Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Scalable Elastomeric Membranes for Alkaline Water Electrolysis

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Los Alamos National Laboratory
4/30/2019

Project ID # P159

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Project Overview

Project Partners

PI	Yu Seung Kim,	Los Alamos National Laboratory
Co-PI	Chulsung Bae,	Rensselaer Polytech Institute

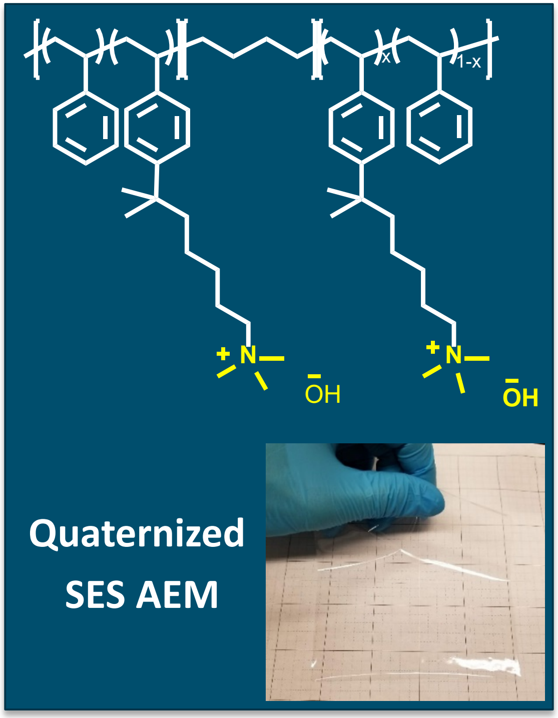
Award #	2.2.0.401
Start/End Date	10/01/2017 – 09/30/2020
Year 1 Funding* Year 2 Funding*	$250,000 $423,000

Project Vision

Preparing advanced alkaline hydroxide conducting SES materials and demonstrating the performance and durability in alkaline membrane water electrolysis.

Project Impact

This technology will bring the alkaline membrane-based water electrolysis technology to a maturity level at which it can be further developed by industry for commercialization.



** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project Motivation

Los Alamos team has demonstrated > 2,000 h alkaline electrolyzer durability using polyaromatic electrolytes in 2013. In this project, we are aiming to develop economically viable elastomeric ionomers that may be used for advanced alkaline membrane electrolyzer.

Barriers

- Alkaline stability
- Hydroxide conductivity
- Mechanical properties
- Performance of AEM electrolyzer
- Durability of AEM electrolyzer

Key Impact

Metric	State of the Art	Expected Advance
Hydroxide conductivity (mS/cm)	*30-40*	*40*
% Loss conductivity after 300 h, 1 M NaOH, 80 °C	*30*	*< 5*
Tensile toughness (MPa × % elongation)	2000	3000

Partnerships

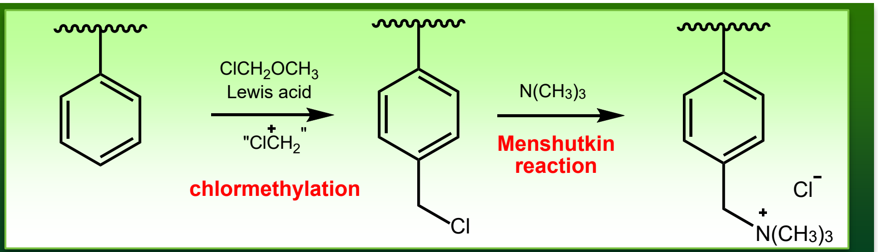
- Yu Seung Kim (LANL): Project managing, ionomer preparation, identification of performance- and durability- limiting factors for AEM electrolyzers
- Chulsung Bae, Sangwoo Lee (RPI): Polymer synthesis & characterization
- Kathy Ayers (Proton Onsite): Alkaline membrane electrolyzer testing (from the 2nd year)

Approach- Innovation

Synthesize highly conductive, alkaline stable styrene-ethylene-styrene block copolymer by inexpensive acid catalyzed route.

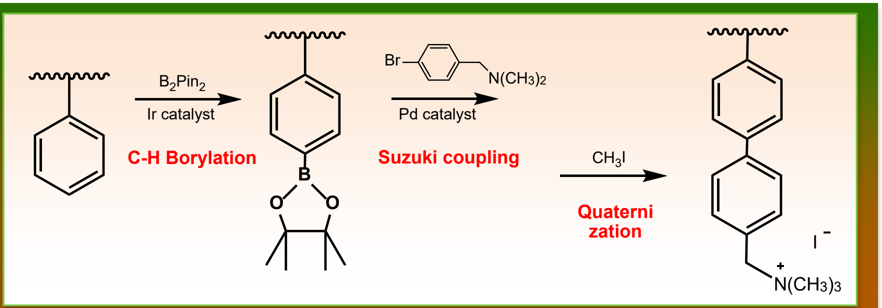
Conventional Chloromethylation

- Low level of functionalization & gelation
- Only allow benzyl ammonium functionalization
- Toxic and expensive reagents



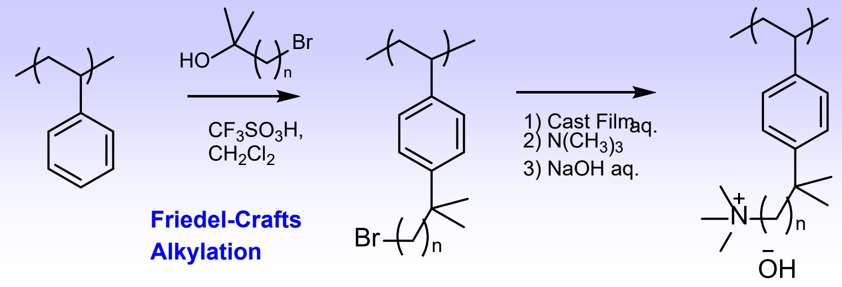
Metal-catalyzed coupling (M-Cat)

- Good control of IEC (1.5 meq./g)
- High hydroxide conductivity (40 mS/cm)
- Excellent chemical stability
- Not practical due to expensive metal catalysts



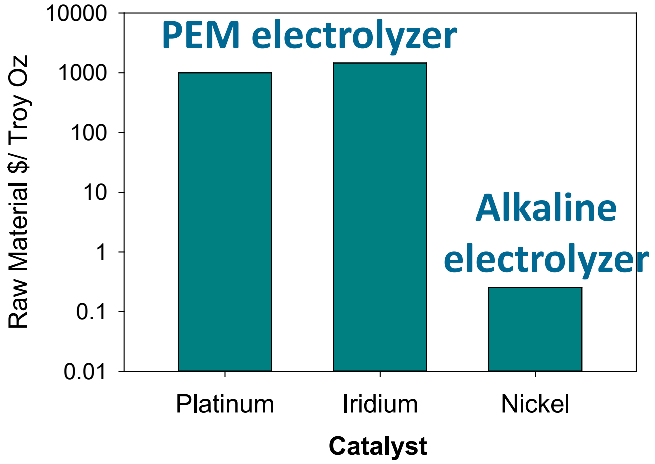
Acid catalyzed (Proposed)

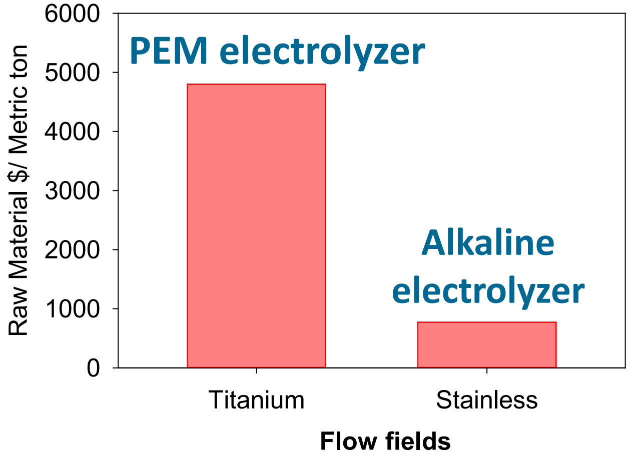
- IEC, conductivity and chemical stability are similar to that from metal-catalyzed coupling
- Multi-cation structure is feasible
- No use of expensive metal catalysts



Relevance & Impact

- ☐ Benefits of AEM electrolyzer over PEM electrolyzer





- ☐ Technical challenges of AEM electrolyzers
  - Low performance and durability are two technical challenges for AEM electroyzers. This project focuses on developing alkaline stable AEMs and ionomers to improve AEM electrolyzer performance and durability.

- ☐ Node utilization and other types of resources
  - Node utilization: modeling, Ionomer thin film study, electrochemical measurement (SNL, LBNL, and NREL).
  - Other types of resources: Alkaline Membrane Fuel Cell Project (FCTO).

Budget Period 1 Go/No-Go Milestone

Milestone progress

Description	Criteria	Planned date	Progress
Baseline SEBS synthesis	5 × 5 inch, 3 membranes (IEC > 1.5 meq.g)	12/31/17	100% (12/19/17)
Chemical stability (baseline polymer)	< 5% σ loss after 300 h, 1 M NaOH, 80 °C	3/31/18	100% (2/28/18)
Conductivity & stability assessment	40 mS cm^{-1} at 30 °C, <5% loss σ after 300 h 1 M NaOH, 80 °C	9/30/18	100% (9/25/18)
Mechanical property	Mechanical toughness (mechanical strength (MPa) x % elongation) > 1,400 at 50 °C, 90% RH	9/30/18	100% (9/25/18)

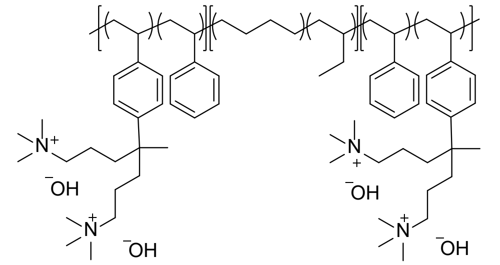
Go-no-Go Decision (9/30/2018) – needs to meet the criteria simultaneously

1. Hydroxide conductivity: > 40 mS cm^{-1} at 30 °C.
2. Less than 5% loss in hydroxide conductivity after 300 h, 1 M NaOH treatment at 80 °C.
3. Mechanical toughness (mechanical strength (MPa) × % elongation) > 1,400 at 50 °C, 90% RH.

Progress on the Chemical Structure Optimization of the Block Copolymers

Quaternized SEBS(QA)

Di-quaternized SEBS (Di-QA)



Semi-crystalline SES

(see the synthesis of QA and di-QA in Technical Backup Slide #1)

Cross-linked SES

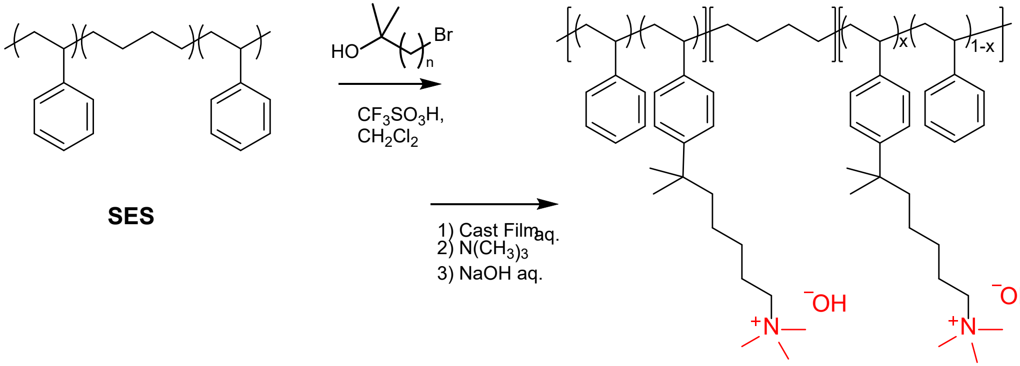
IEC, water uptake, and hydroxide conductivity of QA and Di-QA.

Samples	IEC (mequiv./g)[a]	WU (OH^-, wt.%)	OH^- σ (mS/cm)		
			30 °C	60 °C	80 °C
SEBS-C_3-TMA-0.8 (QA)	**1.55**	**150 (±10)**	**47**	72	93
SEBS-C_3-2TMA-0.4 (Di-QA)	**1.55**	**173 (±13)**	**40**	56	70

[a] from titration

- The mechanical properties of the QA and di-QA SEBS AEMs are poor due to lack of crystallinity.
- Decided not to proceed the direction of QA and di-QA synthetic strategy

Synthesis, Crystallinity, and Hydroxide Conductivity of Semi-Crystalline SES



Ion exchange capacity (IEC), water uptake (WU), and conductivity (σ) of SES.

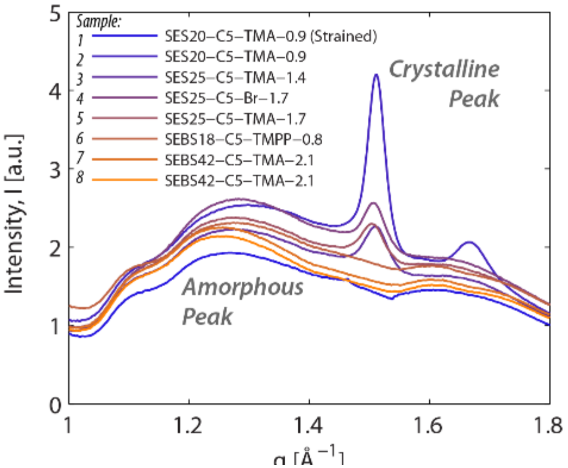
Samples	IEC[a] (meq./g)	OH^- WU (wt %)	Crystallinity (%)	OH^- σ (mS/cm)		
				30°C	60°C	80°C
SES20-C_5-TMA-0.9	0.87	35	40	25	42	53
SES25-C_5-TMA-1.4	1.41	80	25	36	56	65
SES25-C_5-TMA-1.7	**1.71**	**144**	**21**	**42**	54	63

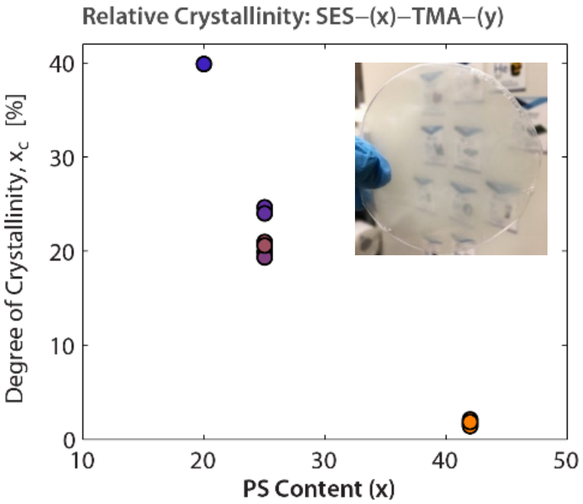
[a] from titration

- Series of semi-crystalline SES polymers were successfully synthesized by Friedel-Craft reaction.

Highlight: SES25-C5-TMA-1.7 met the hydroxide conductivity milestone (> 40 mS cm^{-1} at 30 °C)

WAXS characterization of SES





Alkaline Stability and Mechanical Properties of Semi-Crystalline SES

The property change after stability test (1 M NaOH at 80°C for 300 h)

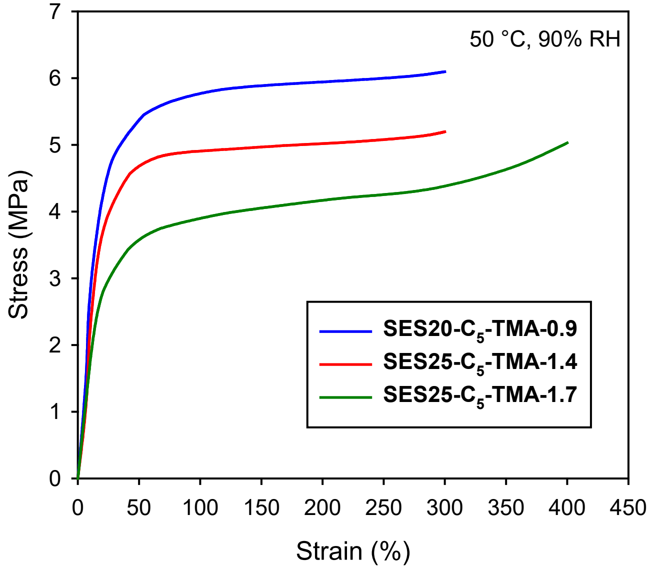
Membrane	Titration IEC (meq./g)[a]		OH^- σ (mS/cm) 80 °C[b]		
	0 h	300 h[c]	0 h	300 h[c]	% loss
SES25-TMA-1.7	1.71	1.78	63	64	**0**

[a]Titration IEC values from Mohr titration method. [b]All OH^- *σ* were measured in water under argon atomosphere. [c]After alkaline test in 1 M NaOH Solution at 80 °C for 300 h

Mechanical properties of SES at 50 °C, 90% RH.

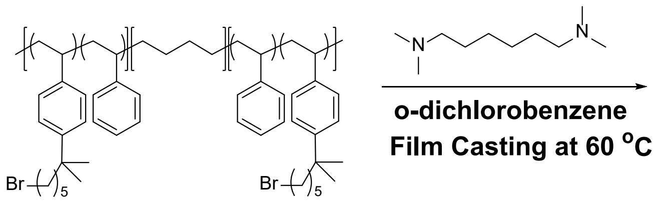
Membrane	Strength (MPa)	Strain (%)	Toughness
SES20-TMA-0.9	6.1	300	1830
SES25-TMA-1.4	5.2	300	1560
SES25-TMA-1.7	5.1	410	**2091**

Tensile stress-strain curves of SES membrane (50 °C, 90% RH)

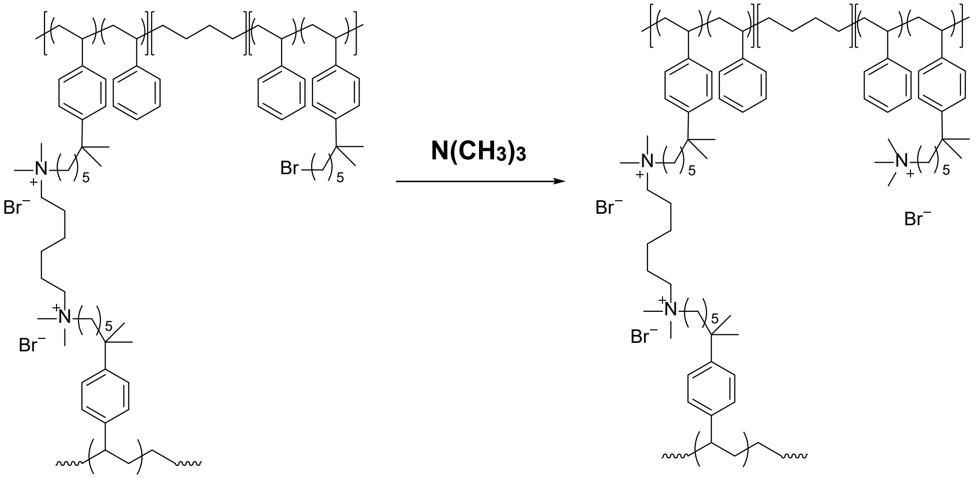


- SES25-C5-TMA-1.7 met the alkaline stability milestone (Milestone: < 5% conductivity loss after 300 h, 1 M NaOH treatment at 80 °C).
- SES25-C5-TMA-1.7 met the mechanical property milestone (Milestone: mechanical strength (MPa) × % elongation > 1400 at 50 °C, 90% RH).

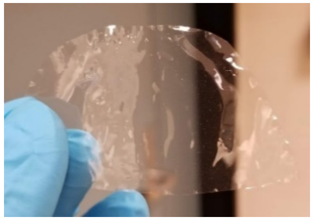
Mechanical Property Improvement Through Crosslinking



o-dichlorobenzene
Film Casting at 60 °C



$N(CH_3)_3$



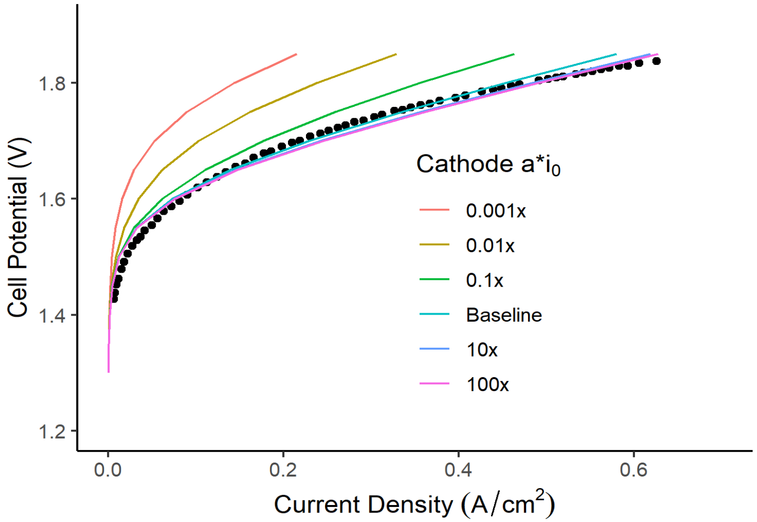
XL-SESx-TMA-y

Samples	IEC (mequiv./g)		WU OH^- (wt. %)	Tensile toughness* (MPa × %)	OH^- σ (mS/cm)[d]		
	^{1}H NMR[a]	Titration[b]			30 °C	60 °C	80 °C
SES25-TMA-1.7	1.73	1.71	144	2091	42	54	63
XL100-SES25-TMA-1.7	**1.66**	**1.50**	**72**	**6055**	**43**	**55**	**82**

* *See Technical backup slide #2 for details*

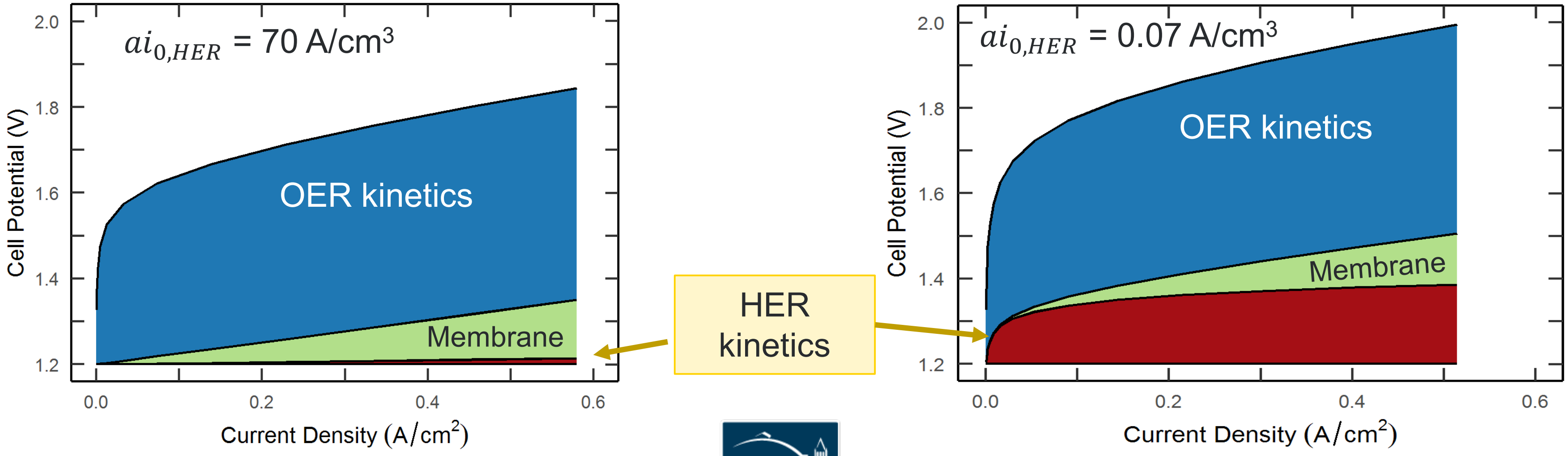
Highlight: Further improved mechanical properties was obtained with crosslinked SES AEMs.

AEM Electrolyzer Model Developed



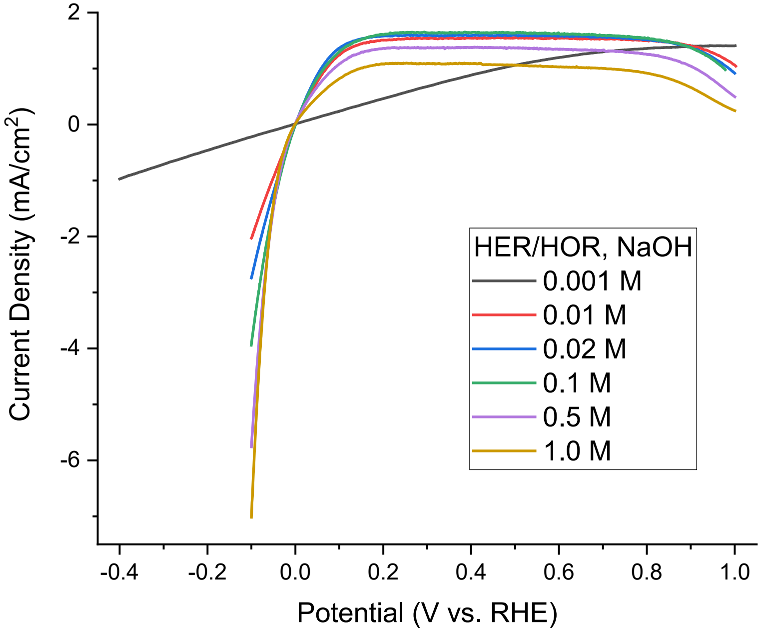
- Electrolyzer model approximates literature data[1] for KOH electrolyte
- Preliminary applied voltage breakdowns illustrate cell limitations
- Next step: improve electrochemical kinetics model to study its importance
  - Current model: Butler-Volmer at each electrode
    - $i_{0,HER}$: 0.7 mA/cm^2
    - $i_{0,OER}$: 1×10^{-4} mA/cm^2
    - Specific surface area: 10^5 cm^2/cm^3

[1] C. C. Pavel *et al.*, *Angew. Chemie - Int. Ed.*, vol. 53, no. 5, pp. 1378–1381, 2014.

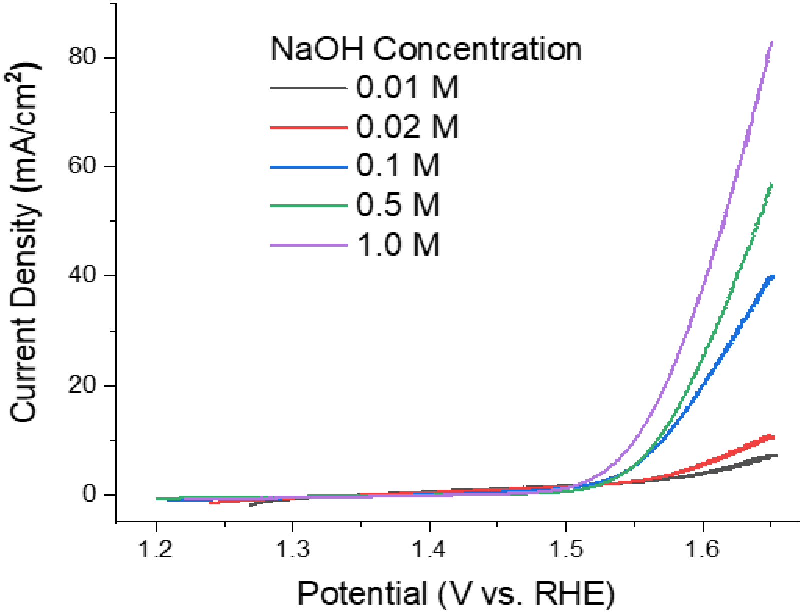


pH Effect of HER/HOR and OER Activity

pH effect of HER/HOR on Pt polycrystal



pH effect of OER on IrO_2

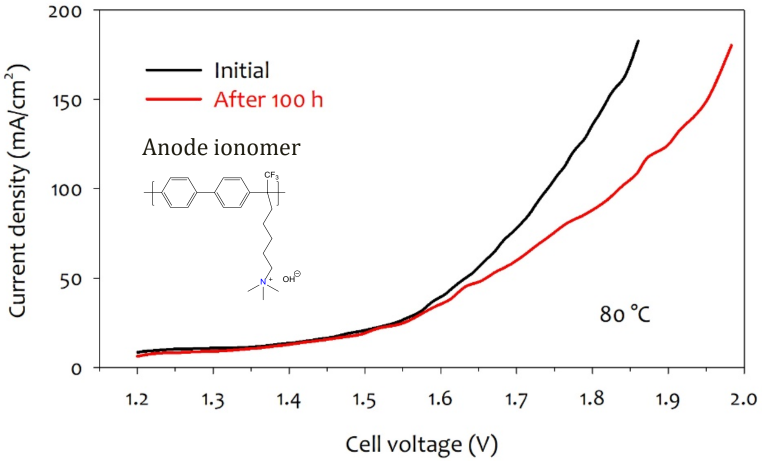


- Both HER and OER activity increases with increasing the concentration of NaOH.
- Stark contrast with HOR which has the best activity at 0.01 – 0.1 M NaOH probably due to cation-hydroxide-water coadsorption.
- **Note:** It is essential to understand that any factor can reduce the pH at the ionomer-catalyst interface.

Identify Durability-Limiting Factor of Alkaline Membrane Electrolyzer

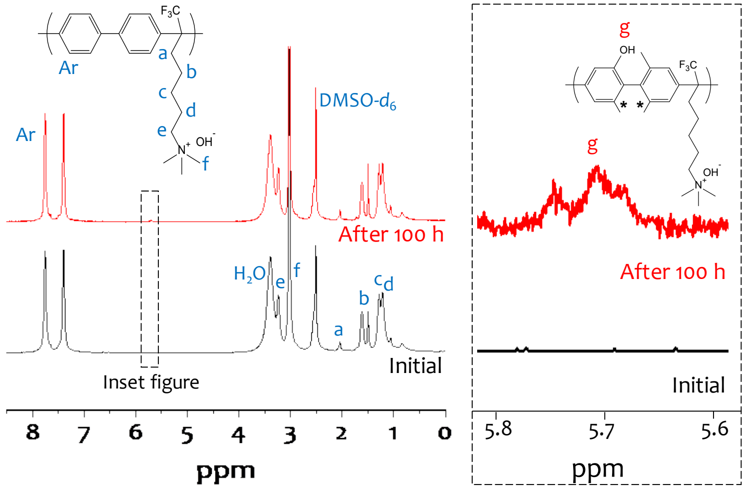
Performance change of AEM electrolyzer after 100 h test at a constant voltage of 2.1 V at 80 °C

(polyphenylene AEM*, Pt/C cathode, IrO_2 anode)

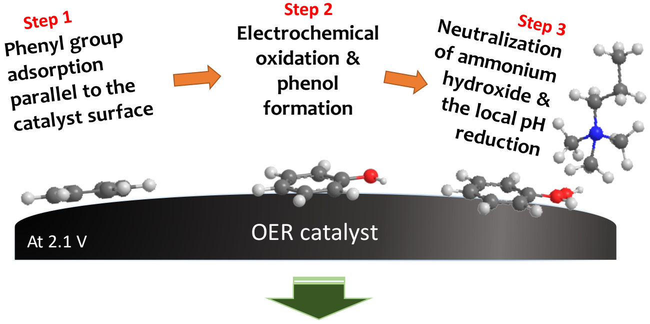


* AEM provided from EMN node SNL

^1H NMR analysis of ionomeric binder of the IrO_2 OER catalyst after the 100 h test



Performance decay mechanism of AEM electrolyzer*



Step 1 Phenyl group adsorption parallel to the catalyst surface

Step 2 Electrochemical oxidation & phenol formation

Step 3 Neutralization of ammonium hydroxide & the local pH reduction

Performance decay of AEM electrolyzer over time

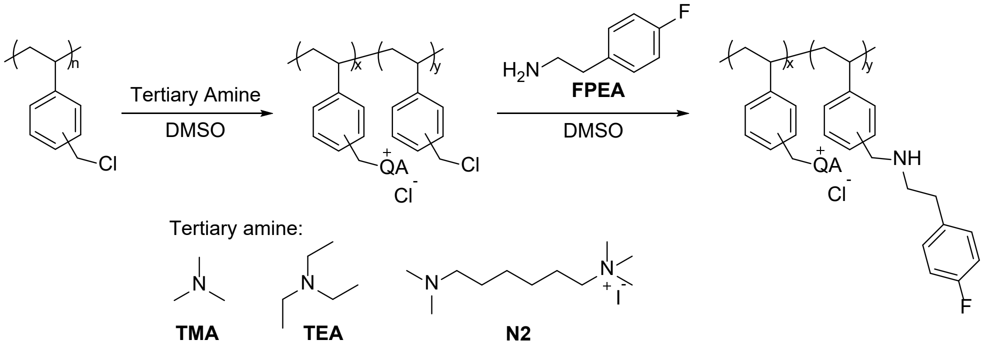
- Acidic phenol formation at the OER catalyst and ionomer interface may detrimental for the OER reaction due to acidic nature of the phenol group.

Highlight: Identify the durability-limiting factor of alkaline membrane electrolyzer.*

*D. Lee et al. ACS Appl. Mater. & Interf. 11, 9696 (2019)

Preparation of Polyolefinic Ionomeric Binders

Synthesis of Quaternized Poly(vinylbenzyl chloride), MW 20-50K



IEC Chart (mmol/g)

Ionic group (x)*	100%	75%	50%	25%
TMA	5.18	3.60	2.23	1.04
TEA	4.26	3.13	2.04	1.00
N2	5.92	4.73	3.37	1.81

* The rest of the percentage (y) is FPEA

Solubility Chart (mmol/g)

	Polymer	IEC (mmol/g)	H_2O	MeOH	EtOH	*i*-PrOH	Ethylene glycol	CH_3CN	Acetone	THF	DMSO
Solubility (Cl⁻ form)	TMA-75	3.60	++	++	+	±	+	−	−	−	++
	TMA-50	2.23	−	++	+	+	+	−	−	−	+
	TEA-75	3.13	+	++	+	+	+	−	−	−	+
	TEA-50	2.04	−	++	+	+△	+	−	−	−	+
	N2-50	3.37	+	++	+	−	+	−	−	−	+△
	N2-25	1.81	−	++	+	−	+	−	−	−	+△
Ion exchange using dialysis membranes and 1M NaOH, washed with DI water and dried under vacuum at room temperature											
Solubility (OH⁻ form)	TMA-50	2.23	−	±	±		±				−
	TEA-50	2.04	−	±	±		±				−
	N2-25	1.81	−	+△	+△		+△				+△

++: soluble instantly; +: soluble at rt; −: insoluble; ±: partially soluble/swollen; +△: soluble when heated and sonicated

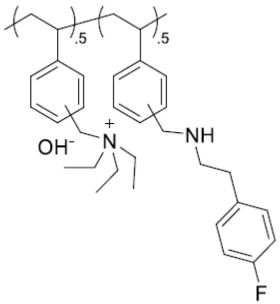
- Acidic phenol formation at the OER catalyst and ionomer interface may detrimental for the OER reaction due to acidic nature of the phenol group.
- Investigated the impact of electrolyte pH effect (Technical backup slide #2)

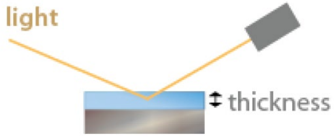
Highlight: Identify the durability limiting factor of alkaline membrane electrolyzer.

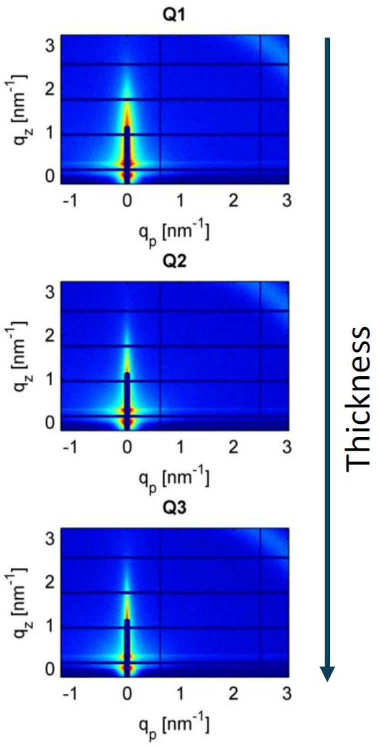
Characterization of Ionomer Thin Film

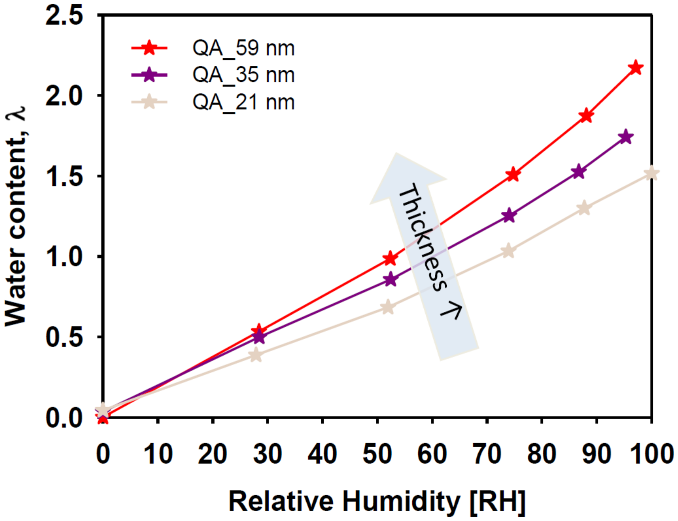
2D GISAXS study

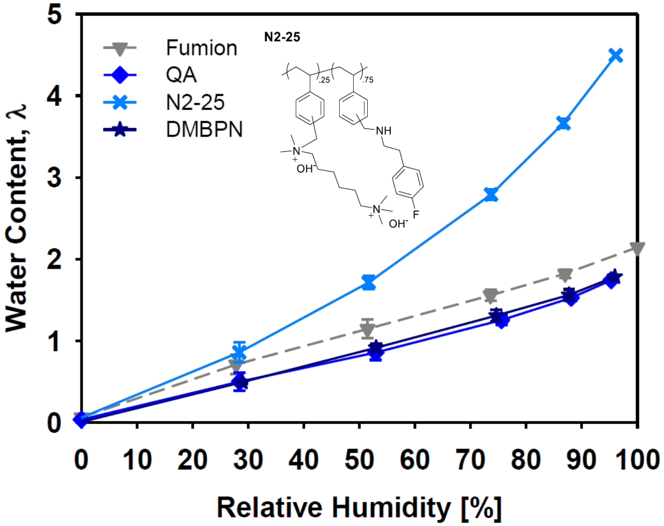
QA











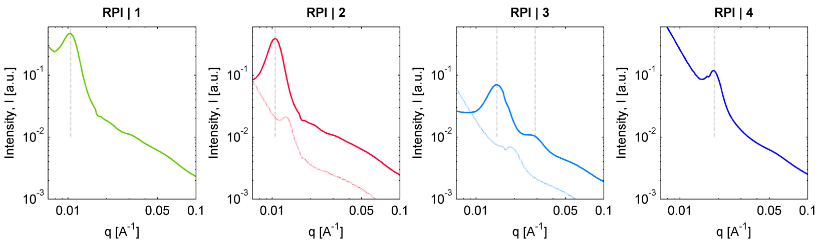
- Ionomer thin film study indicates that within thin-film λ increased with increasing film thickness.
- For a similar thickness 936 nm, significant higher water uptake was obtained with multi-cation group functionalized ionomer.

Collaboration: Effectiveness

Task 1: Synthesis and characterization of SES

Collaborator: LBNL (**Jessica Luo and Amhet Kusoglu**)

- WAXS experiment: crystallinity of SES
- Water sorption: water uptake of SES



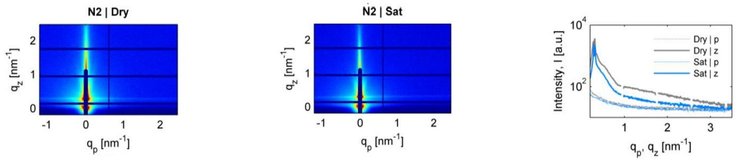
Task 2: Synthesis and characterization of ionomeric binder

Collaborator: LBNL (**Jessica Luo and Amhet Kusoglu**)

- 2D GISAXS Patterns: thin ionomer film morphology

Collaborator: LBNL (**Nemanja Danilovic**)

- Micro electrode study (started from 2nd year)



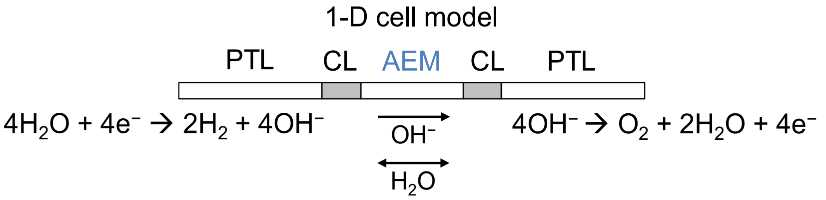
Task 3: AEM performance study

Collaborator: LBNL (**Adam Weber)**

- Performance modeling (thermodynamics, Kinetics and transport)

Collaborator: SNL (**Cy Fujimoto)**

- Provide baseline AEMs (quaternized polyphenylene)



1-D cell model

$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

OH^-

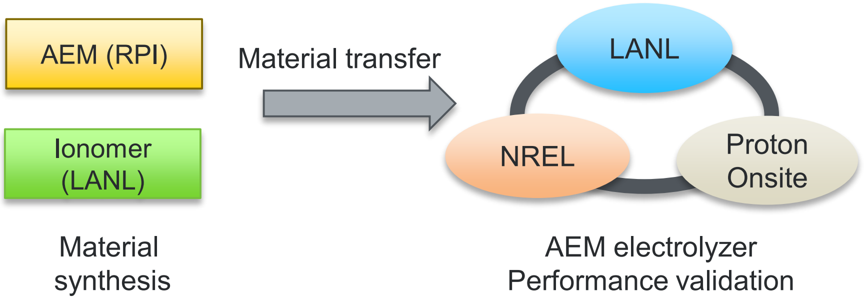
H_2O

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Task 4: AEM performance and durability validation

Collaborator: NREL (**Guido Bender**)

- AEM performance evaluation (started from 2nd year)



Material synthesis

AEM electrolyzer Performance validation

Proposed Future Work

Remainder of FY 2019

- Optimization of IEC, block size, cationic group and crosslinking density of SES.
- Characterization of cross-linked SES (LBNL node collaboration).
- Completion of AEM electrolyzer degradation study (LBNL node collaboration).
- Evaluation of baseline AEM electrolyzer performance (SNL and NREL node collaboration).
- Characterization of ionomer and ionomer performance evaluation (NREL node collaboration).

GNG2: Target electrolyzer MEA performance: 1 A/cm^2 at 2.0 V under ambient pressure.
Target electrolyzer MEA durability: < 0.2 mV/hr degradation rate over 300 hr continuous run with an initial voltage of ~1.8 V.

Remainder of FY 2020

- Down-select AEM and ionomer based on their performance.
- Optimization of the operating conditions in terms of differential pressure, operating temperature and alkaline electrolyte carriers (LBNL, SNL, and NREL node collaboration).
- Scale-up synthesis of AEM and ionomers.

GNG3: Target electrolyzer MEA durability: < 0.05 mV/hr degradation rate over 1,000 hr continuous run with an initial voltage of ~1.8 V.

Any proposed future work is subject to change based on funding levels.

Project Summary

Objective:	Preparing advanced alkaline hydroxide conducting SES materials and demonstrating the performance and durability in alkaline membrane water electrolysis.
Relevance:	Aiming to make AEM electrolyzer system competitive to PEM electrolyzers in terms of performance and durability. AEM electrolyzers can utilize PGM-free catalysts, as well as low-cost metal flow fields which account for more than 70% of the stack cost.
Approach:	Preparing highly alkaline stable SES block copolymer AEM and polyolefinic ionomeric binder which minimizes the undesirable interaction with electrocatalysts.
Accomplish-ments (FY 18)	▪ Prepared polyolefinic SES block copolymer which showed no chemical degradation for 300 h in 1 M NaOH at 80 °C, hydroxide conductivity > 60 mS/cm at 80 °C and mechanical toughness. ▪ Initiate the modeling study to understand alkaline electrolyzer performance and durability. ▪ Identify a durability-limiting factor of AEM electrolyzer and synthesized soluble polyolefinic ionomeric binder.
Collaborations:	Work together with 5 EMN nodes at three different National Labs (LBNL, SNL and NREL). Work closely with Proton Onsite (subcontractor) for the electrolyzer performance and durability evaluation.

Publications & Presentations

Publications:

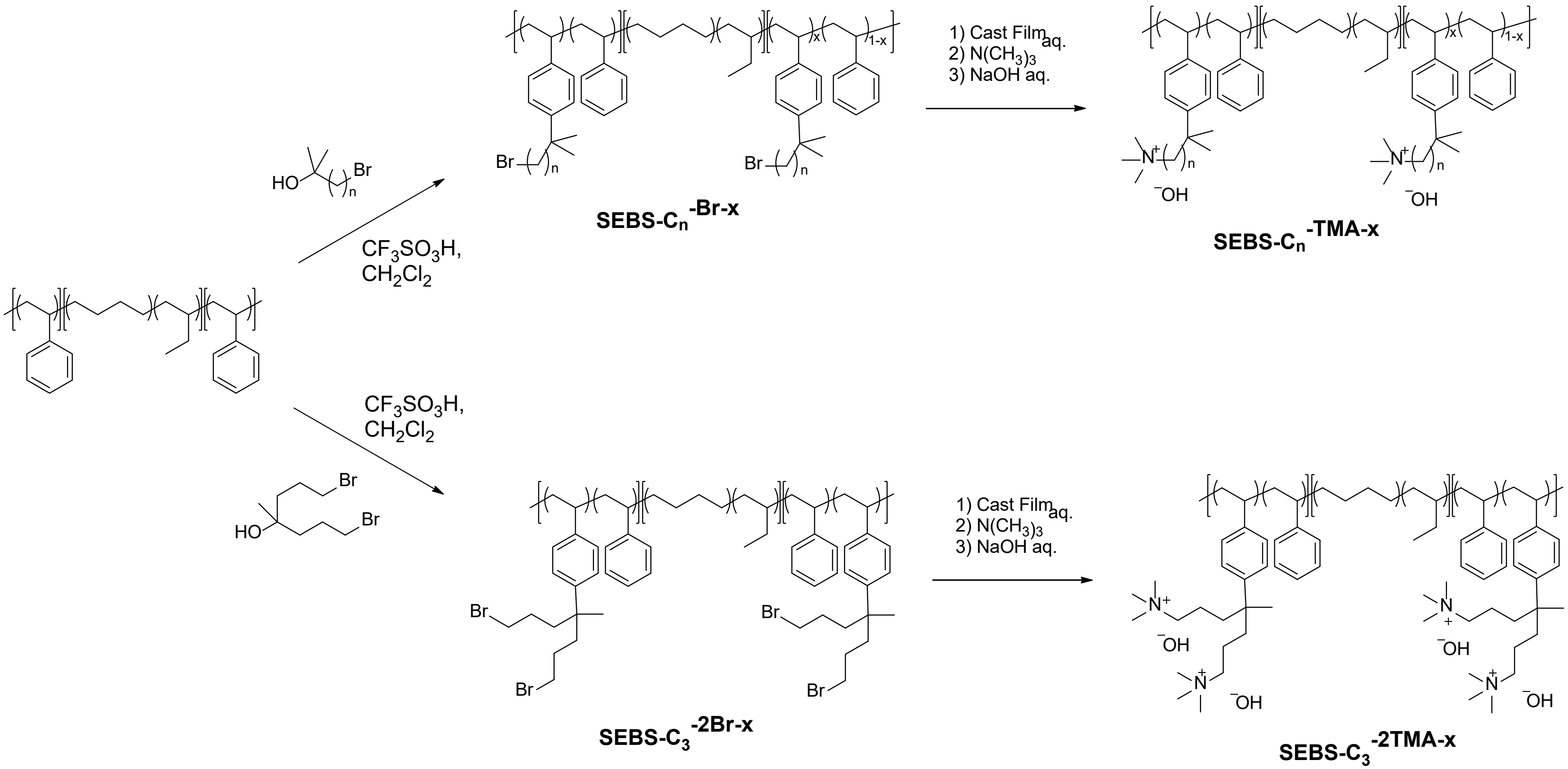
- Synthesis of Aromatic Anion Exchange Membranes by Friedel-Crafts Bromoalkylation and Cross-Linking of Polystyrene Block Copolymers, Jong Yeob Jeon, Sungmin Park, Junyoung Han, Sandip Maurya, Angela D. mohanty, Ding Tian, Nayan Saikia, Michael A. Hickner, Chang Y. Ryu, Mark E. Tuckerman, Stephen J. Paddison, Yu Seung Kim, and Chulsung Bae, *Macromolecules*, 52, 5, 2139-2147 (2019).
- Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer, Dongguo Li, Ivana Matanovic, Albert S. Lee, Eun Joo Park, Cy Fujimoto, Hoon T. Chung, and Yu Seung Kim, *ACS Applied Materials & Interfaces*, 11, 10, 9696-9701 (2019).

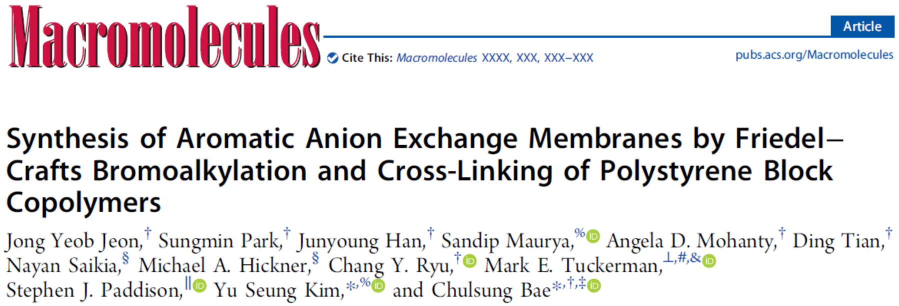
Presentation:

- Phenyl Oxidation at Oxygen Evolution Potentials, D. Li, I. Matanovic, Albert S. Lee, Eun Joo Park, Cy Fujimoto, Hoon T. Chung, and Yu Seung Kim, Polymers for Fuel Cells, Energy Storage and Conversion, Feb. 24-27, 2019, Asilomar Conference Ground, Pacific Grove, CA, USA.
- Caveat of High Temperature Accelerated Stability Test of Anion Exchange Membrane, E. J. Park, S. Maurya, M. R. Hibbs, C. H. Fujimoto, Y. S. Kim, Polymers for Fuel Cells, Energy Storage and Conversion, Feb. 24-27, 2019, Asilomar Conference Ground, Pacific Grove, CA, USA.
- Carbon-free Perovskite Oxide OER Catalysts for AEM Electrolyzer, H. T. Chung, A. S. Lee, Y. S. Kim, P. Zelenay, C. Fujimoto, L.-W. Wang, G. Teeter, G. Bender, Abstract number IO3-1687, 233rd ECS Meeting, May 13-17, 2018 Seattle, Washington.

Technical Back-Up Slides

Mono-QA and di-QA Functionalized SEBS AEMs

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Article

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Synthesis of Aromatic Anion Exchange Membranes by Friedel−Crafts Bromoalkylation and Cross-Linking of Polystyrene Block Copolymers

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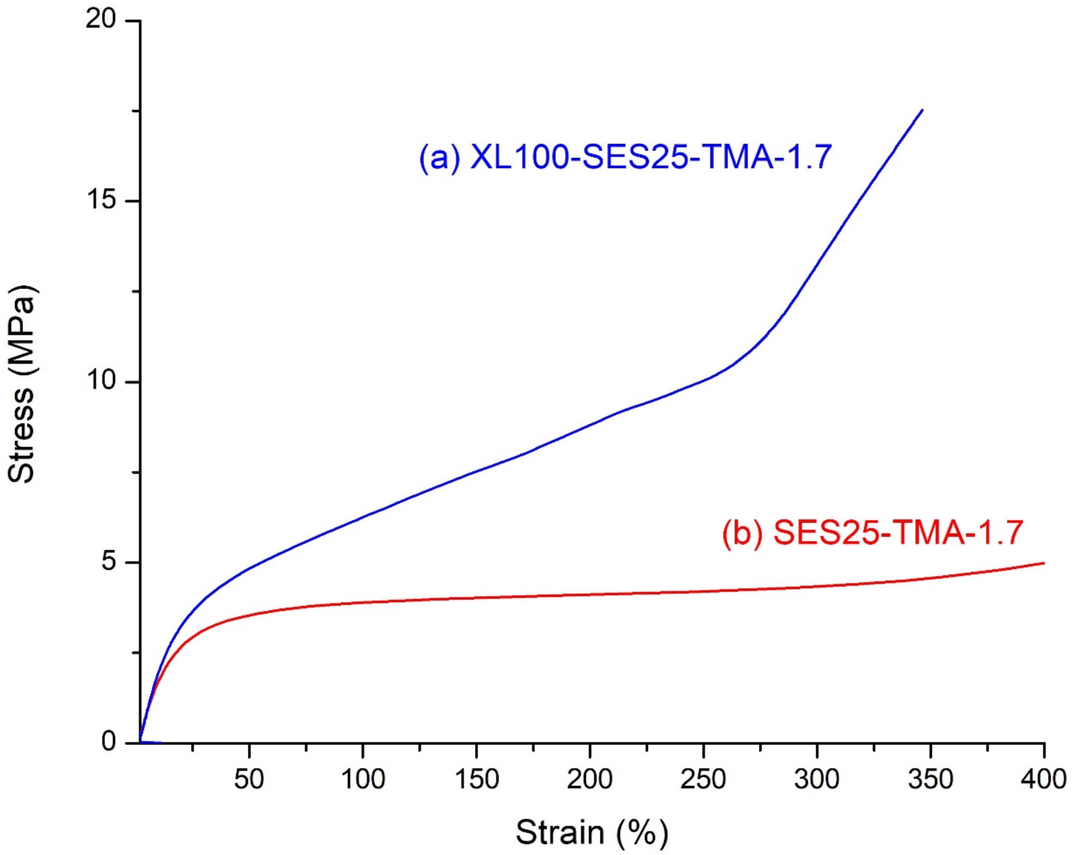
Stress-strain Curves of Crystalline SES AEMs

50 °C and 90% RH



17.5 MPa, 346%

17.5 x 346 = 6055

5.1 MPa, 410%

5.1 x 410 = 2091

Q4 (SMART, go-no-go decision point):
iii) Mechanical toughness (mechanical strength (MPa) x % elongation) > 1,400 at 50 °C, 90% RH