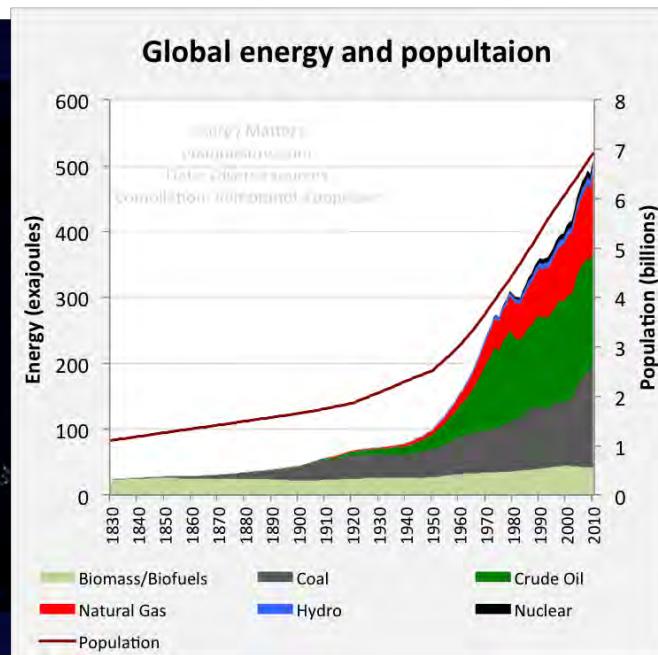


Ion Conducting Polymer Electrolyte Membranes for Energy Conversion Technology



Chulsung Bae

**Department of Chemistry & Chemical Biology
Department of Chemical & Biological Engineering (*joint appointment*)**

**Rensselaer Polytechnic Institute (RPI)
Troy, New York**

April 10, 2019 (RPI CFES Symposium)



Rensselaer

Overview of Bae Group Research

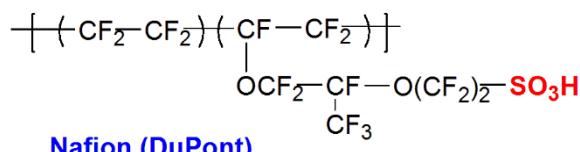
Molecular Engineering of Polymers

- Application-driven, Technology-focused
- Solid Electrolyte, Membranes, Separation

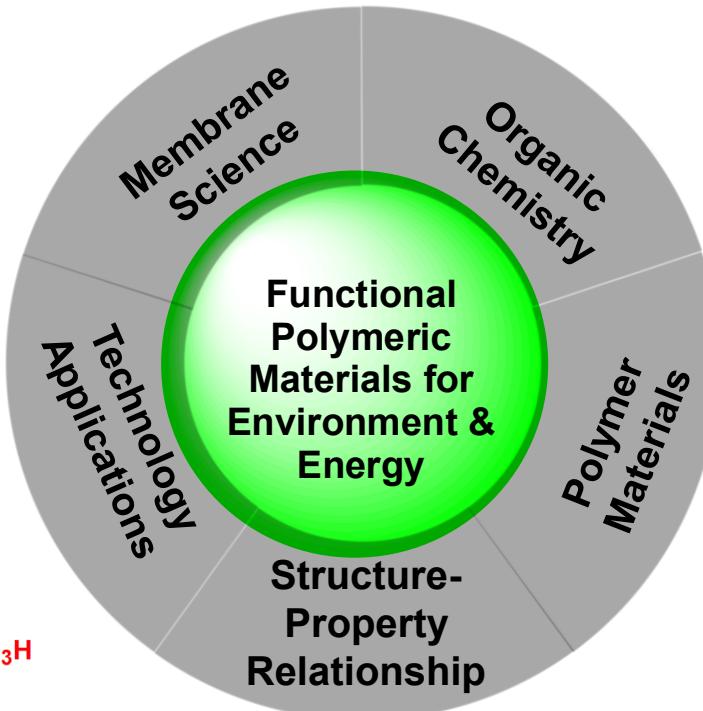
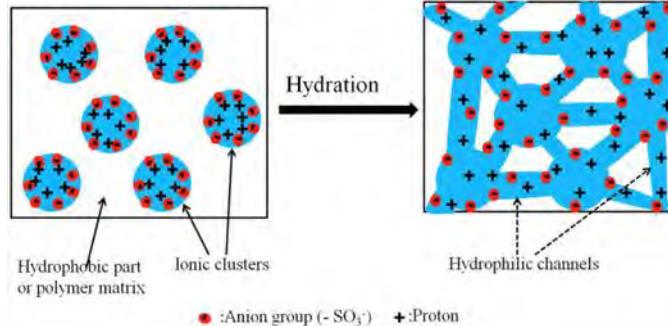
Clean Energy

Ion-conducting (H^+ , OH^-) polymer electrolytes for *electrochemical* devices

- Fuel cells
- Electrolysis
- Redox flow battery
- Actuators/Sensors

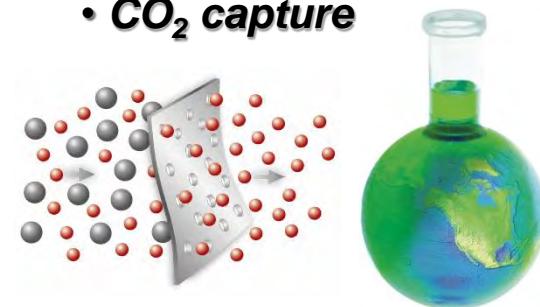


Nafion (DuPont)

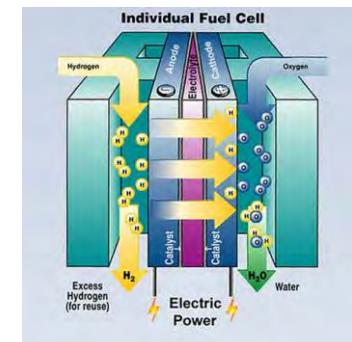


Clean Environment

- Gas separation
- CO_2 capture

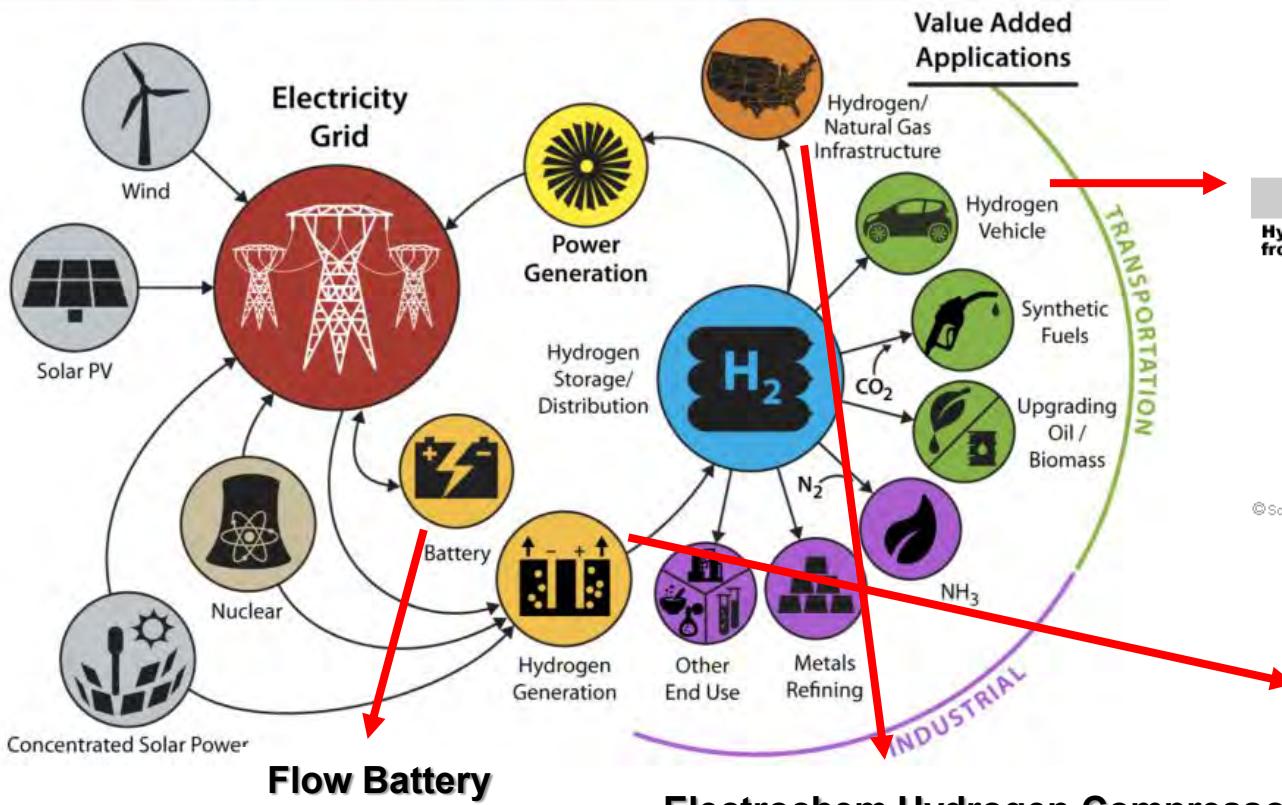


- University
- Gov. labs
- Industry

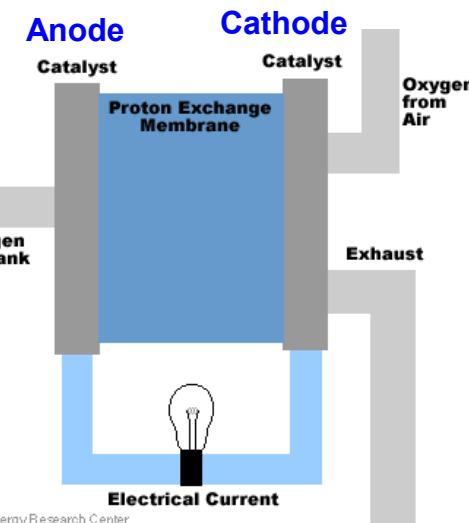


Hydrogen Economy: Future Energy System

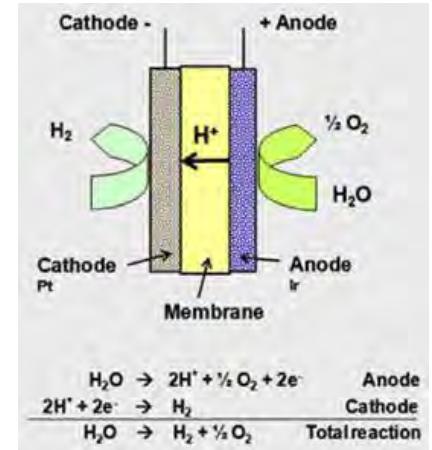
Future H₂ at Scale Energy System DOE H2@Scale



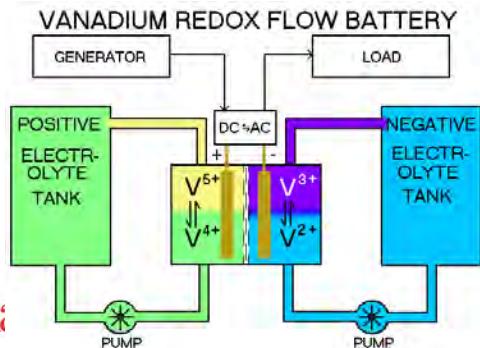
PEM Fuel Cell



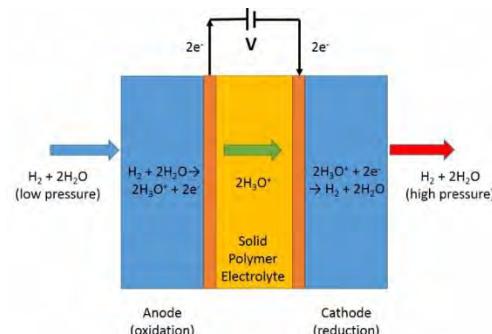
PEM Electrolyzer



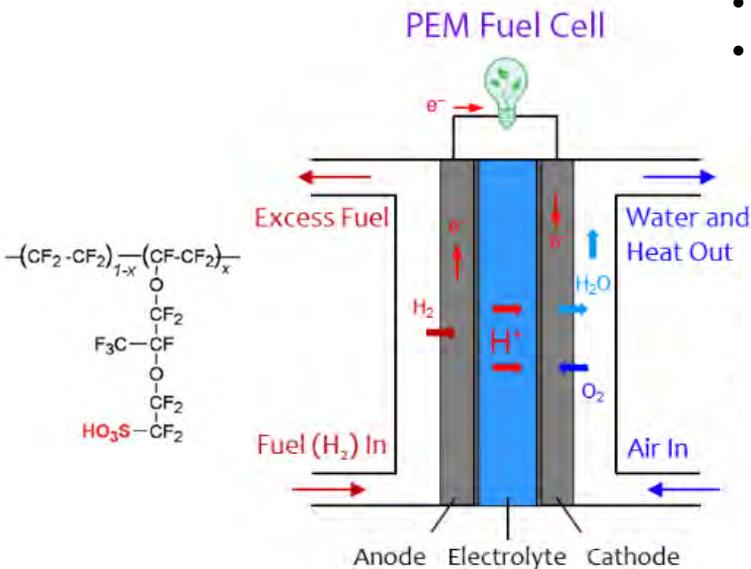
Flow Battery



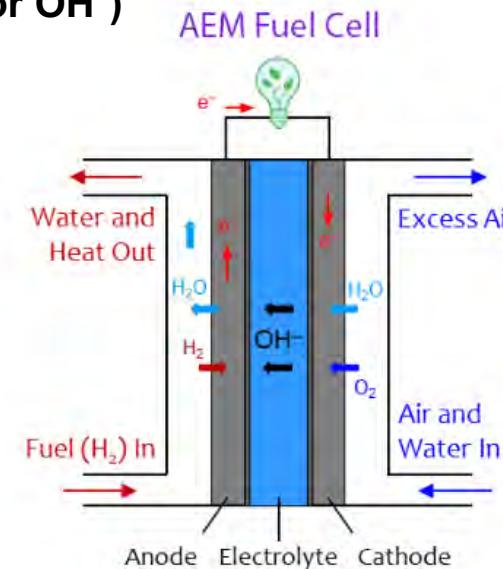
Electrochem Hydrogen Compressor



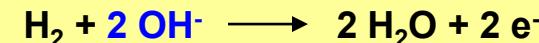
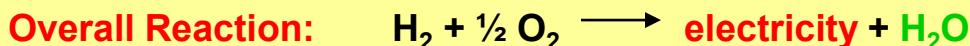
Solid Electrolyte in Electrochemical Energy Conversion: Acidic Membrane (H^+) vs. Alkaline Membrane (OH^-)



- Transport ion (H^+ or OH^-)
- Stable
 - Chemical
 - Mechanical



?



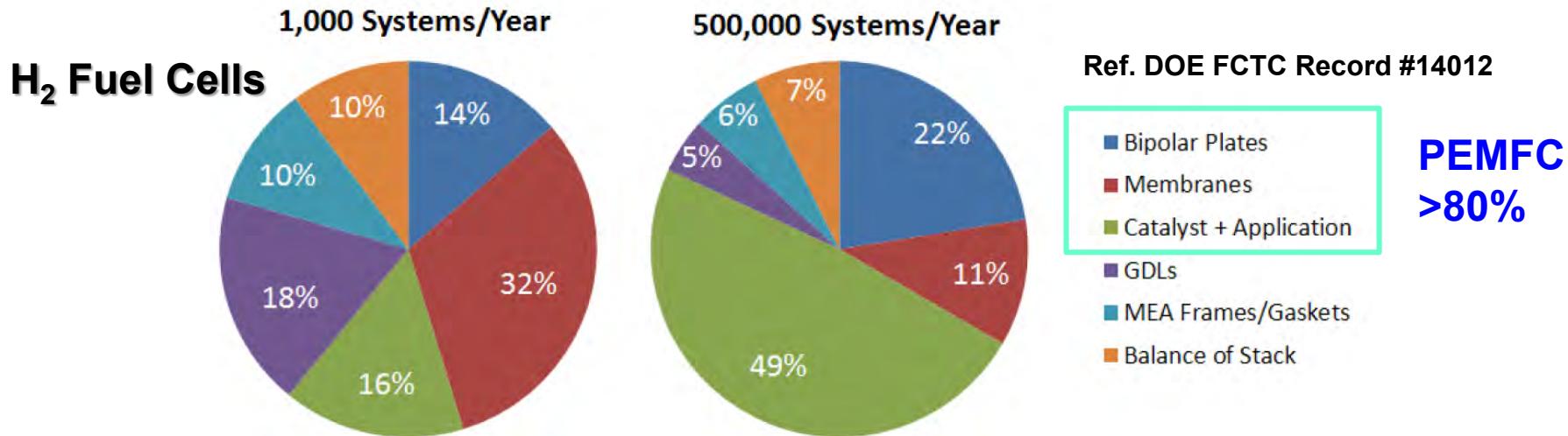
- Since 1970s (most advanced fuel cells)
- **Acidic** environment
- Bipolar plate: titanium
- Catalyst: expensive Pt (or PGMs)
- **PEM**
 - High cost of Nafion
 - High crossover of fuels & ion

- Since 2010s (a new concept)
- **Basic** environment
- Bipolar plate: stainless steel
- Catalyst: non-noble metals possible (Ag, Ni)
- **AEM**
 - No standard membrane
 - Low OH^- conductivity (<100 mS/cm)
 - poor stability against OH^- (>80 °C)
 - poor mechanical stability (wet)

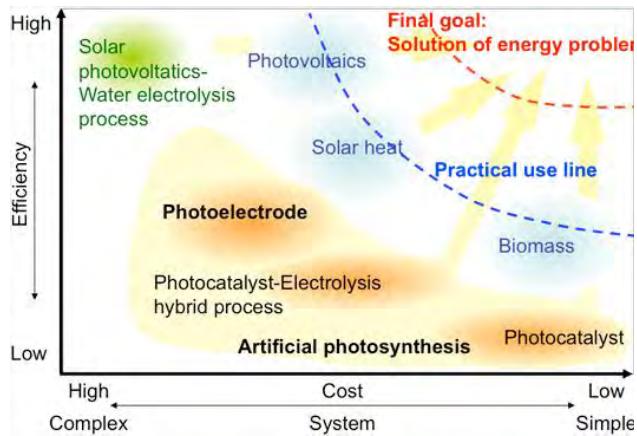


Cost Analysis in PEM Fuel Cells & Electrolysis

Materials Cost Issue: *Membranes, Catalyst, Bipolar Plates*



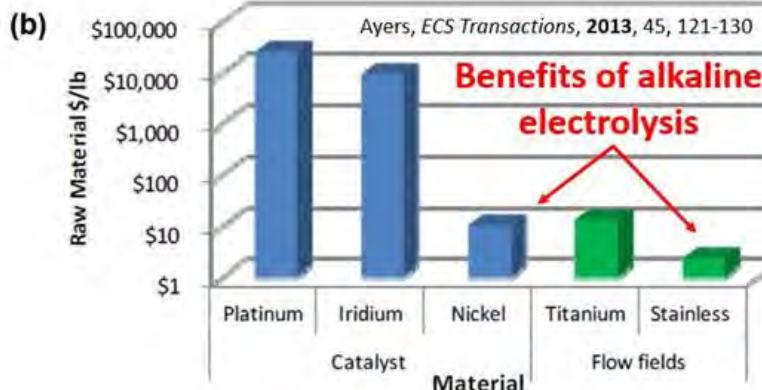
H₂ Production



(a) Comparison of different electrolyser technologies.

Technology	Efficiency	Maturity
Alkaline electrolyser	59–70% ^a	Commercial
PEM electrolyser	65–82% ^a	Near term
Solid oxide electrolysis cells	40–60% ^b	Mediate term
Photoelectrolysis	2–12% ^a	Long term

Zeng, *Progress in Energy and Combustion Science*, 2010, 36, 307-326



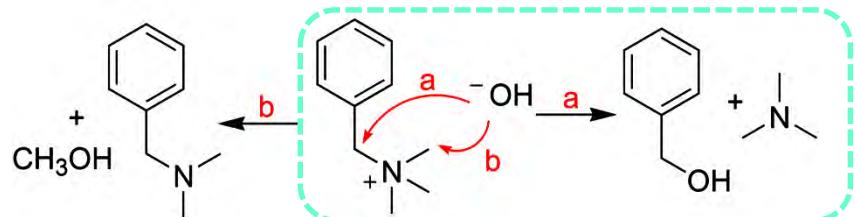
www.dailymetalprice.com
(November 2018)

Metal	\$/lb
Pt	12,500
Ir	21,500
Ru	3,900
Ag	210
Ni	5
Fe	0.03

Chemical Degradation of AEM by OH⁻ Attack

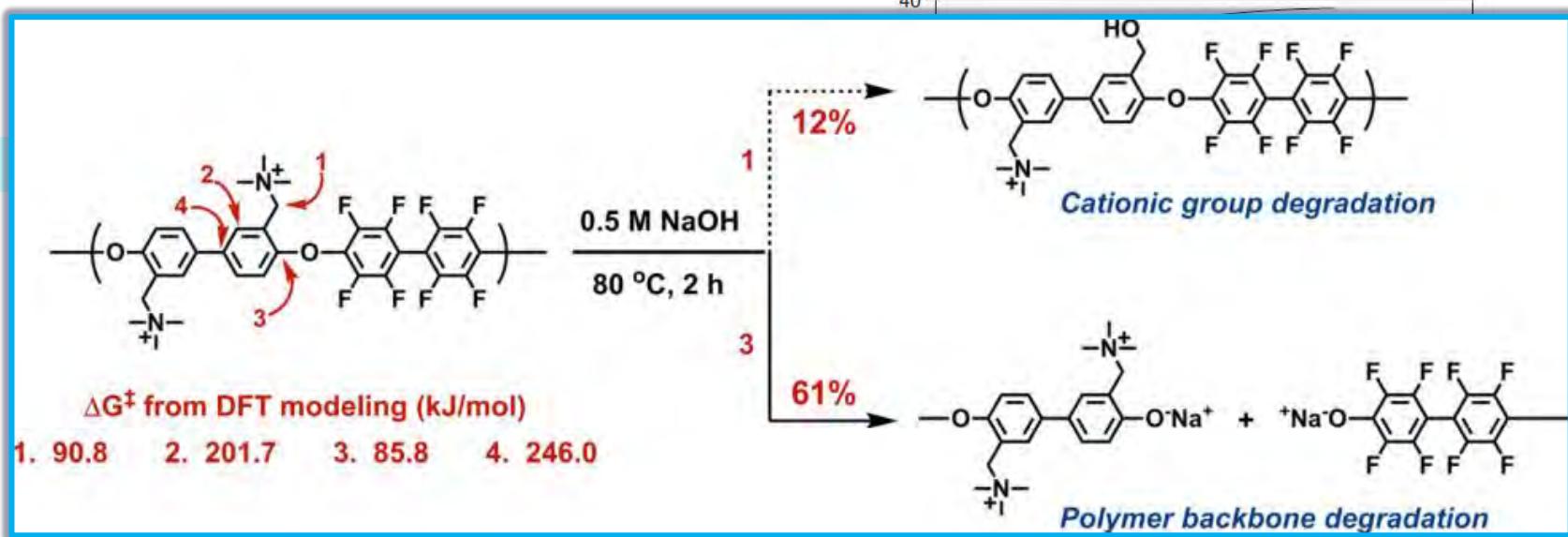
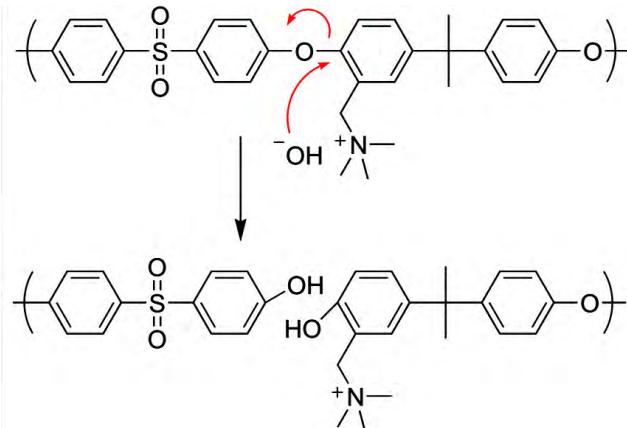
Degradation at Cation Group

» S_N2 substitution

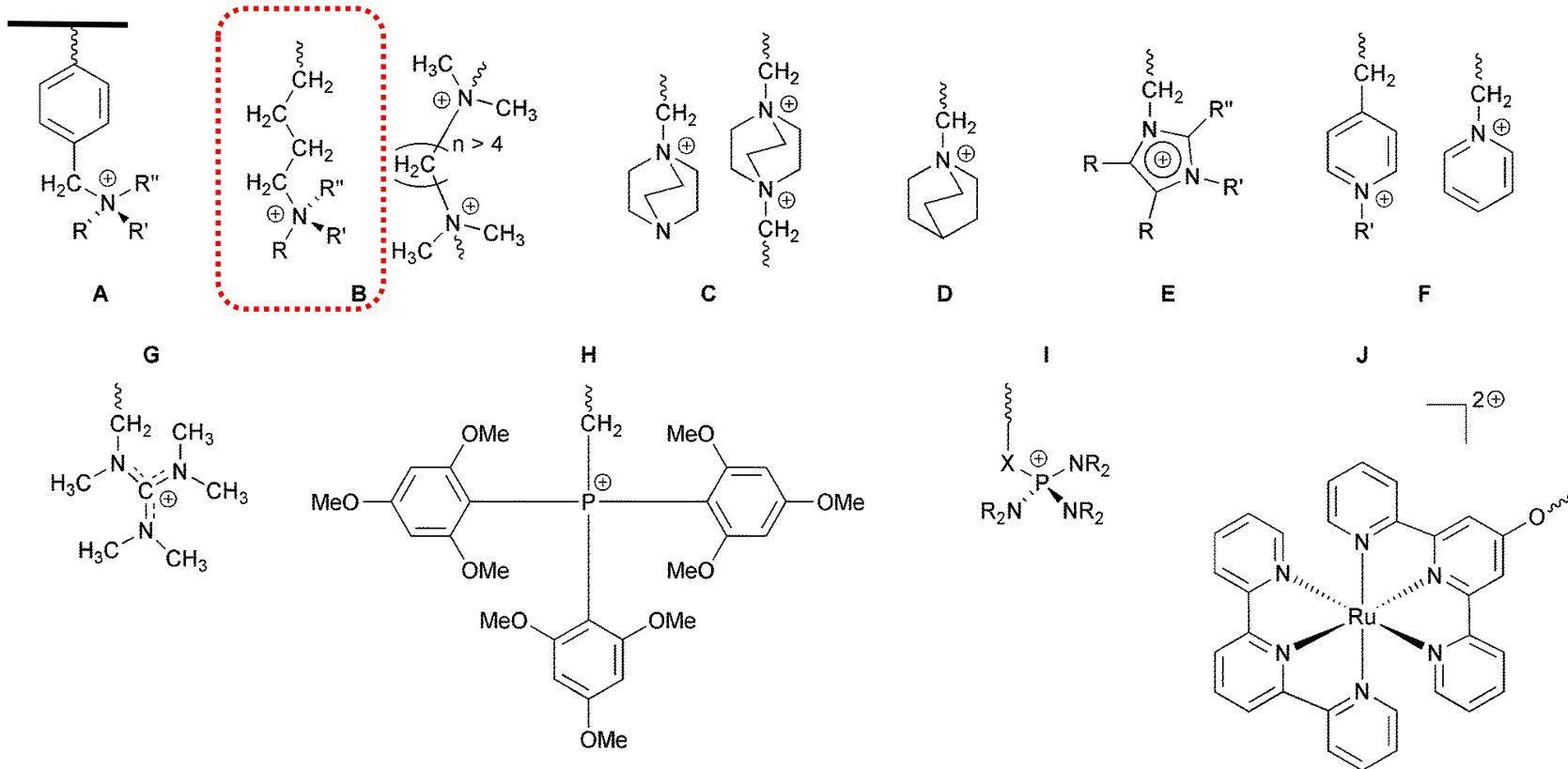


Degradation at Polymer Backbone

» Chain cleavage at aryl C–O bond



Current AEMs: Cation & Backbone

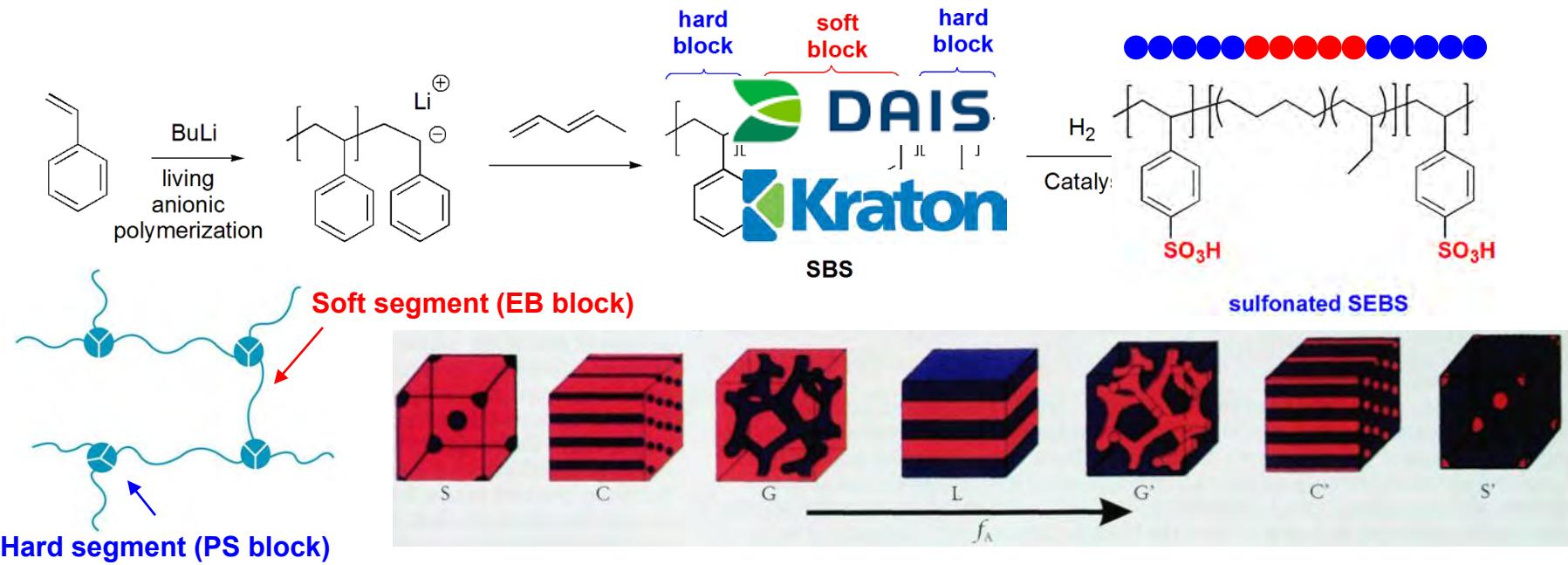


Reviews and Articles on AEM and AEM Fuel Cells:

- Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T.; Zhuang, L. *Energy Environ. Sci.* **2014**, 7, 3135
- Gottesfeld, S.; Dekel, D. R.; Page, M.; Bae, C.; Yan, Y.; Zelenay, P.; Kim, Y. S. *J. Power Sources* **2018**, 375, 170
- Dekel, D. R. *J. Power Sources* **2018**, 375, 158
- Maurya, S.; Shin, S.-H.; Kim, Y.; Moon, S.-H. *RSC Adv.* **2015**, 5, 37206
- Park, E. J.; Kim, Y. S. *J. Mater. Chem. A* **2018**, 6, 15456
- Olsson, J. S.; Pham, T. H.; Jannasch, P., *Adv. Funct. Mater.* **2018**, 28, 1702758
- Miyatake, K. et al. . *J. Am. Chem. Soc.* **2011**, 133, 10646-
- Wright, A. G.; Weissbach, T.; Holdcroft, S., *Angew. Chem. Int. Ed.* **2016**, 55, 4818



Commercial Styrene-Diene Block Copolymers

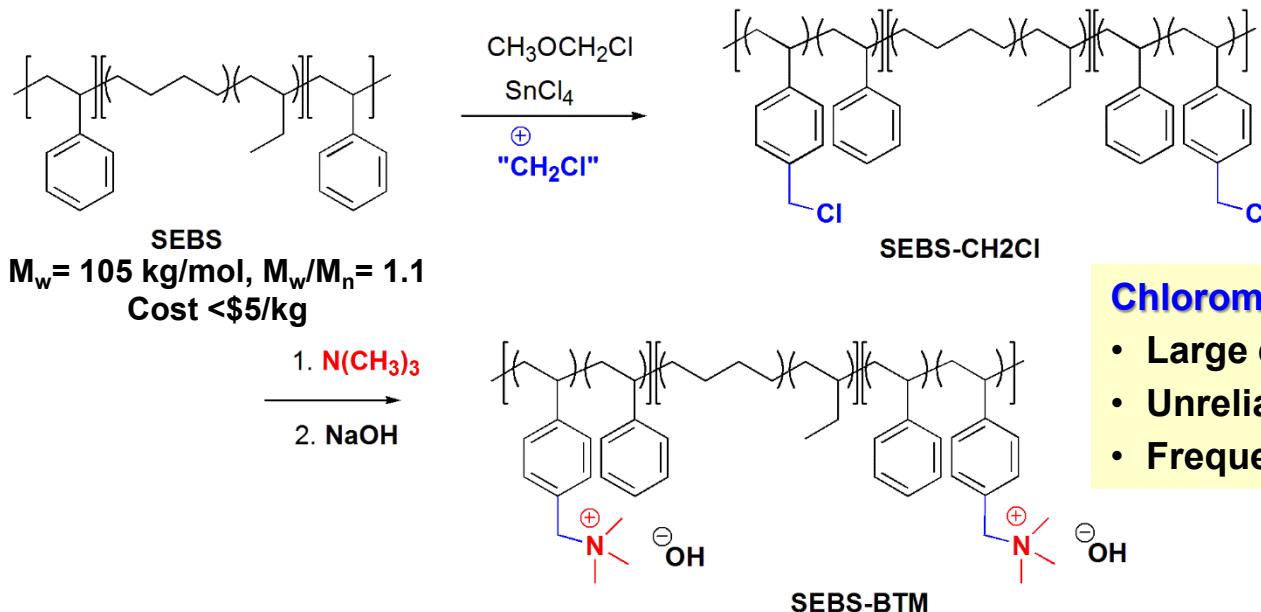


Commercial Samples	Hard block Styrene mol.% (vol.%)	Rubbery block		
		total rubbery (mol.%)	Ethylene (mol.%)	Butylene (mol.%)
SBS #1	25 (38)	72	67	8
SEBS #4	18 (29)	82	51	31
SEBS #6	20 (32)	78	73	7



Prior Attempts for SEBS AEMs

- Ionic triblock copolymer: nano-scale phase-separated morphology
- No cleavable C–O bond



Chloromethylation

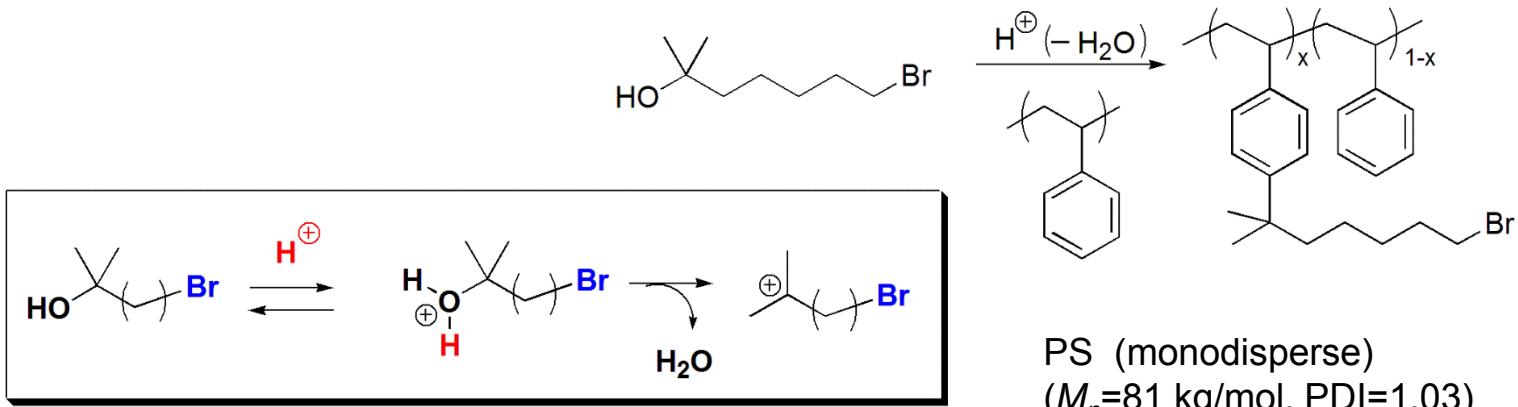
- Large excess of toxic CMME
- Unreliable functionalization degree
- Frequent gelation

Source	Styrene block mol.%	$\text{IEC}_{\text{theo}} (\text{meq/g})$	$\text{IEC}_{\text{exp}} (\text{meq/g})$
SEBS #4 (Sigma-Aldrich)	18	2.21	0.30^a

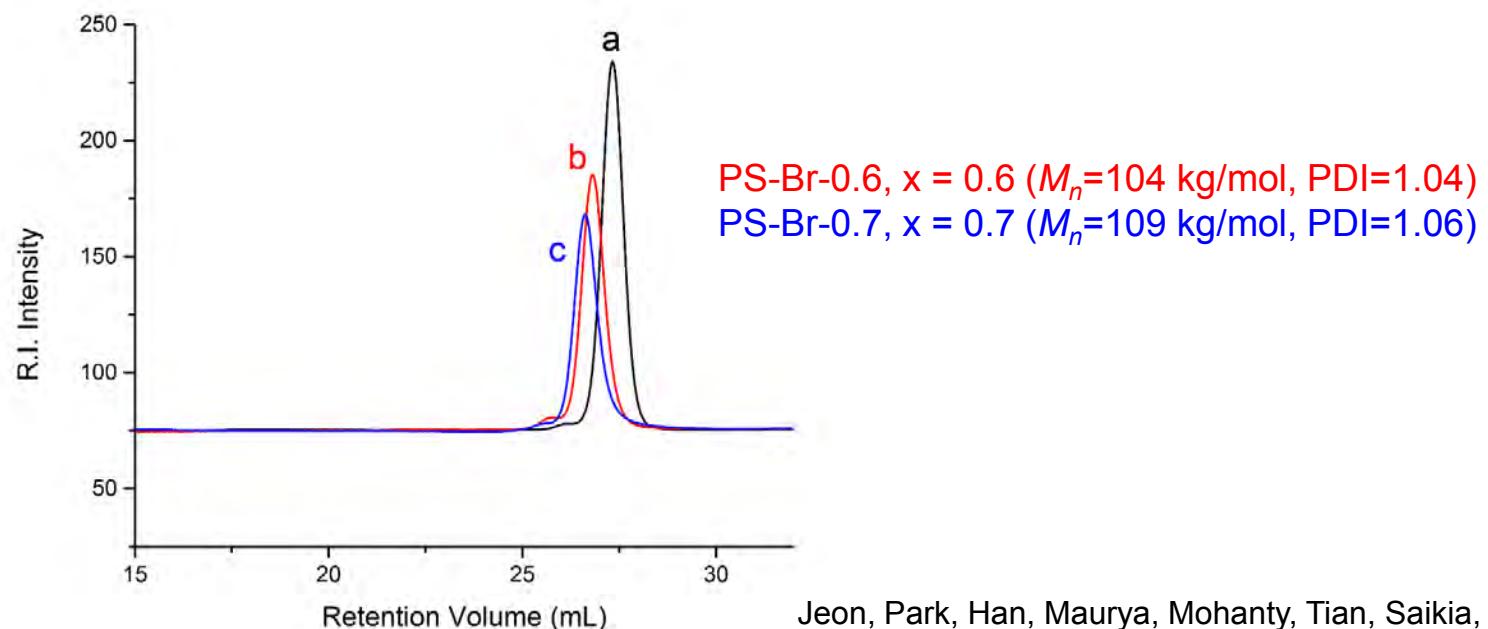
Liu, *et al.* *J. Membrane Science* **2010**, *349*, 237
Chen, *et al.* *J. Power Sources* **2012**, *202*, 70

^a Gelation occurred above the IEC

Friedel-Crafts Bromoalkylation of Monodisperse PS



PS (monodisperse)
($M_n=81 \text{ kg/mol}$, PDI=1.03)

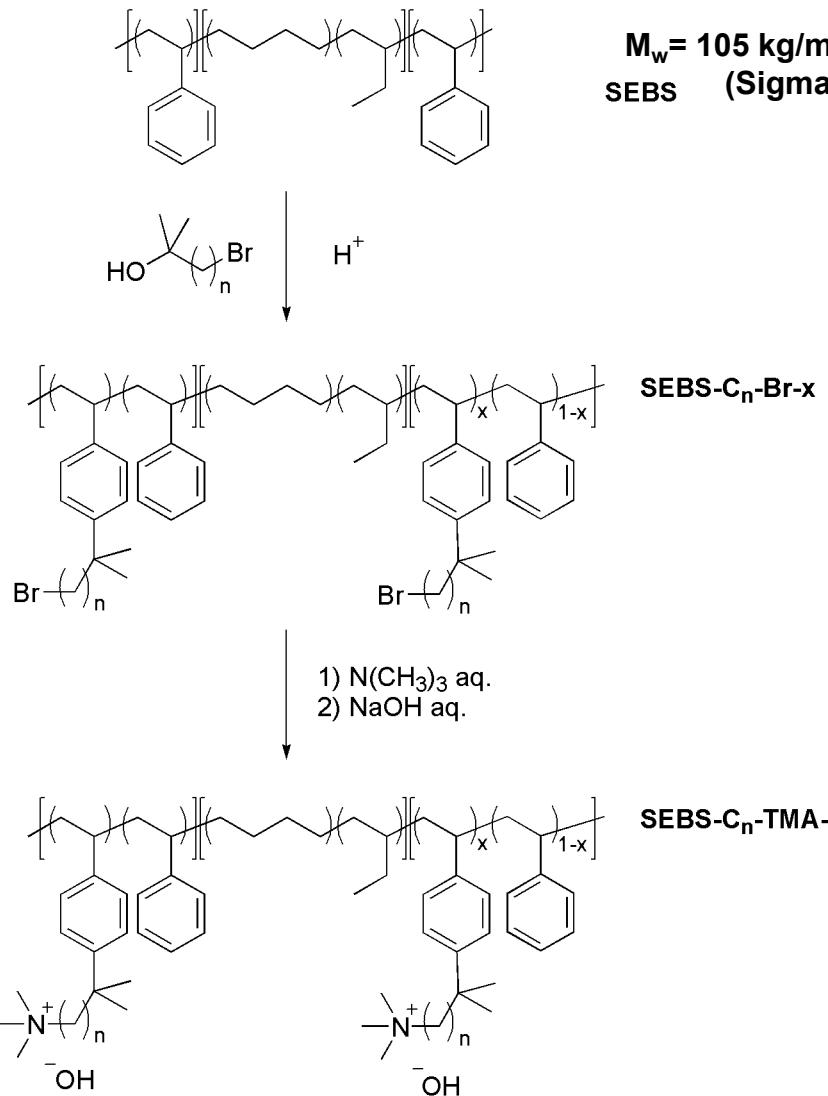


Jeon, Park, Han, Maurya, Mohanty, Tian, Saikia,
Hickner, Ryu, Tuckerman, Paddison, Kim, Bae,
Macromolecules. 2019, 52, 2139



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New Synthetic Route for TMA-Functionalized SEBS



Advantage of SEBS

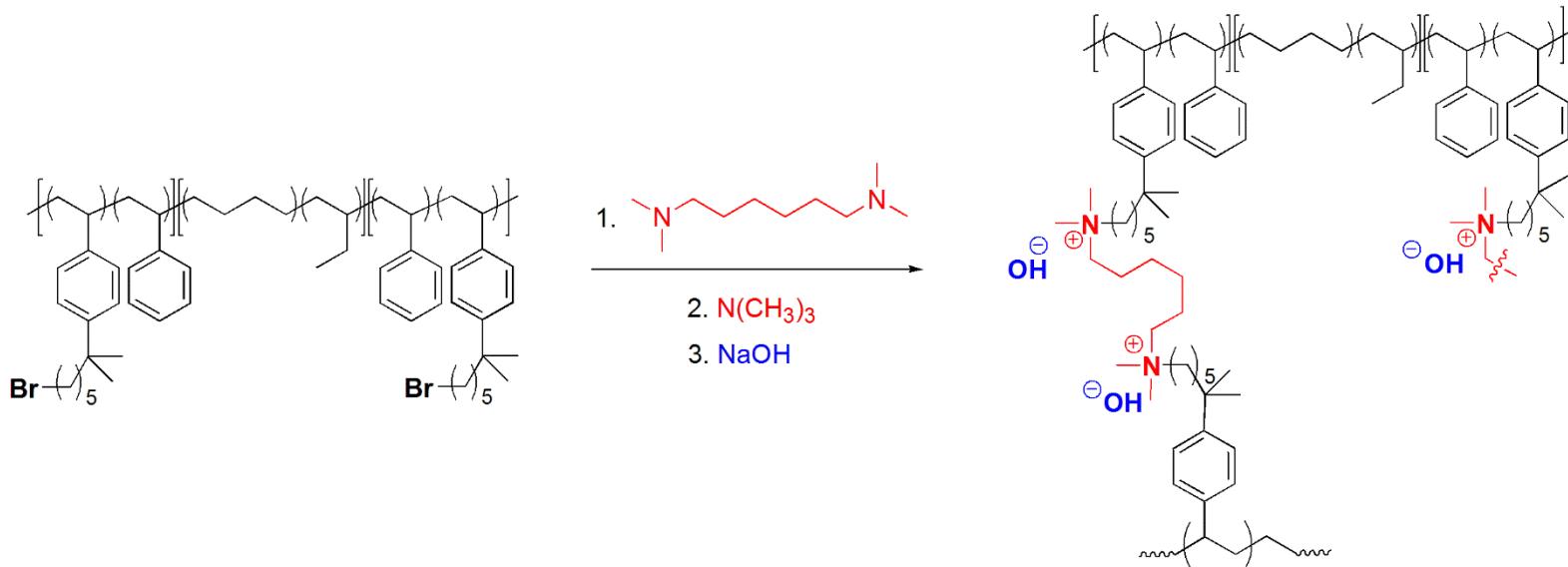
- Thermoplastic elastomer
- Commercially available
- Various compositions (PS & EB)
- Microphase-separated morphology

n = side chain length
(carbon number of spacer)

x = functional degree on PS block



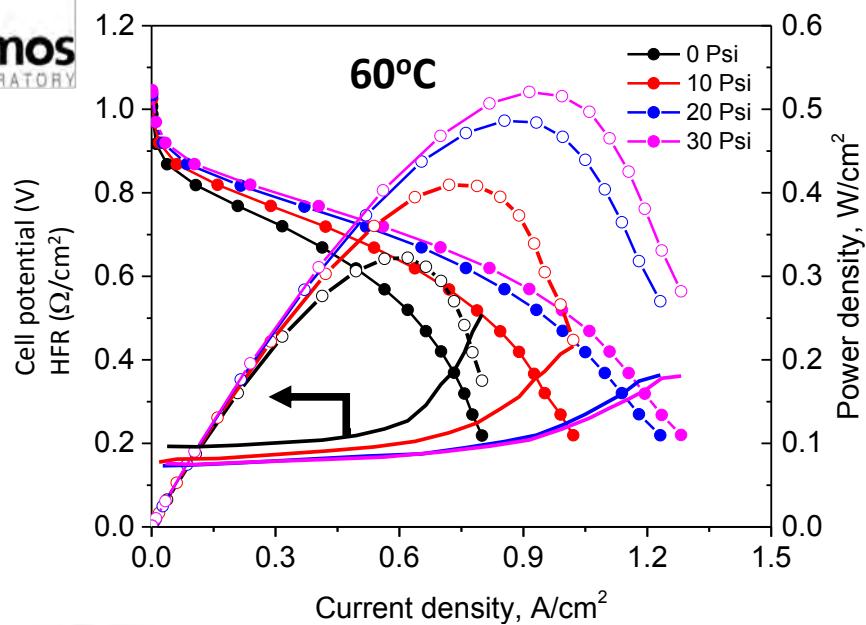
Crosslinked SEBS AEMs: Lower Water Uptake



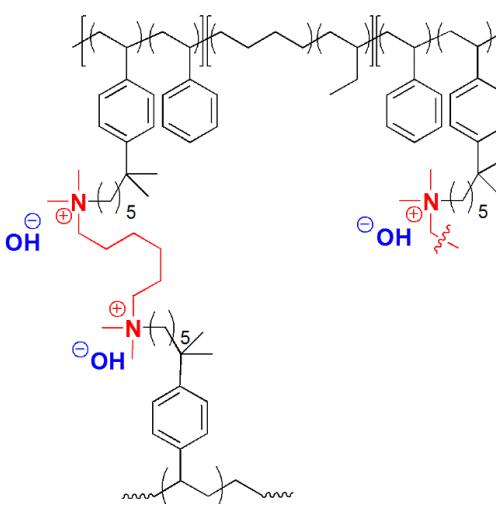
Samples	TMHD N:Br (%)	IEC (meq/g) NMR (Titration)	Water Uptake (OH ⁻ wt %)	Cl ⁻ σ (mS/cm) 60°C	OH ⁻ σ (mS/cm)		
					30°C	60°C	80°C
SEBS-C ₅ -TMA-0.8	0	1.50 (1.41)	155 (± 10)	20	23	41	-
XL20-SEBS-C ₅ -TMA-0.8	20	1.49 (1.41)	70 (± 3)	17	30	42	62
XL60-SEBS-C ₅ -TMA-0.8	60	1.47 (1.42)	46 (± 1)	15	33	50	65
XL100-SEBS-C ₅ -TMA-0.8	100	1.45 (1.42)	28 (± 1)	13	29	41	65



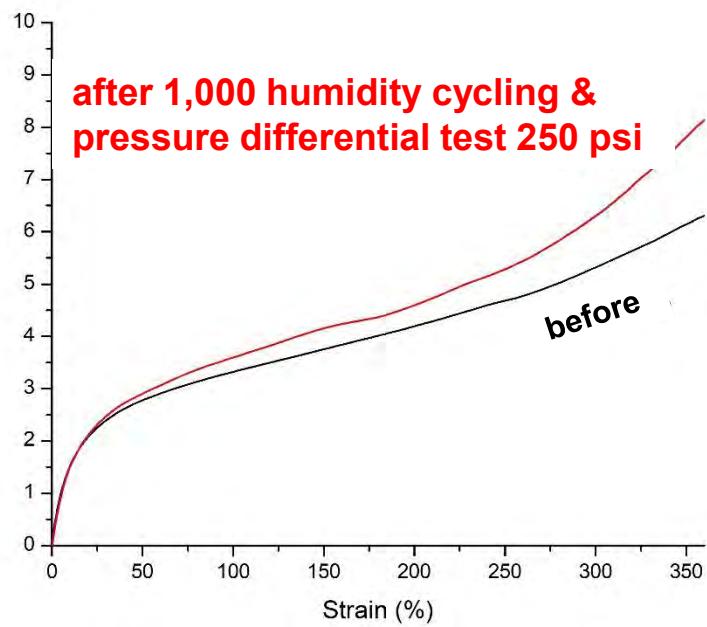
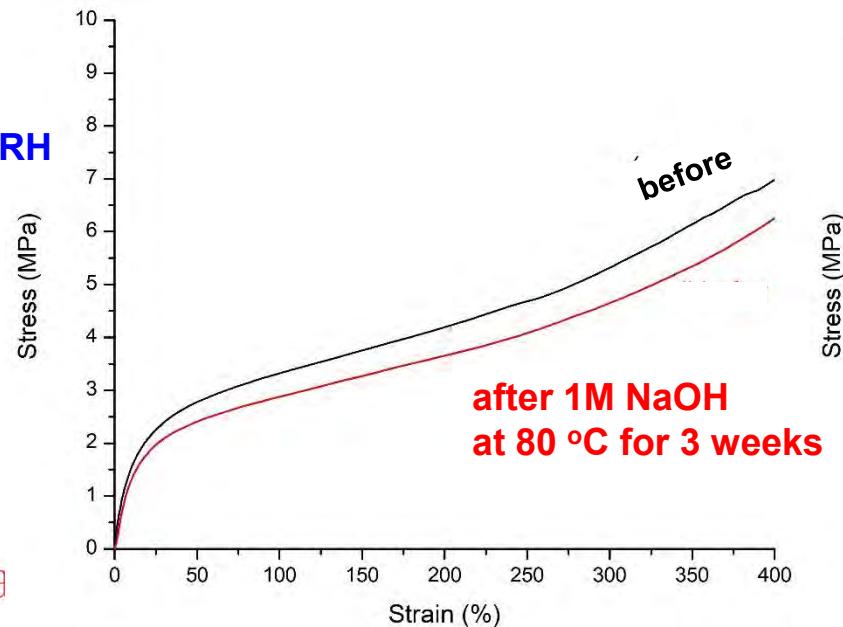
Fuel Cell Performance & Stability of Crosslinked SEBS AEM



XL-100-SEBS-C₅-TMA-0.8
IEC = 1.45 meq/g

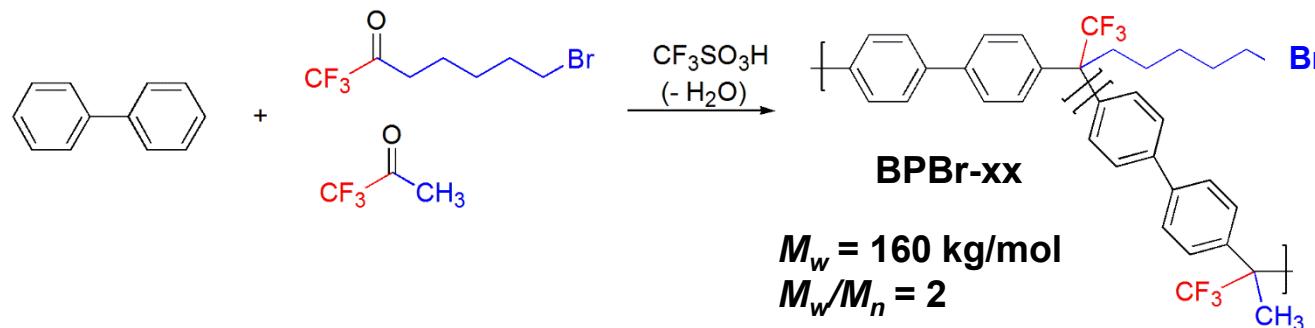


Condition:
50 °C, 50% RH



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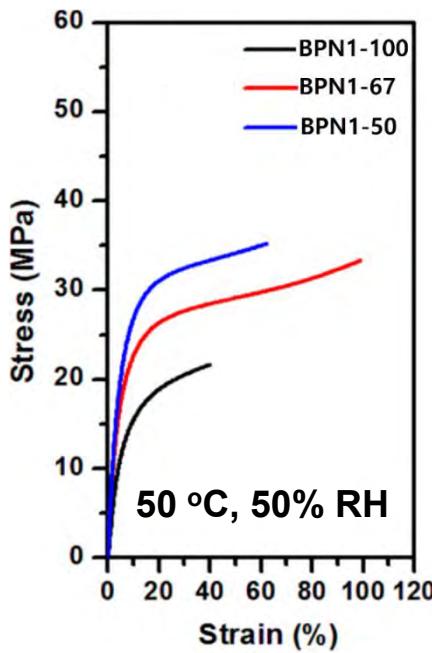
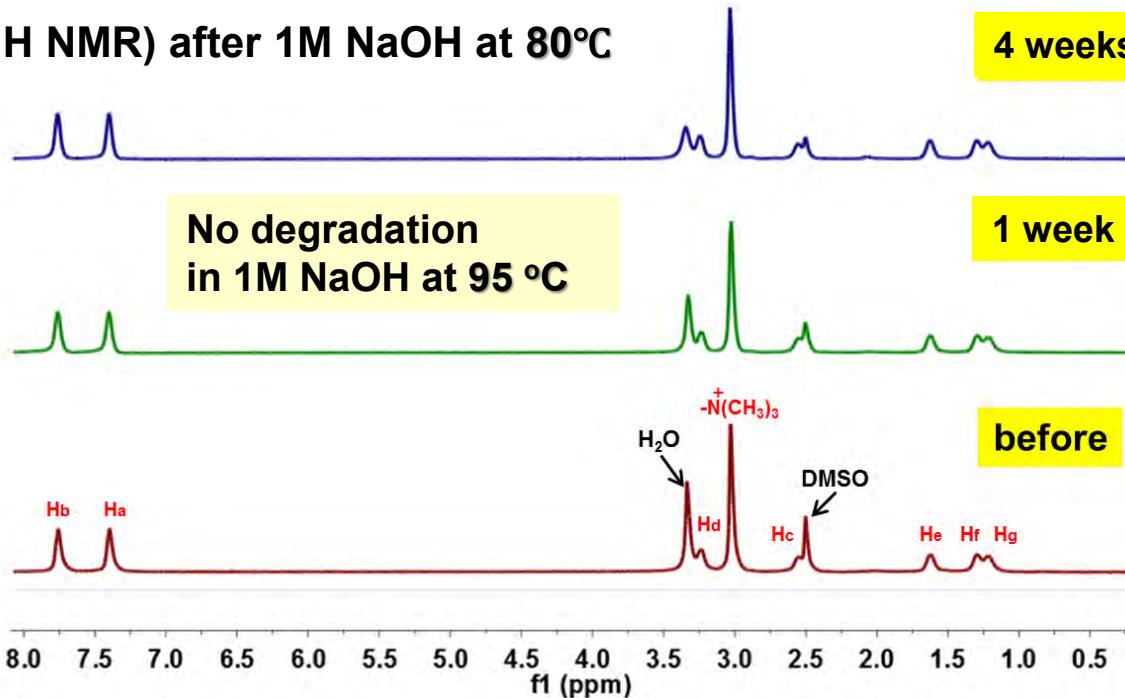
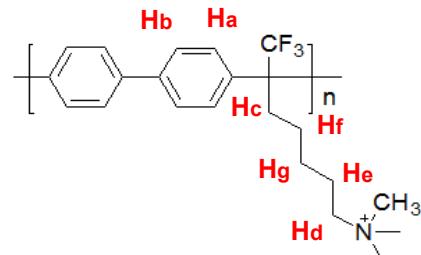
Biphenyl Polymer AEM: Stable, Tough, Scalable



- Long-alkyl chain tethered ammonium: more stable than benzyl ammonium against OH^- attack
- Repeating unit composed of rigid **biphenylene** with one C_{sp^3}
 - all C–C bonds (no cleavable C–O bonds, no backbone degradation)
 - kinked backbone: improve polymer solubility & molecular weight
 - incorporate a tethered cation group
- Soluble in alcohol
- No need to use expensive metal catalysts in synthesis
- Further modifications are possible to tune structures & properties

Alkaline Stability & Mechanical Property of Biphenyl AEMs

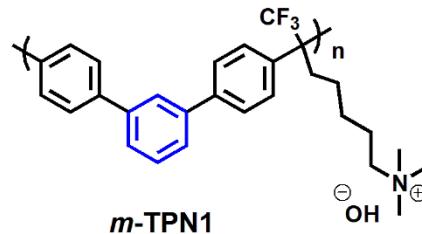
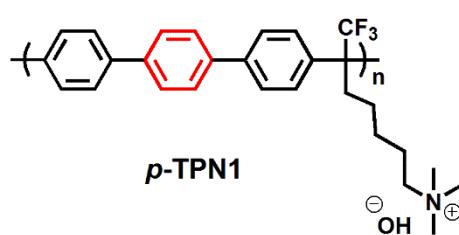
Alkaline stability test (^1H NMR) after 1M NaOH at 80°C



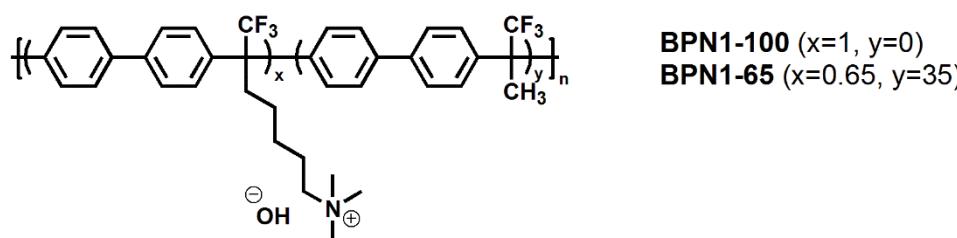
Sample -N ⁺ (CH ₃) ₃	IEC (meq/g) Before test		IEC 80 °C, 4 weeks	
	NMR	titration	NMR	titration
BPN1-100	2.61	2.70	2.60	2.65
BPN1-67	1.91	1.94	1.93	1.92
BPN1-50	1.45	1.46	1.46	1.48



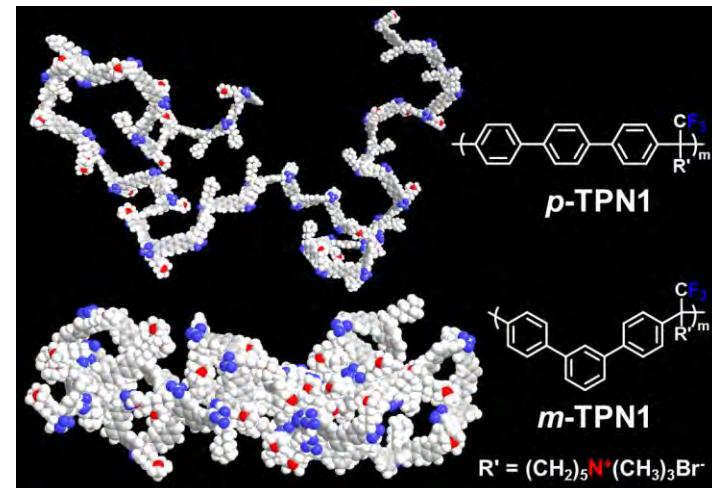
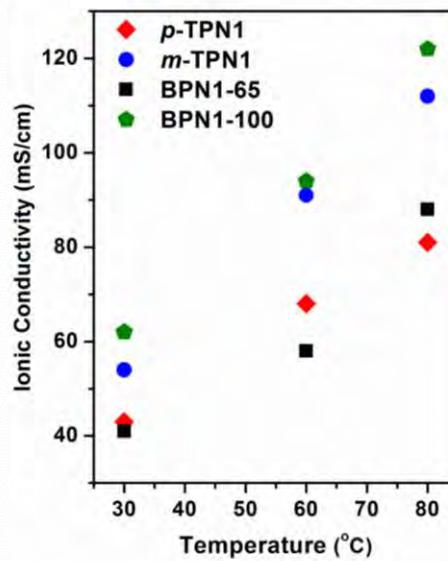
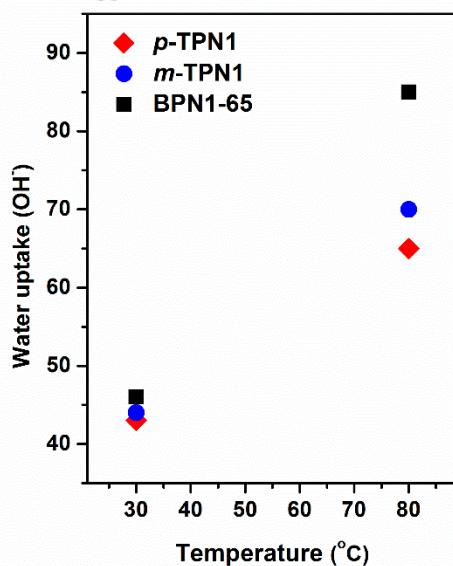
Backbone Effect on AEM: Biphenyl vs.Terphenyl



IEC = 2.15 (*para*) mequiv/g
2.12 (*meta*)

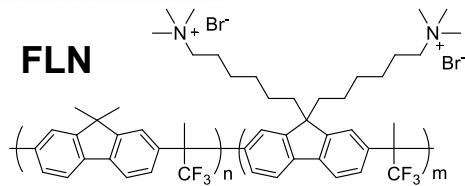
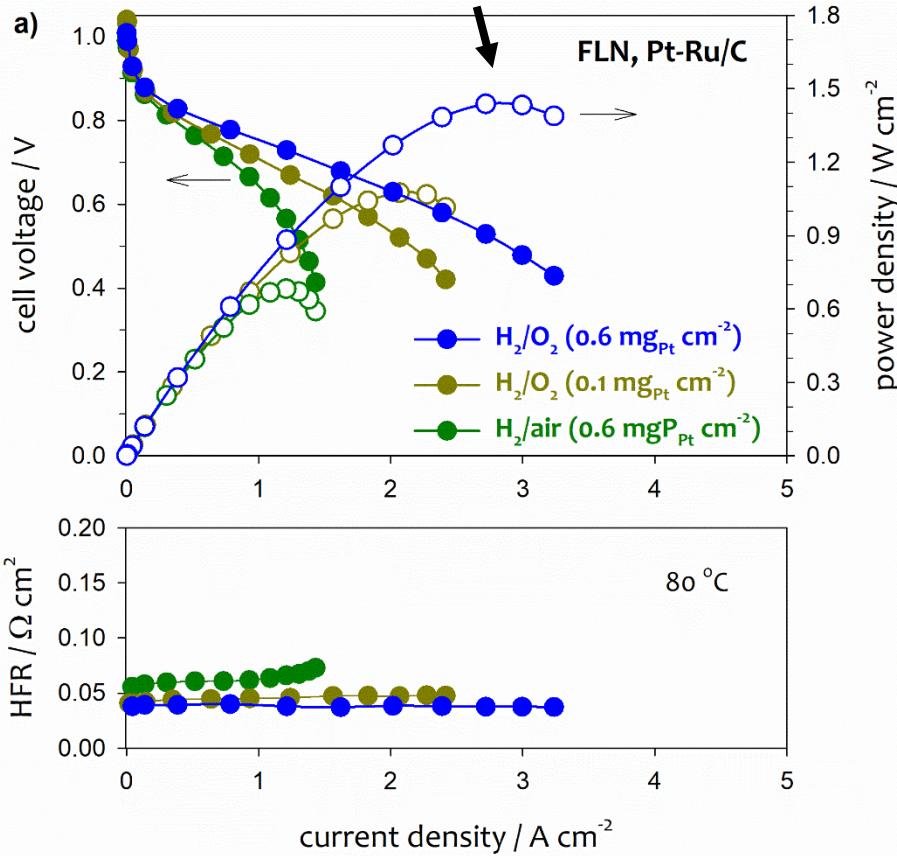


2.70 ($x = 1.0$)
1.94 ($x = 0.65$)



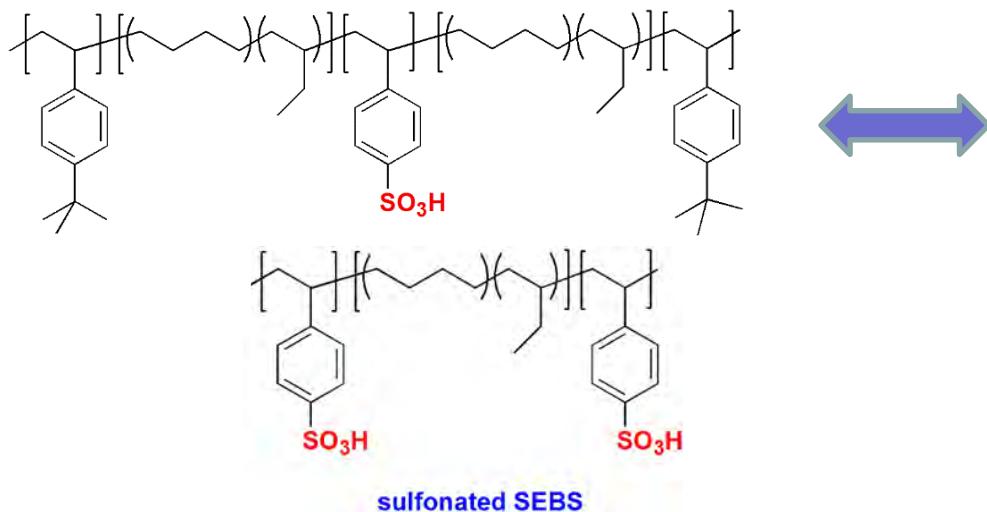
Progress of AEM Fuel Cell Performance (April 2018)

m-TPN1 (AEM) 1.5 W/cm²
Alkaline condition, <3 yr

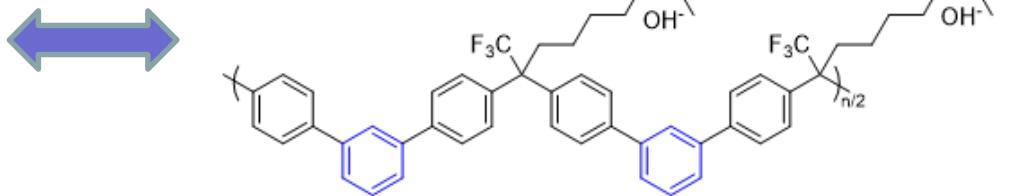
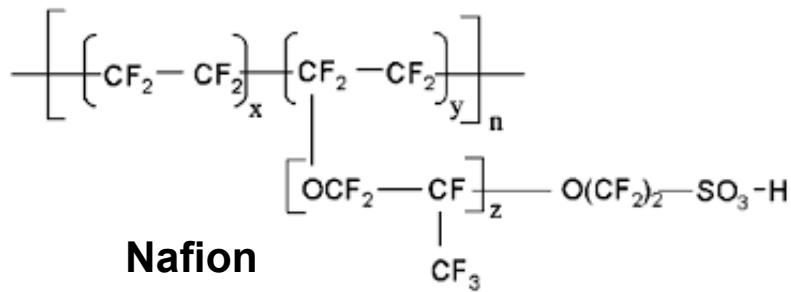
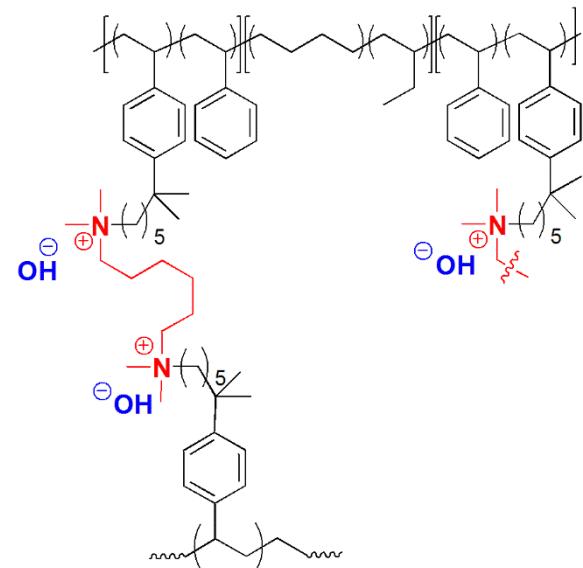


Summary

PEM: H⁺ acidic



AEM: OH⁻ basic



More are coming



Acknowledgment



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



U.S. DEPARTMENT OF
ENERGY

Energy Efficiency &
Renewable Energy



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POWERED BY SBA



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- Kwang J. Kim (UNLV)
- Sangil Kim (UIC)
- Paul Kohl (Georgia Tech)
- Haiqing Lin (SUNY Buffalo)
- Stephen Paddison (U. Tennessee)
- Chang Ryu / Sangwoo Lee (RPI)
- Mark Tuckerman (NYU)
- Yushan Yan/Shimshon Gottesfeld (UDel)

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- Yu Seung Kim (LANL)
- Bryan Pivovar (NREL)
- Jia Wang/Radoslav Adzic (BNL)
- Adam Weber/Ahmet Kusoglu (LBNL)
- Sungsool Wi (NHMFL)

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- Giner
- Orion Polymer
- POCell Tech
- Proton Onsite
- Skyre
- StorEn
- Xergy

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Gregory Kline
Asheesh Singh
Bharat Shrimant
Sungmin Park
- Sangtaik Noh
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