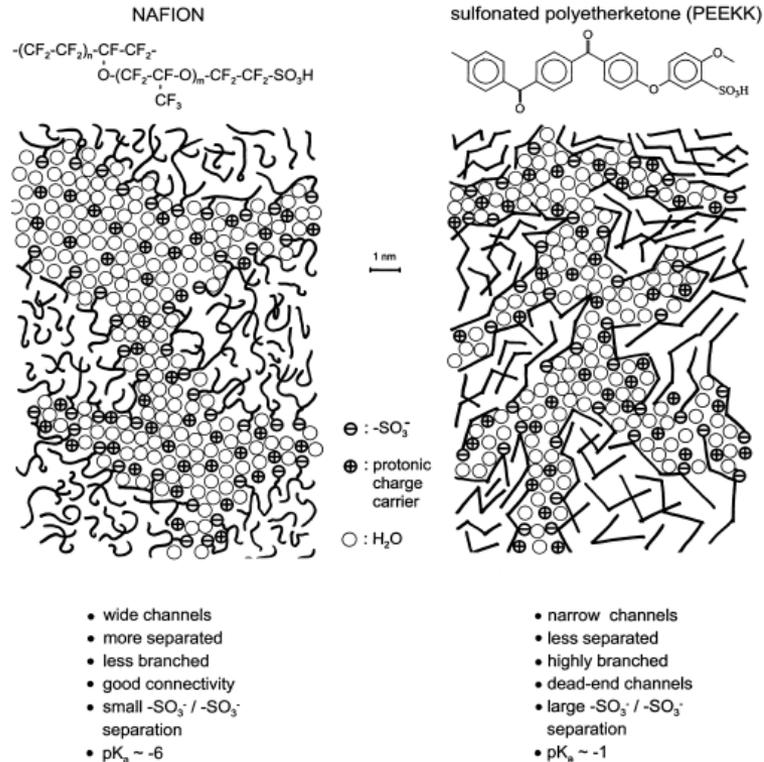


Fig. 2. Schematic representation of the microstructures of NAFION and a sulfonated polyetherketone (derived from SAXS experiments [19]) illustrating the less pronounced hydrophobic/hydrophilic separation of the latter compared to the first.

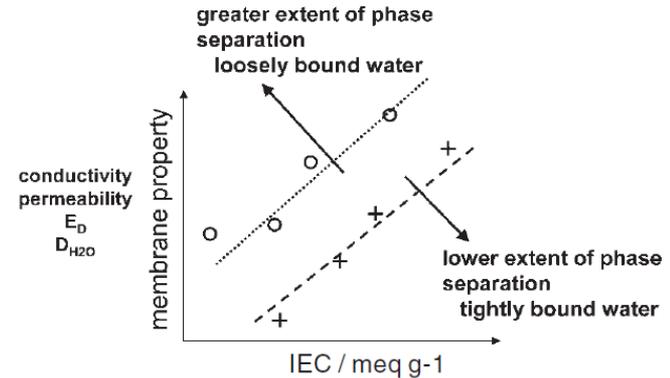


Fig. 12 Example comparison of the properties of a strongly and weakly phase separated system.

Hickner, M.A. and B.S. Pivovar, Fuel Cells, 2005. 5(2): p. 213-229

- Numerous examples of how structure and chemistry have been used to interpret PEM properties. Trends observed likely consistent between cation and anion exchange membranes.



# Chemistry and Morphology

- Numerous tools not yet applied to AEMs
- Morphology
  - Stress-Strain (mm)
  - SAXS (nm –  $\mu\text{m}$ )
  - Nano-Indentation ( $>10\text{s nm}$ )
  - Microscopy ( $\text{\AA}$  – nm)
  - Neutron scattering (nm –  $\mu\text{m}$ )
- Chemistry
  - IR/Raman/UV
  - NMR



# Break Out Session Focus

## Anion Exchange Membranes – Stability

Consider (Primary):

- Stability of Alkaline Membranes (How long do today's materials last, what is reasonable intermediate target, what is ultimate goal – compare to PEMs)
- Importance/Effect of conditions (Temperature, Hydration, Counterion, Peroxide?, Mechanical, RH cycling, other?)
- Cations: Traditional/Alternative or Advanced
- Membranes: Backbones (systems explored, impact on durability)

(Secondary):

- Issues that crossover with Session 2 (for example impact of Water Uptake or phase separation on stability)

# Break Out Session Focus

## Anion Exchange Membranes – Transport/Conductivity

Consider (Primary):

- Conductivity (Today's materials, targets, impact of counterion, comparison with PEMs)
- Water transport (Today's materials, targets, impact of counterion, comparison with PEMs)
- Water Uptake (Today's materials, targets, impact of counterion, comparison with PEMs)
- Membrane Chemistries and how they impact structure and transport properties

(Secondary):

- Issues that crossover with Session 1 (for example impact of Water Uptake or phase separation on stability)

