Status and Challenges of Hydroxide Ion-Conducting Polymers for Anion Exchange Membrane Applications

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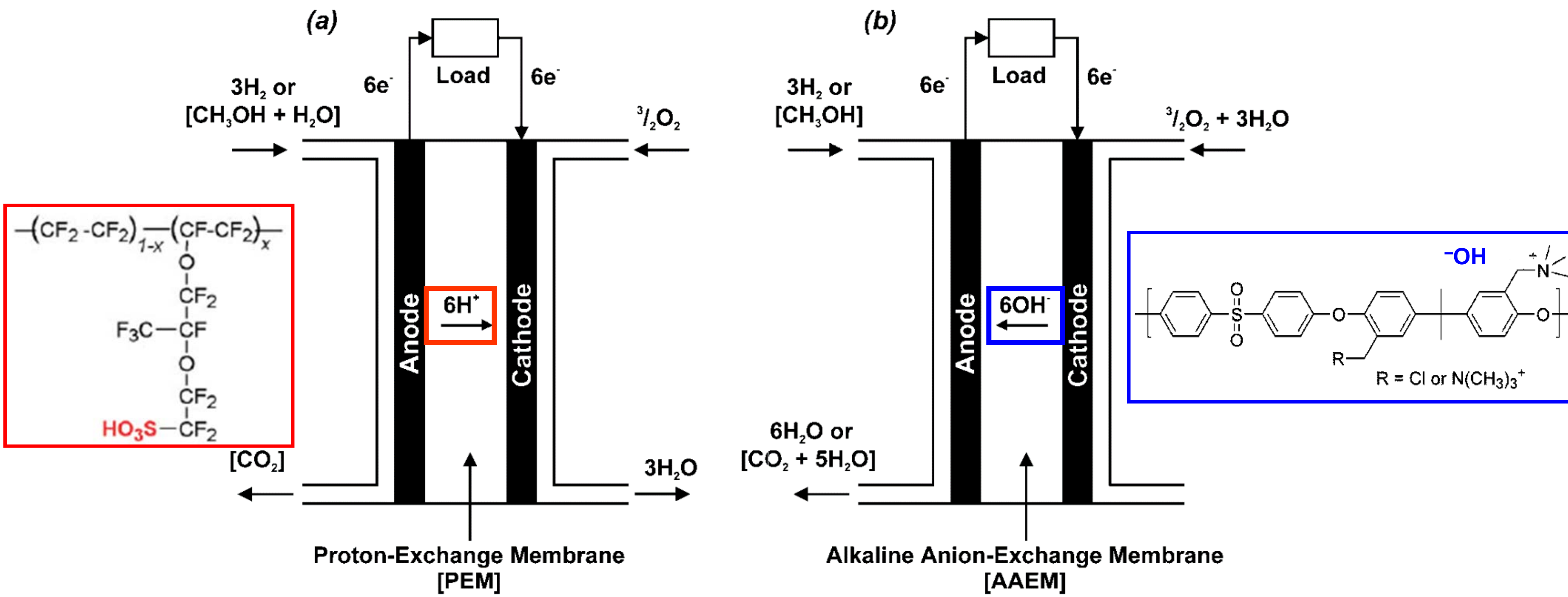
Solid Electrolyte in Fuel Cells: PEM *vs.* AEM



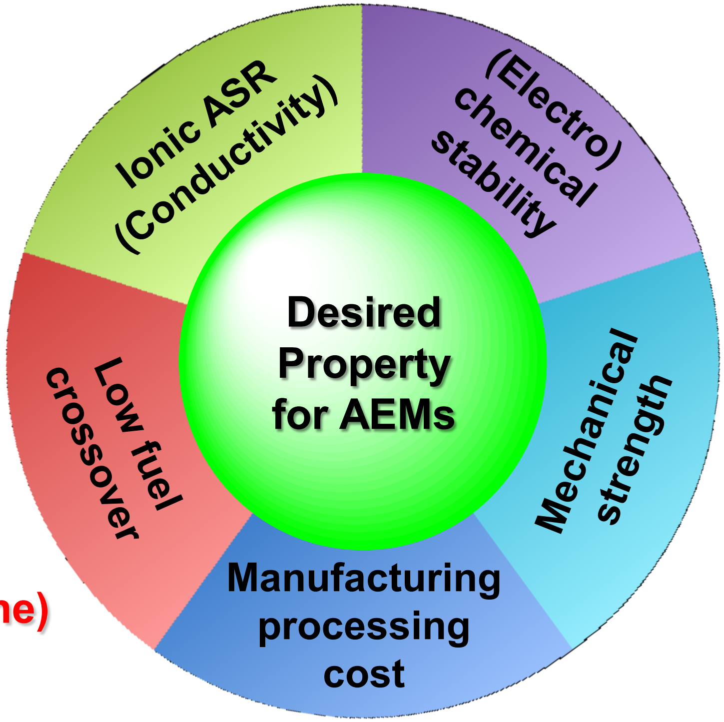
	PEM	AEM
Reaction at Anode:	$H_2 \longrightarrow 2\,H^+ + 2\,e^-$	$H_2 + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^-$
Reaction at Cathode:	$½\,O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O$	$½\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$
Overall Reaction:	$H_2 + ½\,O_2 \longrightarrow$ electricity + H_2O	$H_2 + ½\,O_2 \longrightarrow$ electricity + H_2O

- Since 1960s (most advanced fuel cells)
- **Bipolar plate**: titanium (*acidic* environment)
- **Catalyst**: expensive Pt
- **PEM**: insufficient H^+ conductivity at low RH
  high cost of Nafion

- Since 2010s (new concept)
- **Bipolar plate**: stainless steel (*basic* environment)
- **Catalyst**: non-noble metals possible (Ag, Ni)
- **AEM**: insufficient OH^- conductivity
  poor stability against OH^-

Major Requirements for AEMs

- **Key component in alkaline membrane fuel cells**
  - Transport OH^- (and H_2O)
  - Separate H_2 and O_2
- **Required Properties in AEM**
  - Hydroxide ion-containing polymer materials
  - **Synthesis**
    - **Inexpensive, less hazardous chemicals**
    - **short synthetic steps**
    - **easily scalable, quality controlled process**
    - **high molecular weights**
  - **Good ion conductivity** (*even at low RH*)
    - **low area specific resistance (thin membrane)**
    - **high IEC**
  - **Good stability**
    - **chemical/electrochemical: 1M NaOH, >80 °C**
    - **Mechanical: high tensile strength with good elongation behavior**
  - **Low H_2 and O_2 crossover**

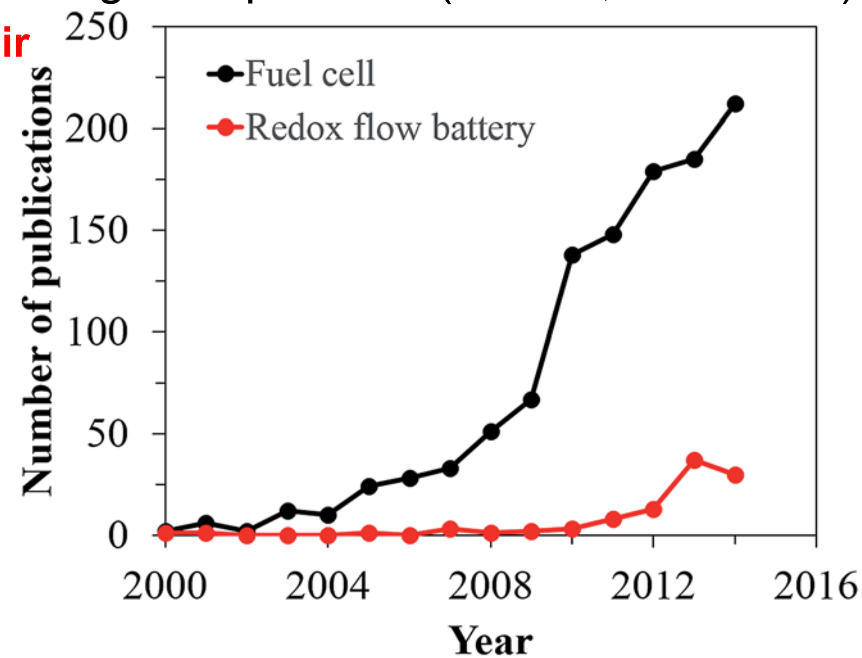


Current Status & Challenges of AEMs for Electrochemical Energy Conversion & Storage

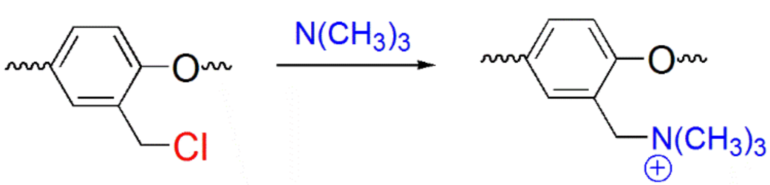
Unlike Nafion in PEM, there is no benchmark membrane in AEM yet!

» Limitation of commercially available AEMs for use in electrochemical energy conversion technology

- Asahi Chemical, Asahi Glass, Tokuyama, FuMa-Tech, Ionics, Solvay, Tianwei Membrane (review: Xu, *J. Membr. Sci.* **2005**, *263*, 1)
- **Too thick:** 100-200 micron (desired <20 micron)
- **Too high area specific resistance:** >1 ohm cm^2 (desired <0.02 ohm cm^2)
- **Moderate IEC:** 1.0–2.0 mequiv/g (or mmol/g)
- **Poor stability** (chemical & mechanical) at high temperature (>80 ^oC, 1M NaOH)
  1. **to avoid HCO_3^- from OH^- and CO_2 in air**
  2. **to generate more power**

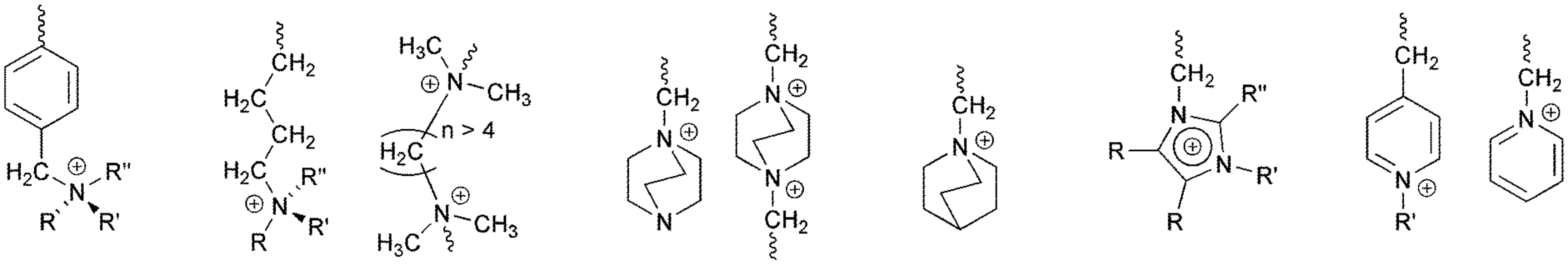


AEM synthesis via chloromethylation



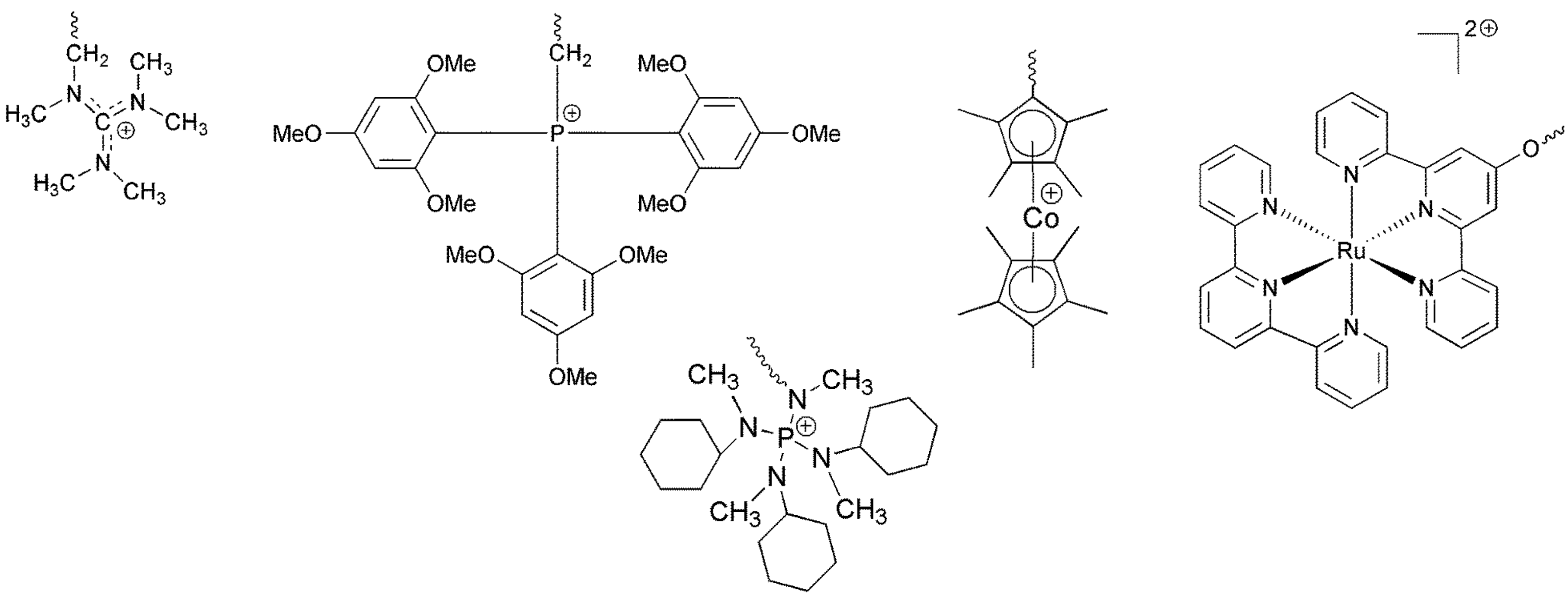
Moon, et al. *RSC Adv.* **2015**, 5, 37206

Tethered Cations in AEMs



A B C D E F

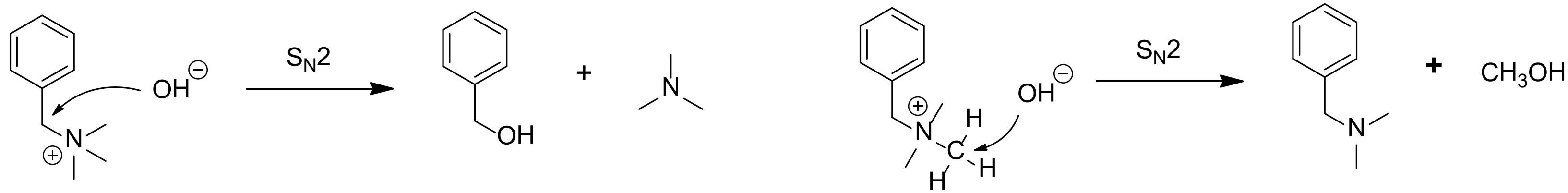
G H I J



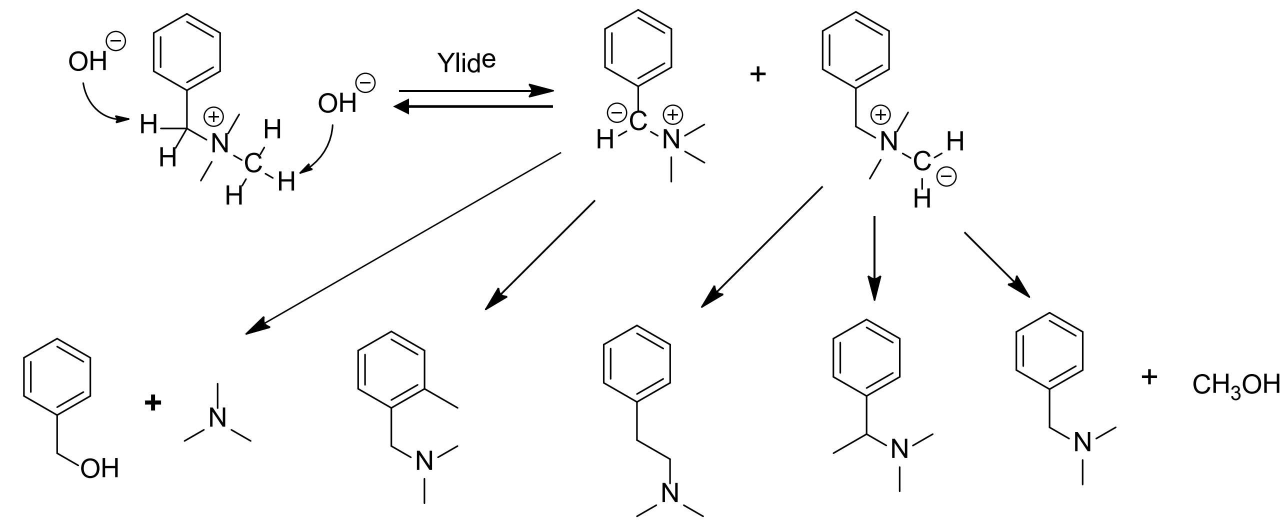
Review: J. R. Varcoe, et al. *Energy Environ. Sci.* **2014**, *7*, 3135

Degradation Routes of Quaternary Ammoniums

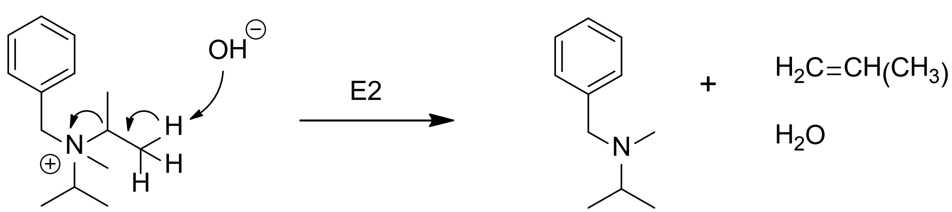
(a) Nucleophilic Substitution Reaction by Hydroxide Ion: Dealkylation



(b) N-ylide formations & Rearrangements



(c) Hofmann Elimination: Hydroxide Ion abstracts β-Hydrogen



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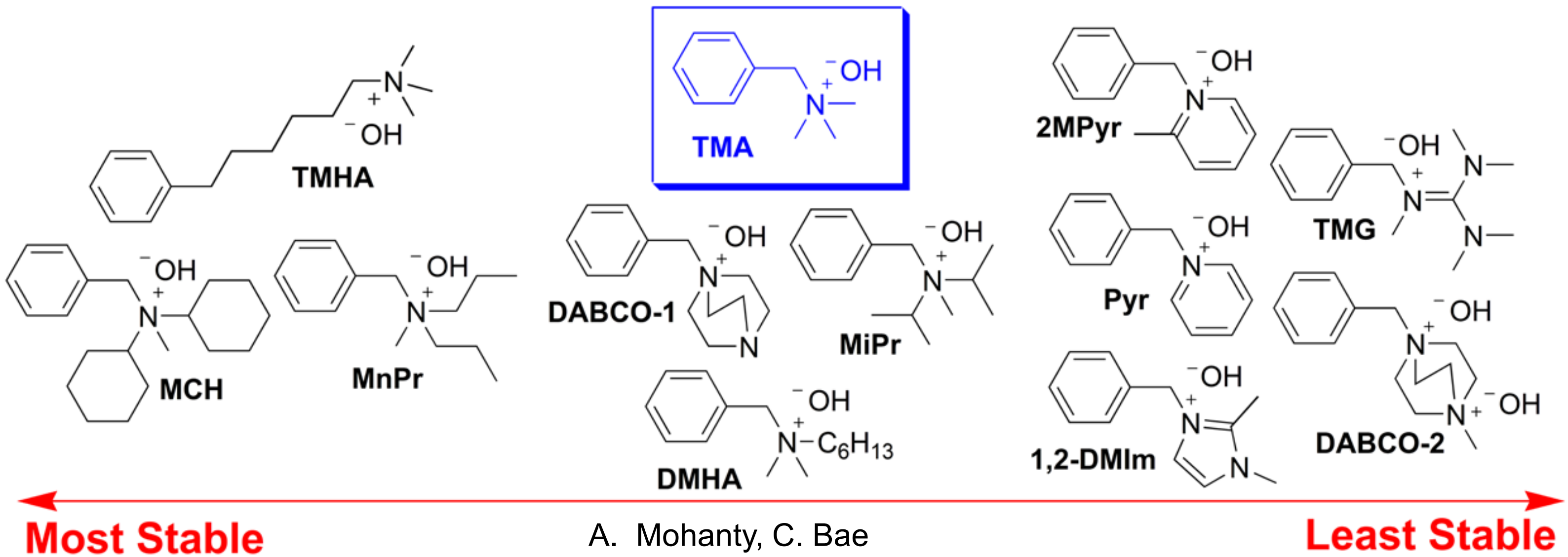
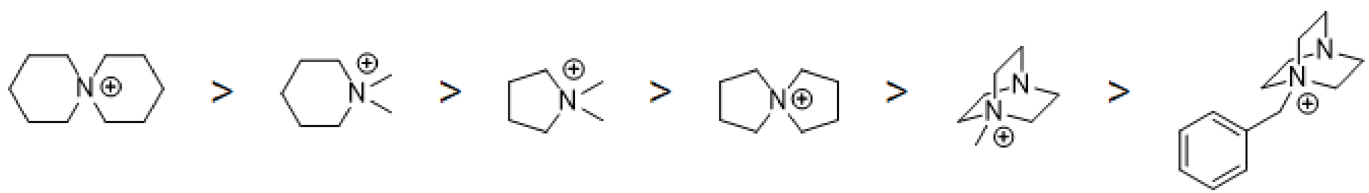
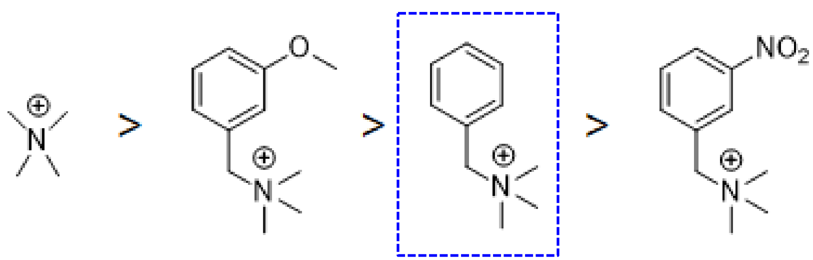
Stability Comparison of Small Molecule Ammoniums



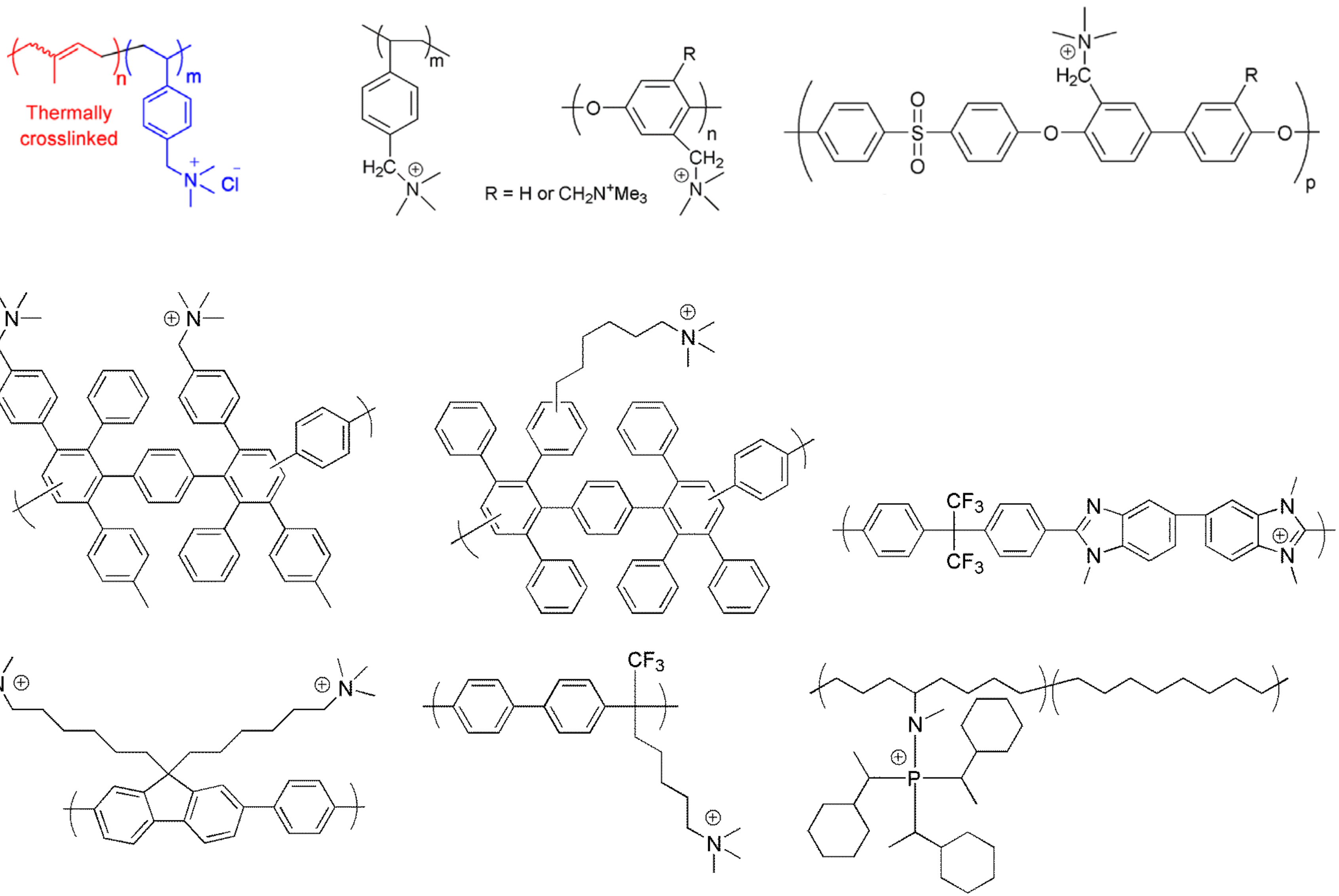
A. Mohanty, C. Bae
J. Mater. Chem. A. **2014**, *2*, 17314





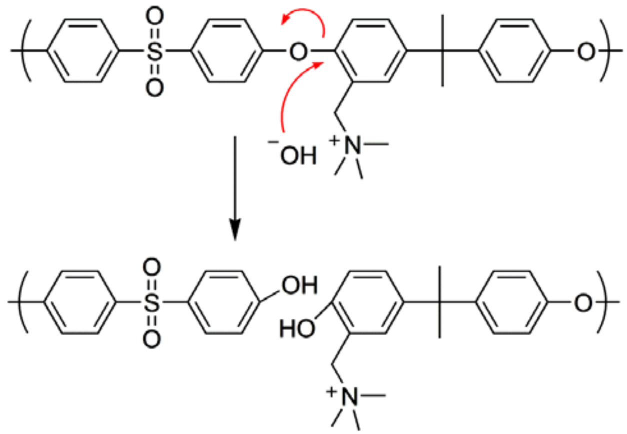
M.G. Marino, K. D. Kreuer
ChemSusChem **2015**, *8*, 513

Polymer Backbones in AEMs

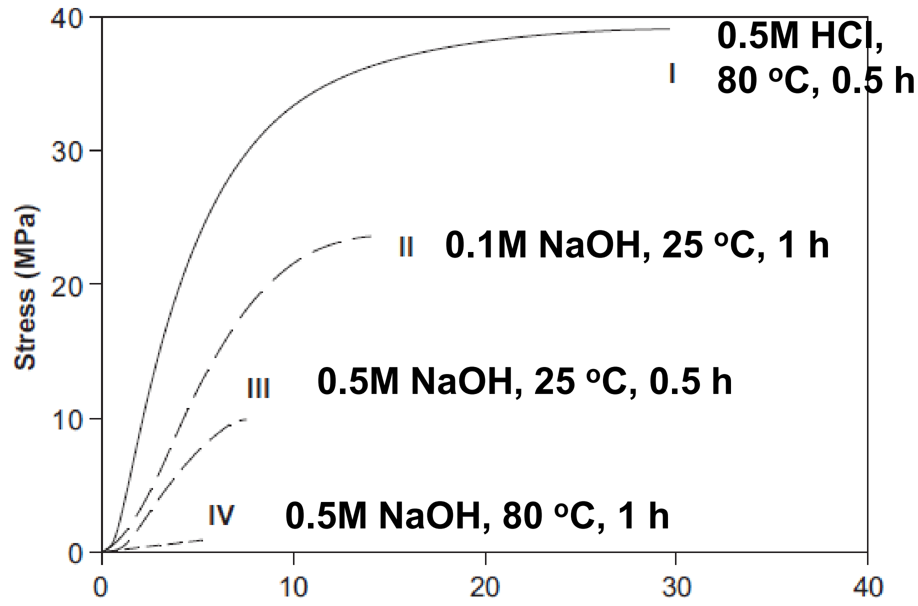


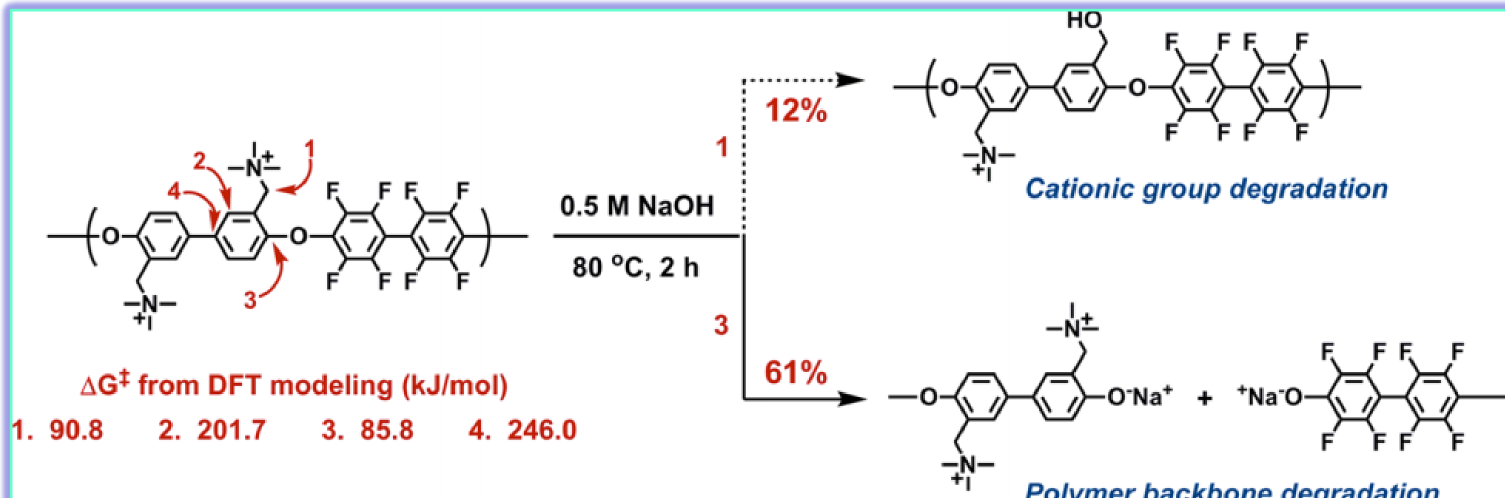
Chemical Degradation of Polymer Backbone in AEM

» **Cleavage at Aryl C–O bond**



Kim, *J. Membr. Sci.* **2012**, *423-424*, 438
Ramani, *PNAS* **2013**, *110*, 2490
Hickner, *ACS Macro Lett*. **2013**, *2*, 49





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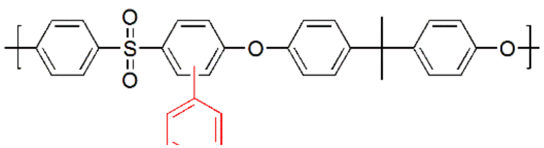
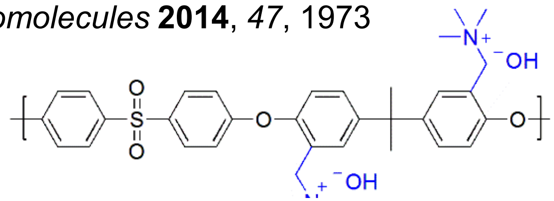
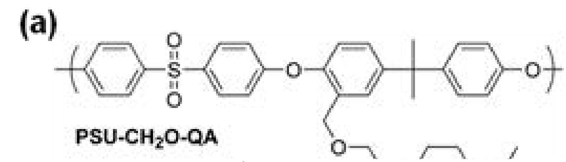
Poor Mechanical Stability of Polysulfone AEMs under Alkaline Conditions

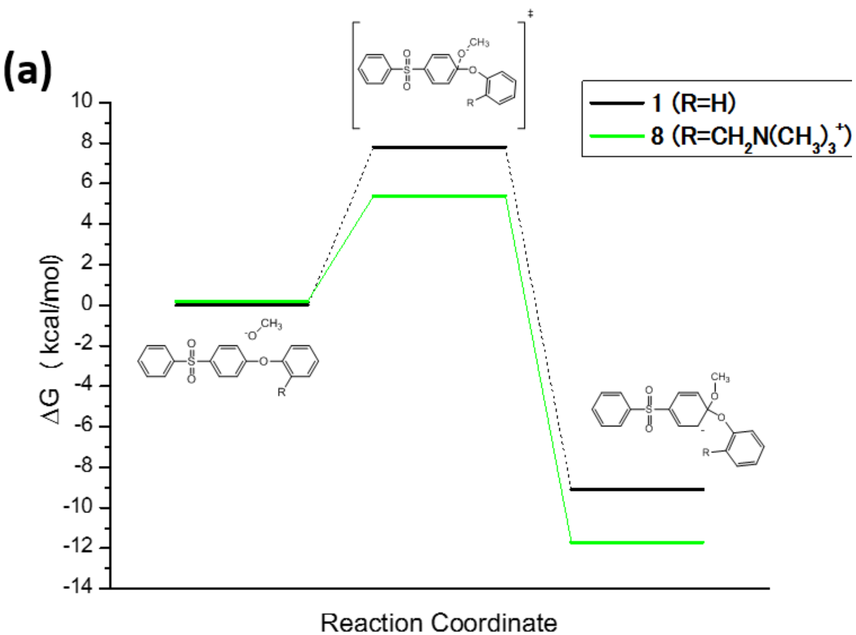
Mohanty, Lee, Zhu, Hickner, Bae, *Macromolecules* **2014**, *47*, 1973

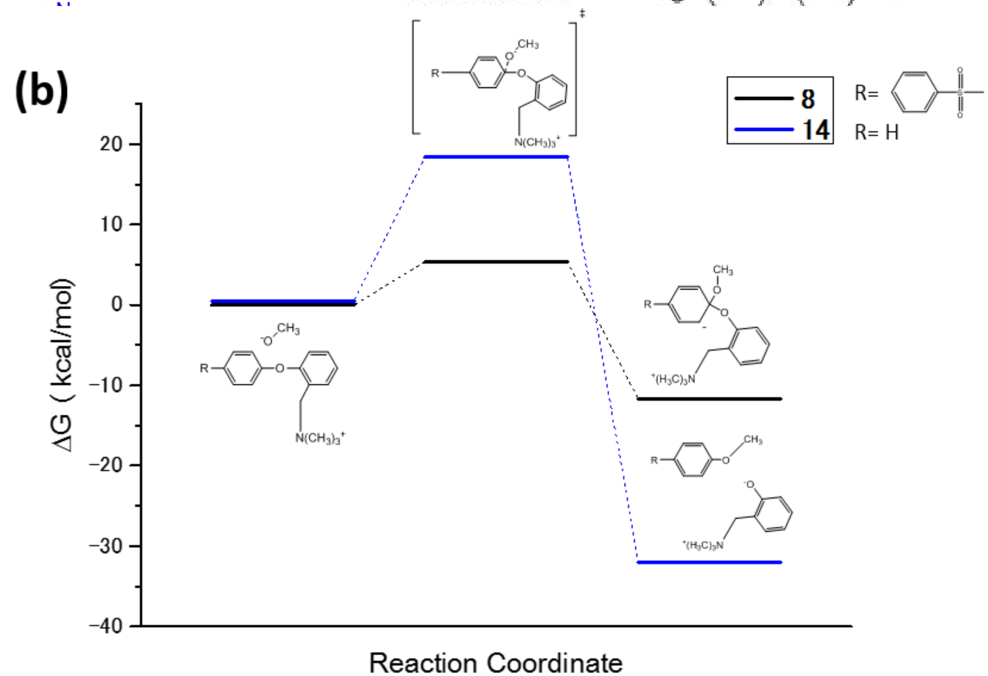
Mohanty *et al.*, *Macromolecules* accepted











Need polymer backbone structures with

- ***Rigid backbone & elastic mechanical property***
- ***High molecular weights***
- ***Avoid aryl C–O bonds if possible***
- ***Convenient synthesis (e.g., avoid metal catalyst in synthesis)***

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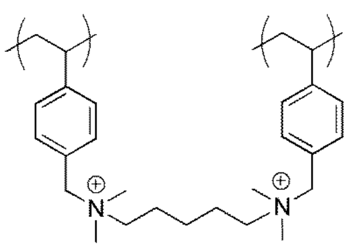
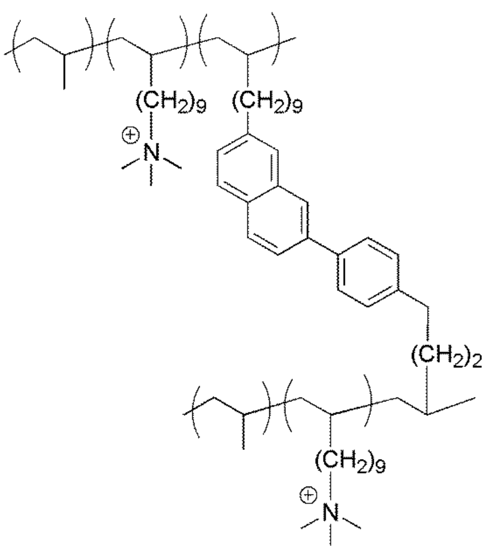
Challenges in AEM: Mechanical Stability

Approaches to enhance mechanical stabilities of AEMs

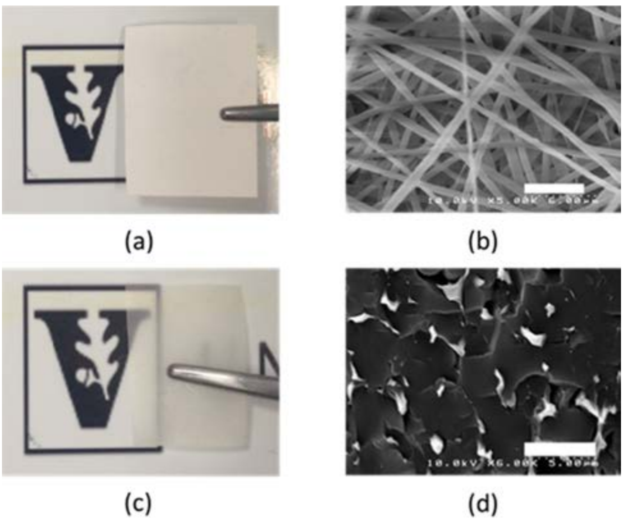
1. Enhance polymer chain entanglement by increasing molecular weights
   – > 100,000 g/mol
2. Decouple the interactions of ionic groups and polymer backbone
   – Longer tether chain for ionic group
   – Phase separation of hydrophilic/hydrophobic domains
3. Crosslinking
4. Composite membranes

Crosslinking



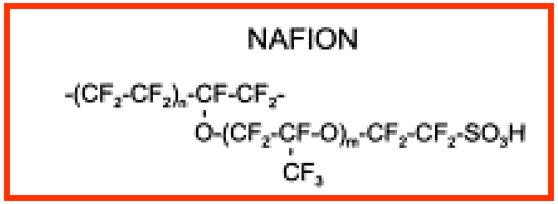


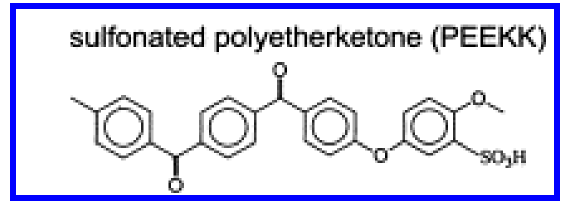
Composite Membrane

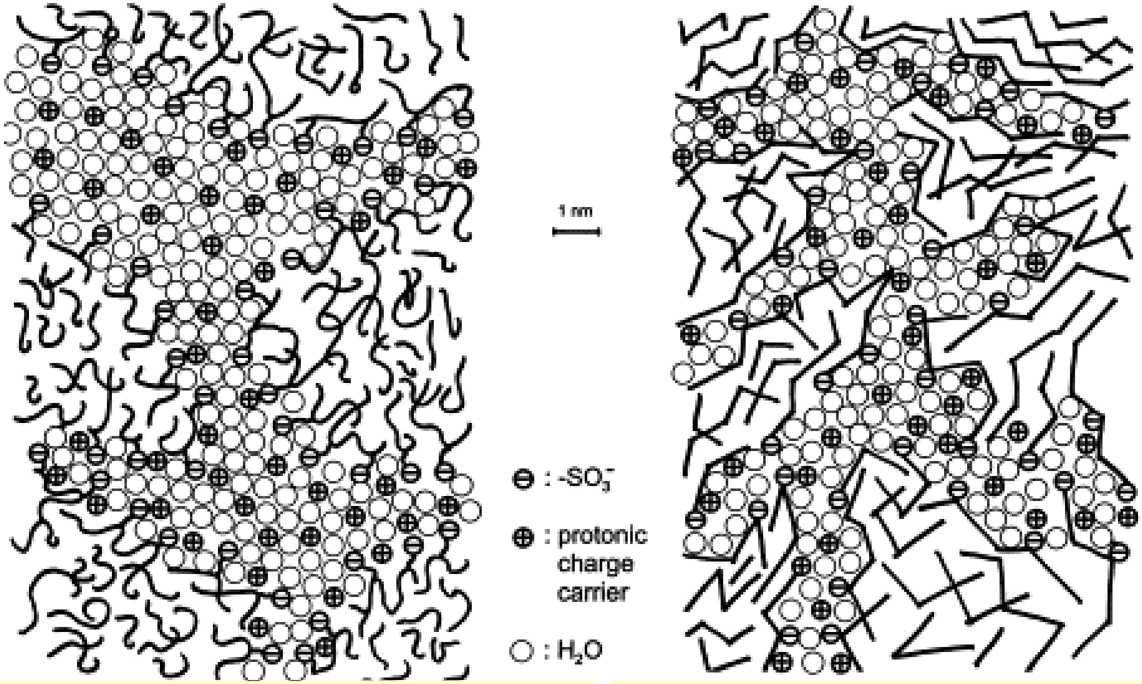


Pintauro, *Macromolecules* **2014**, *47*, 227

Improve Ion Conductivity with Minimum Swelling in Water: Lesson from Nafion







Kreuer, K. D.
J. Membr. Sci.
2001, *185*, 29

Hickner, Pivovar
Fuel Cells **2005**, *5*, 213

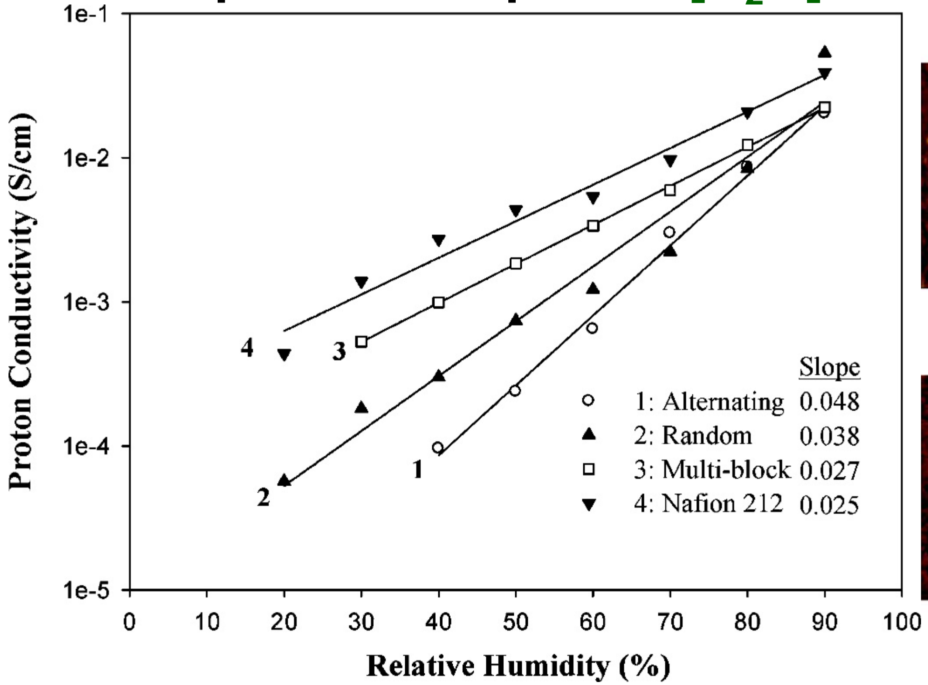
- Close packing of ionic groups
- **Wide channels & good connectivity**
- **Good phase-separated morphology**
- Promotes loosely bound water
- Good water (& H_3O^+) transport

- **Narrow hydrophilic domain channels**
- Highly branched & dead-end channels
- **Lower degree of phase separation**
- More tightly bound water
- Decreased water (& H_3O^+) transport

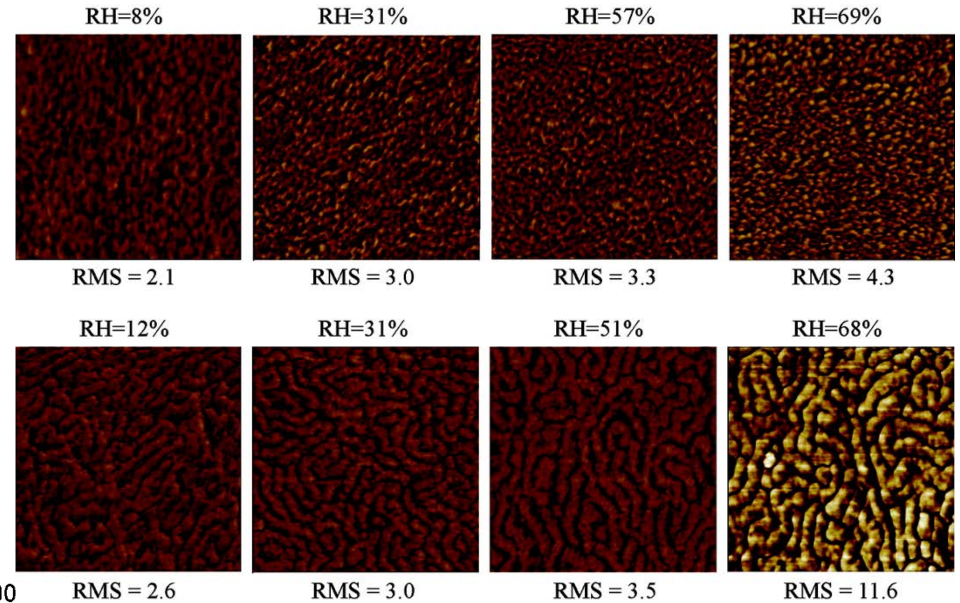
Morphology Control in Hydrophilic-Hydrophobic Sulfonated Block Copolymers

Proton conductivity depends on diffusion of H_3O^+

To improve transport of [H_2O]



Sulfonated *random* copolymer
IEC = 1.53 mequiv/g



Sulfonated *multi-block* copolymer
IEC = 1.51 mequiv/g

Kim, McGrath, Guiver, Pivovar
Chem. Mater. **2008**, *20*, 5636

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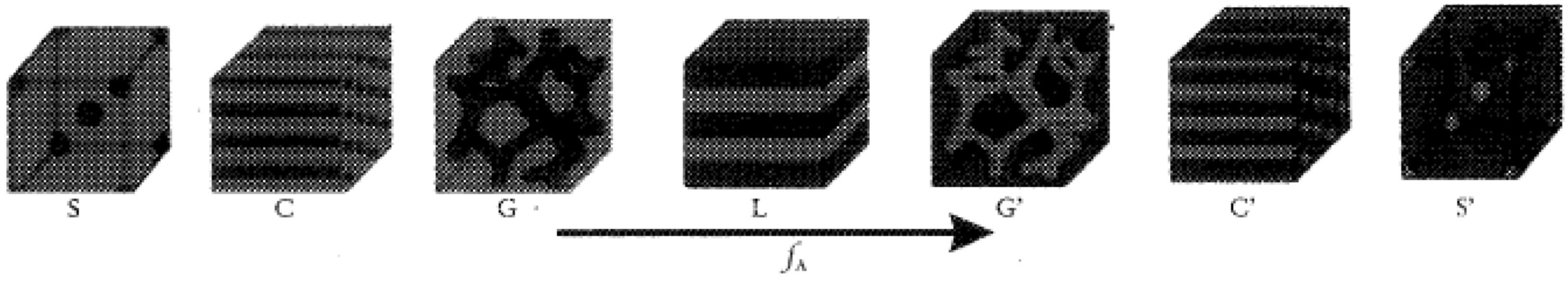
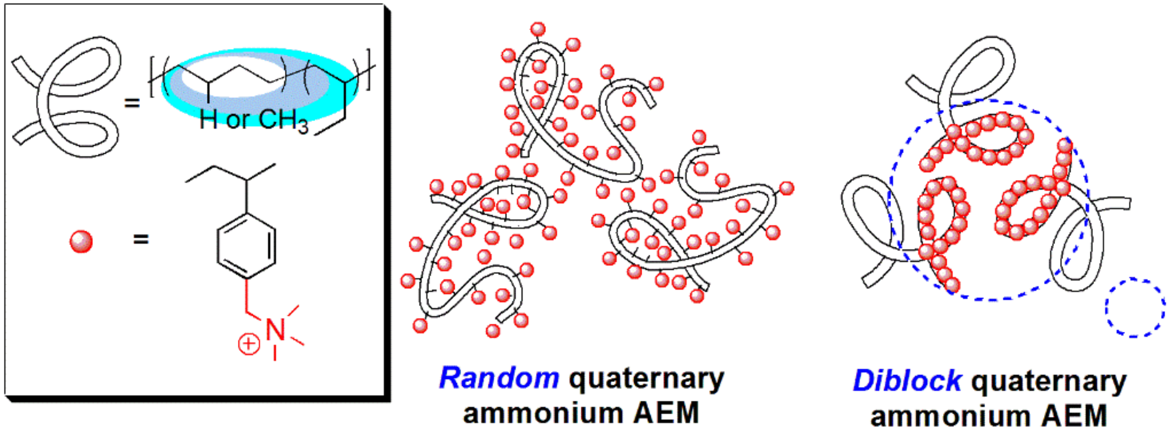
Challenge in AEM: Morphology Control via Polymer Architecture





Morphology of polymer membrane depends on

- ***Structure of ionic groups: short vs. long, bulky vs. compact***
- ***Distribution of ionic groups: random vs. block***
- ***Polarity difference between hydrophilic/hydrophobic units***
- ***Volume fraction (f_x) of hydrophilic/hydrophobic units***

Summary

- **To enhance ionic conductivity (lower resistance)**
  - Add more ionic groups (higher IEC)
  - Create interconnected hydrophilic channels via morphology control
  - Thinner membrane (<20 micron)
- **To improve stability**
  - Avoid vulnerable functional groups at cation and backbone (chemical)
  - Decouple interaction of ionic groups and polymer backbone (chemical & mechanical)
  - High molecular weight polymer backbone, crosslinking, composite membrane (mechanical)
- **To reduce cost**
  - Avoid expensive and toxic chemicals (e.g., chloromethylation)
  - Avoid complicated synthetic process

- **Challenges ahead**
  - **Materials property**: achieve high ion conductivity and good mechanical strength ***simultaneously without sacrificing each other***
  - **Synthesis**: practical process (low cost, easy scalability, quality control, high molecular weight)
  - **Characterization**: understanding of the relationship between polymer structures and membrane property (ion transport, mechanical)

Acknowledgment

- $$$

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- CAREER
- DMR (Polymer)
- CHE (DMREF)
- OISE (PIRE)

KIER

U.S. DEPARTMENT OF ENERGY

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- Paul Kohl (Georgia Tech)
- Stephen Paddision (U. Tennessee)
- Mark Tuckerman (NYU)
- **Chang Y. Ryu (RPI)**

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- Byungchan Bae (KIER)
- **Yoong-Kee Choe (AIST)**
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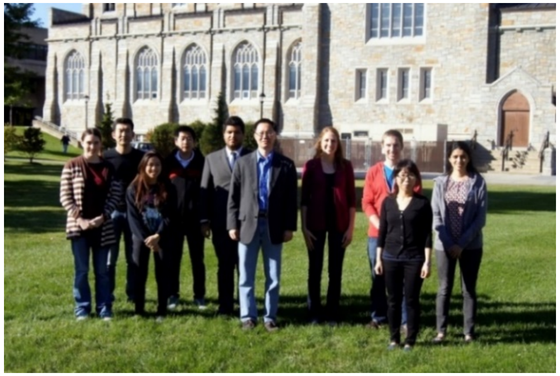
- **Bryan Pivovar (NREL)**
- Sungsool Wi (NHMFL)



- **Current and Past Group Members**
- **Postdoc:**, Jinhee Lee, "Jay" Jong-Yeob Jeon, Dongwon Shin, Woo-Hyung Lee, Ying Chang
- **Graduate student:** Sarah Park, Stefan Turan, Ding Tian, Angela Mohanty, Bhagyashree Date, Jihoon Shin, Se Hye Kim
- **Undergraduate student:** Steven Tignor, Ben Stovall, Alicia Meehan, Rachel de Vera, Jessica Krause