



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  
6/13/2018

Project ID # PD159

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# Project Overview

## Project Partners

**PI** Yu Seung Kim, Los Alamos National Laboratory  
**Co-PIs** Chulsung Bae, Rensselaer Polytech Institute  
Kathy Ayers, Proton Onsite

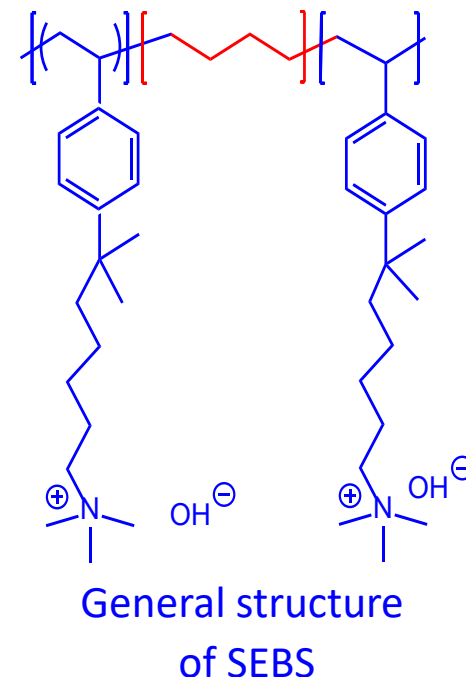
## Project Vision

Preparing durable and economically-affordable alkaline hydroxide conducting materials based on SEBS and demonstrating the performance and durability in alkaline membrane-based 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.

Award #	EE000XXXX
Start/End Date	10/01/2017 - 09/30/2018
Year 1 Funding*	\$250,000



\* 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 (in collaboration with Sandia National Laboratories and Proton Onsite) demonstrated > 2000 h alkaline electrolyzer durability using polyaromatic electrolytes in 2013. In this project, we are aiming to develop economically viable elastomeric ionomers having at least equivalent conductivity with much improved mechanical properties.

## Barriers

- Alkaline stability
- Hydroxide conductivity
- Mechanical properties

## 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, polymer characterization
- Chulsung Bae (RPI): Polymer synthesis & characterization
- Sangwoo Lee (RPI): Polymer design & characterization
- Kathy Ayers (Proton): Alkaline membrane electrolyzer testing



# Approach- Innovation

## Styrene-Ethylene-Butylene-Styrene Block Copolymer

- **Robust polymer backbone**

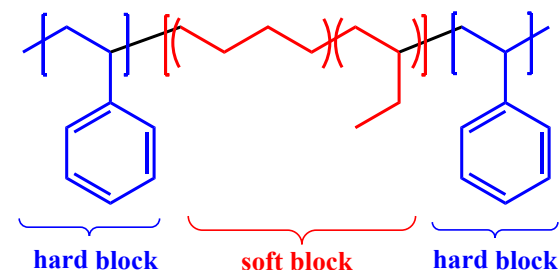
→ No aryl-ether polymer backbone provides chemical stability.

- **Block copolymer architecture**

→ Soft block provides toughness under dry & wet conditions.

- **Cheap base polymer**

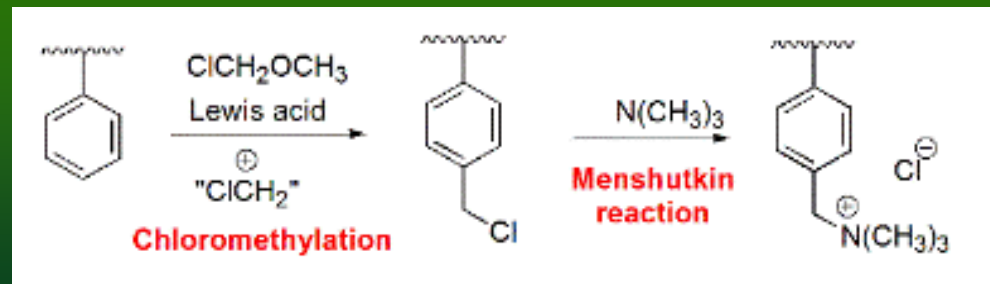
→ Various SEBS are commercially available on the market.



**SEBS**

## Conventional Chloromethylation

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

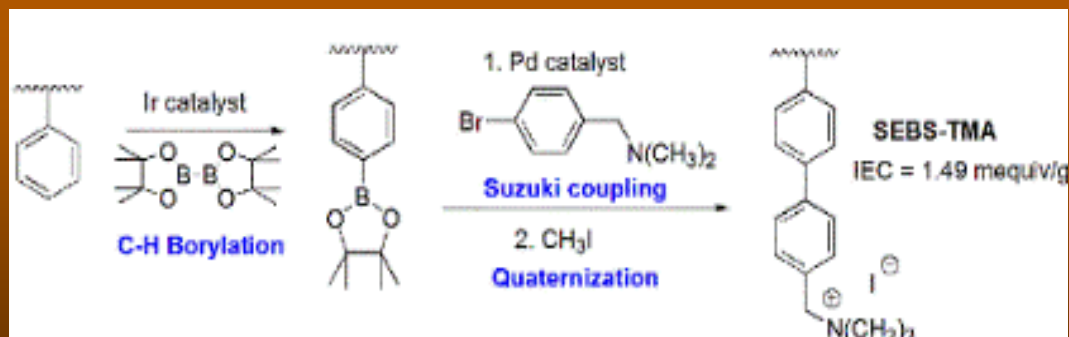




# Approach- AEM Synthesis

## Metal-catalyzed coupling (M-Cat)

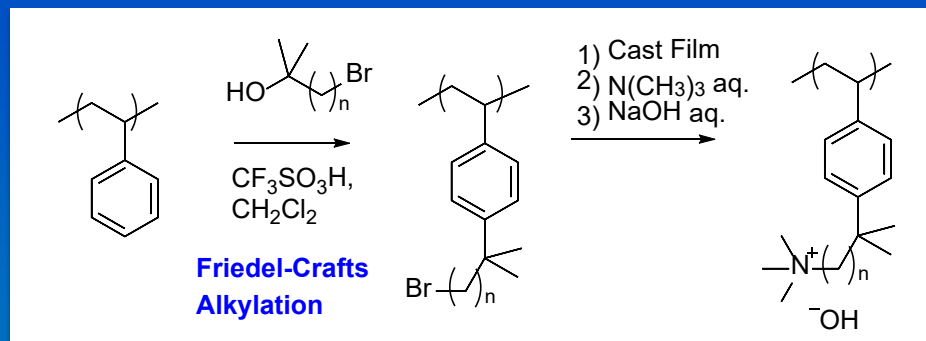
- Good control of IEC (1.5 meq./g)
- High hydroxide conductivity (40 mS/cm)
- Excellent chemical stability (1 M NaOH at 80 °C for 4 weeks)
- **Not practical because of expensive metal catalysts**



*Macromolecules*, 48, 7085 (2015)

## 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





# Scope of Work & Tech Validation

## Scope of Work

- Prepare high molecular weight quaternized SEBS *via* acid catalyzed Friedel-Craft reaction (1<sup>st</sup> year).
- Prepare soluble quaternized styrene ionomers for catalyst dispersion (1<sup>st</sup> year).

## Tech Validation

- Proton Onsite will demonstrate best performance and durability of alkaline electrolyzer using SEBS based polymer electrolytes (2<sup>nd</sup> & 3<sup>rd</sup> year).
- Membrane properties will be validated by LBNL (EMN node) using scattering techniques and thin film characterizations.
- Baseline performance of alkaline membrane based LTE will be validated from modeling works at LBNL.

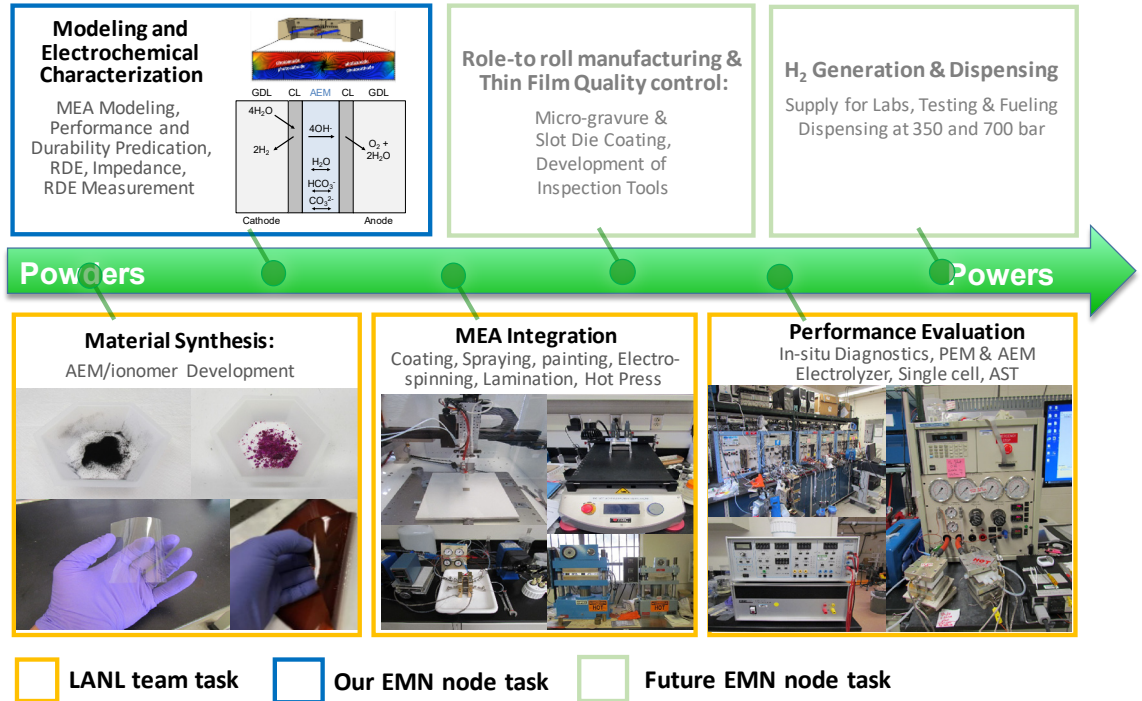


# Relevance & Impact

- ❑ Benefits of alkaline membrane water electrolyzer
  - Lowering capital cost by removing the high noble metal loading requirements.
  - Using relatively cheap cell hardware under high pH conditions.
  - High pressure operation is possible with less cross-permeation.

- ❑ This project directly deals with novel membrane fabrication and development of low temperature electrolysis

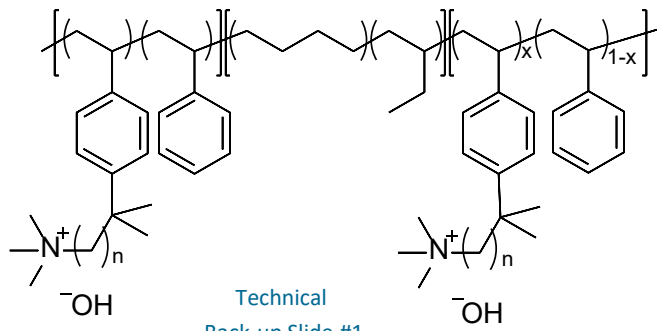
- ❑ Current Node utilization: Modeling and electrochemical characterization.





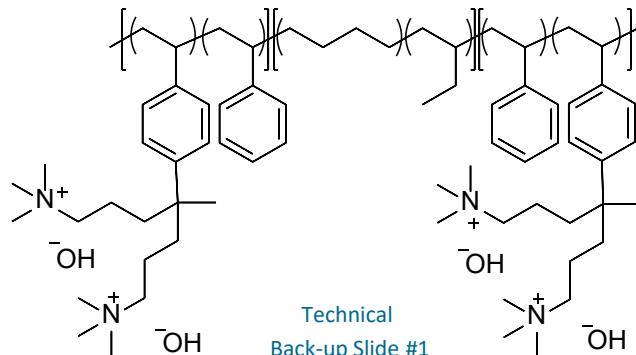
# Membrane Synthesis

## Acid catalyzed base polymer (QA)



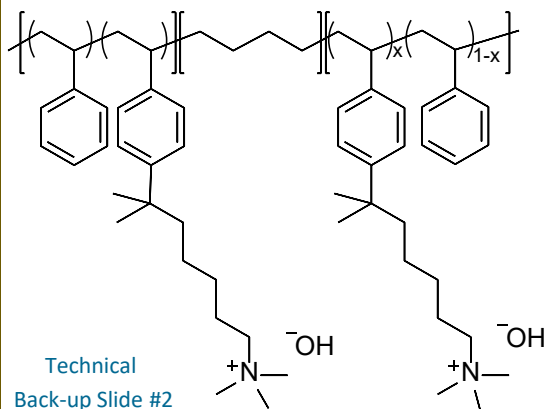
Technical Back-up Slide #1

## Di-Quaternized SEBS (Di-QA)

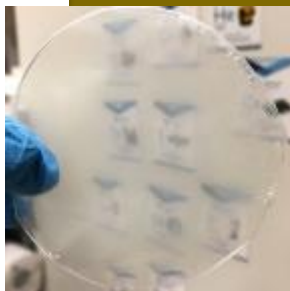


Technical Back-up Slide #1

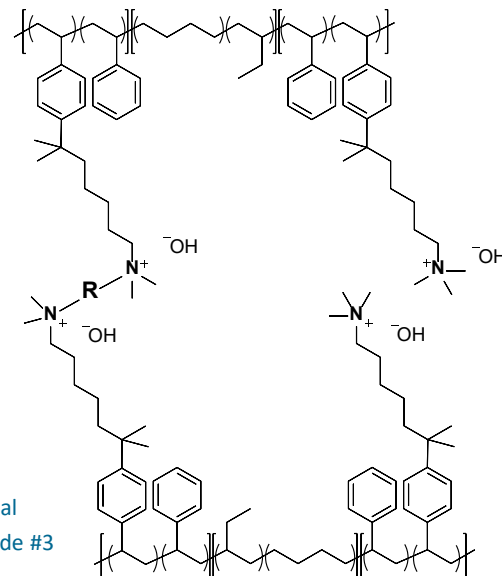
## Semi-crystalline SES (Cryst)



Technical Back-up Slide #2



## Cross-linked SEBS (X-link)

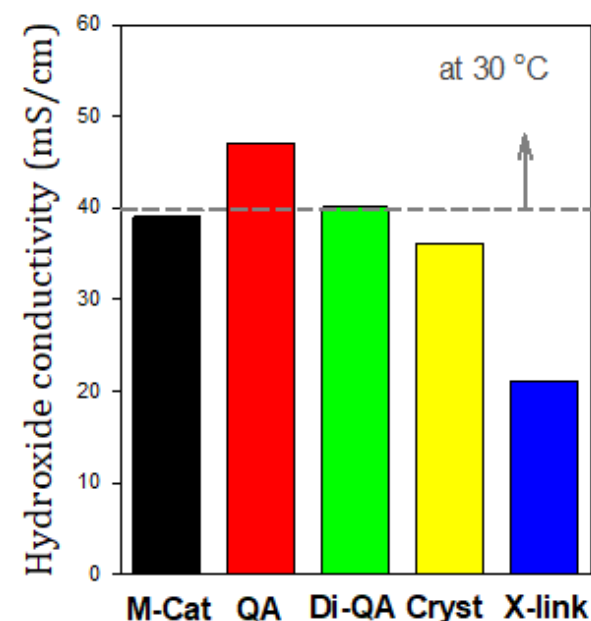
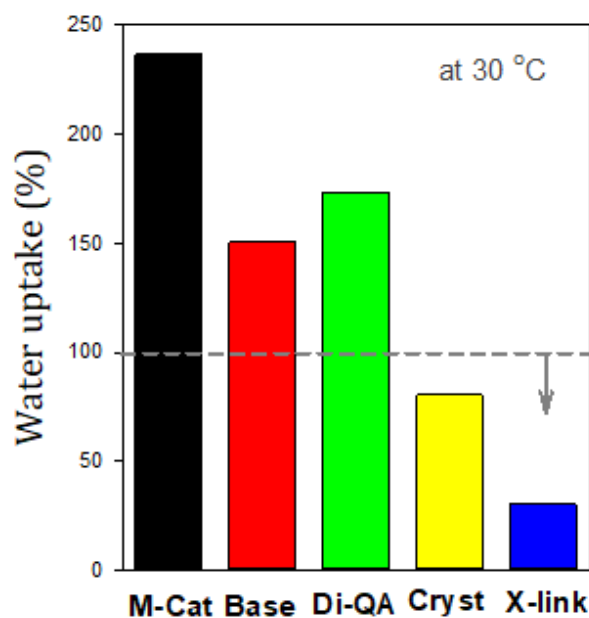
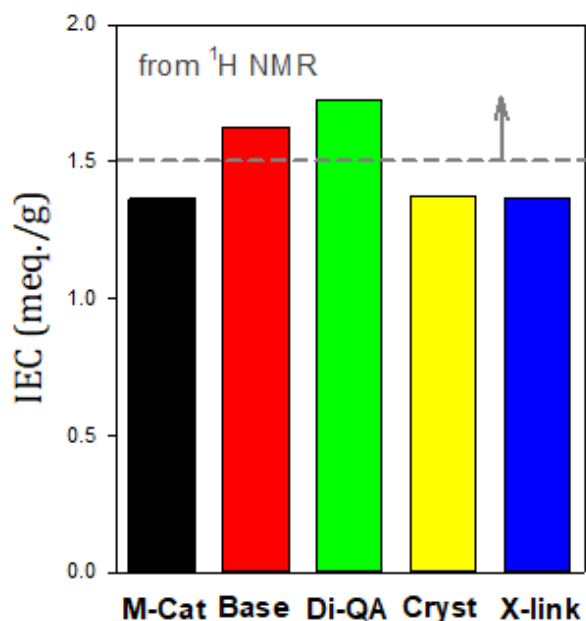


Technical Back-up Slide #3





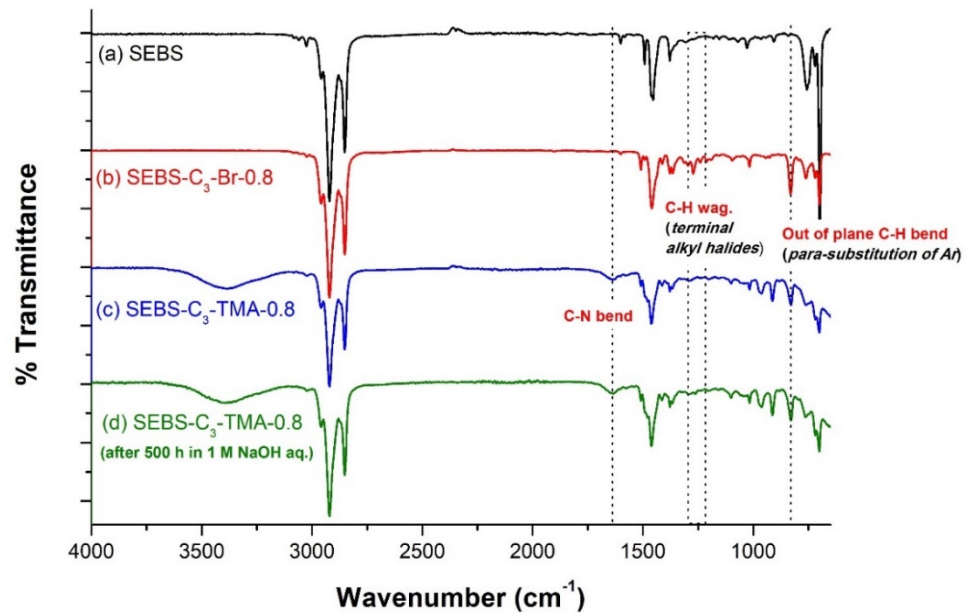
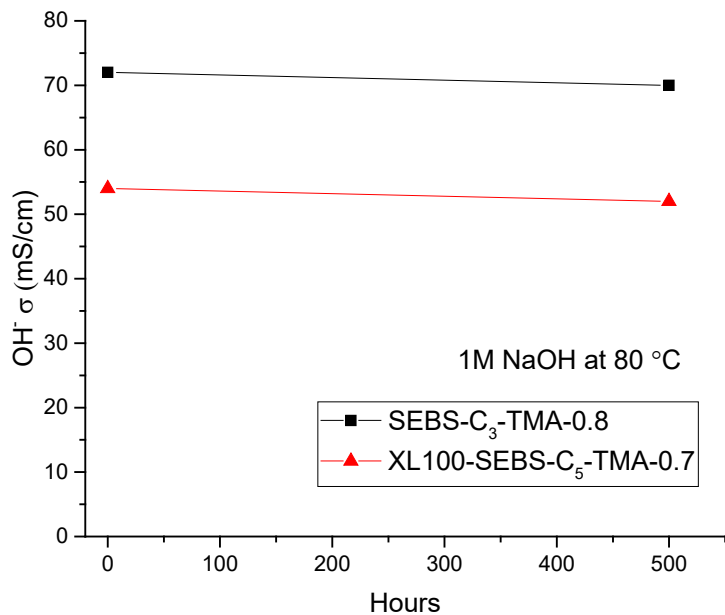
# Membrane Properties



- AEM properties are controlled by IEC and tailoring chemical structure.
- QA and Di-QA SEBS meet the hydroxide conductivity go-no-go decision criteria.
- The hydroxide conductivity of semi-crystalline SEBS is approaching the go-no-go decision criteria → need further optimization.



# Chemical Stability



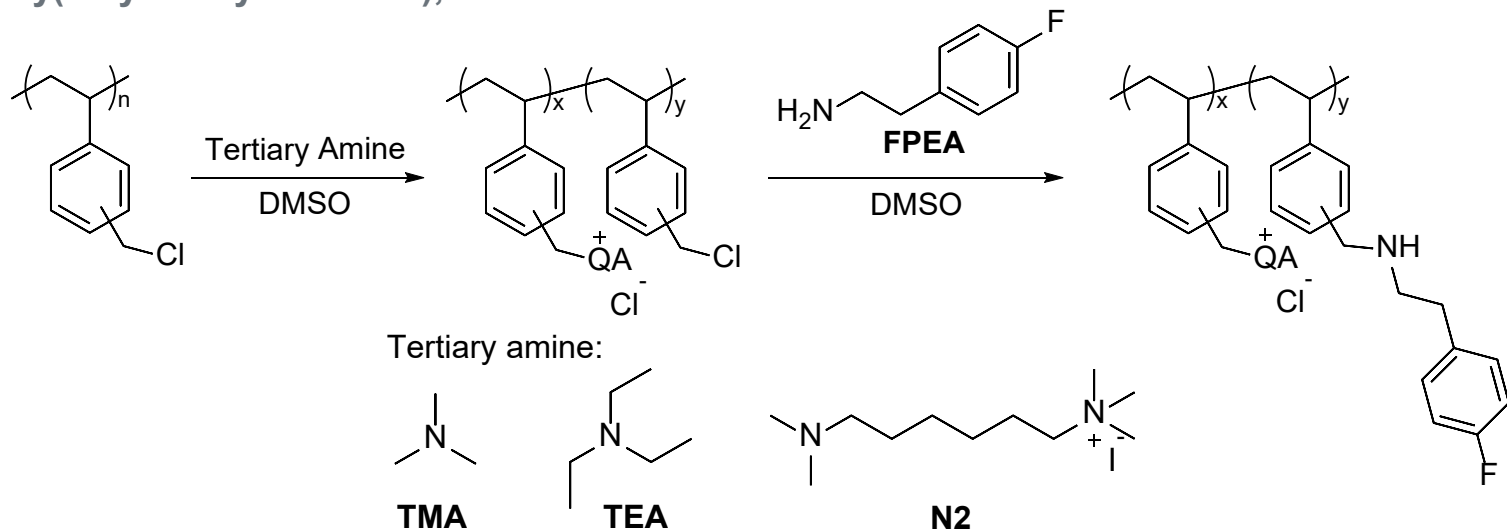
Samples	Titration IEC (mequiv/g) <sup>a</sup>		OH <sup>-</sup> σ (mS/cm) 60 °C <sup>b</sup>	
	0 h	500 h <sup>c</sup>	0 h	500 h <sup>c</sup>
SEBS-C <sub>3</sub> -TMA-0.8	1.55	1.50	72	70
XL100-SEBS-C <sub>5</sub> -TMA-0.7	1.29	1.29	54	52

<sup>a</sup>Mohr titration. <sup>b</sup>OH<sup>-</sup> σ in water under Ar. <sup>c</sup>1 M NaOH aq. at 80 °C.



# Ionomer Synthesis

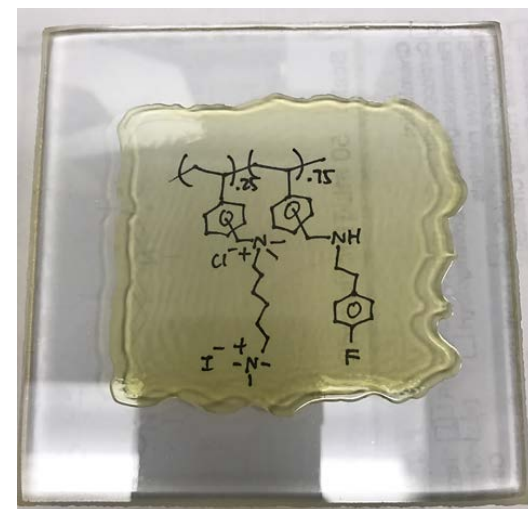
Poly(vinylbenzyl chloride), MW 20-50k



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





# Ionomer Properties

Solubility (Cl <sup>-</sup> form)	Polymer	IEC (mmol/g)	H <sub>2</sub> O	MeOH	EtOH	<i>i</i> -PrOH	Ethylene glycol	CH <sub>3</sub> CN	Acetone	THF	DMSO
	TMA-75	3.60	++	++	+	±	+	-	-	-	++
	TMA-50	2.23	-	++	+	+	+	-	-	-	+
	TEA-75	3.13	+	++	+	+	+	-	-	-	+
	TEA-50	2.04	-	++	+	+Δ	+	-	-	-	+
	N2-50	3.37	+	++	+	-	+	-	-	-	+Δ
	N2-25	1.81	-	++	+	-	+	-	-	-	+Δ
	Ion exchange using dialysis membranes and 1M NaOH, washed with DI water and dried under vacuum at room temperature										
Solubility (OH <sup>-</sup> form)	TMA-50	2.23	-	±	±		±				-
	TEA-50	2.04	-	±	±		±				-
	N2-25	1.81	-	+Δ	+Δ		+Δ				+Δ

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



# Outlook and Projected Outcomes

## Milestone progress

Description	Criteria	Planned date	Progress
Baseline SEBS synthesis	5 × 5 inch, 3 membranes (IEC > 1.5 meq.g)	12/31/17	100% (12/19/2017)
Chemical stability (baseline polymer)	< 5% $\sigma$ loss after 300 h, 1 M NaOH, 80 °C	3/31/18	100% (3% $\sigma$ loss after 500 h, 1 M NaOH, 80 °C )
Deliver SES copolymer	IEC > 1.8 meq./g	6/30/18	60% (made 1.5 meq/g)
Conductivity & stability assessment	40 mS cm <sup>-1</sup> at 30 °C, <5% loss $\sigma$ after 300 h 1 M NaOH, 80 °C	9/30/18	50% (met conductivity target)

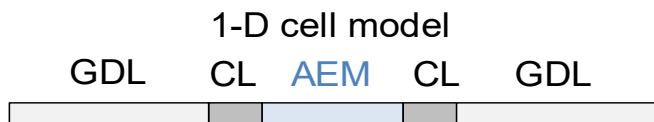
## Go-no-Go Decision (9/30/2018)

Description Criteria	Current status
<ul style="list-style-type: none"><li>▪ <math>\sigma</math>: 40 mS cm<sup>-1</sup> at 30°C,</li><li>▪ &lt; 5% <math>\sigma</math> loss after 300 h 1 M NaOH, 80°C,</li><li>▪ Elongation &gt; 200%, strength &gt; 10 MPa at 50°C.</li></ul>	Three SEBS types (QA, Di-QA and semi-crystalline) met the conductivity target. Alkaline stability test for the SEBS copolymers look promising and need to complete in the next three months. Initial mechanical test assessment indicates all SEBS copolymers prepared have low strength (~ 5 MPa). LANL team makes an effort to reinforce membrane to increase the mechanical properties.

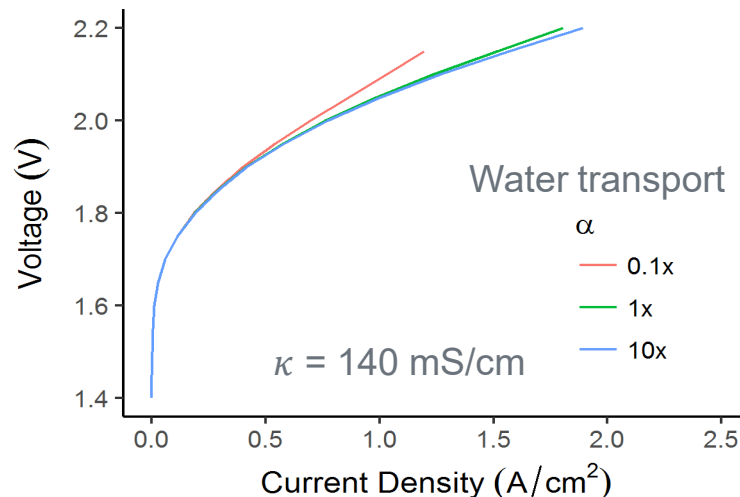
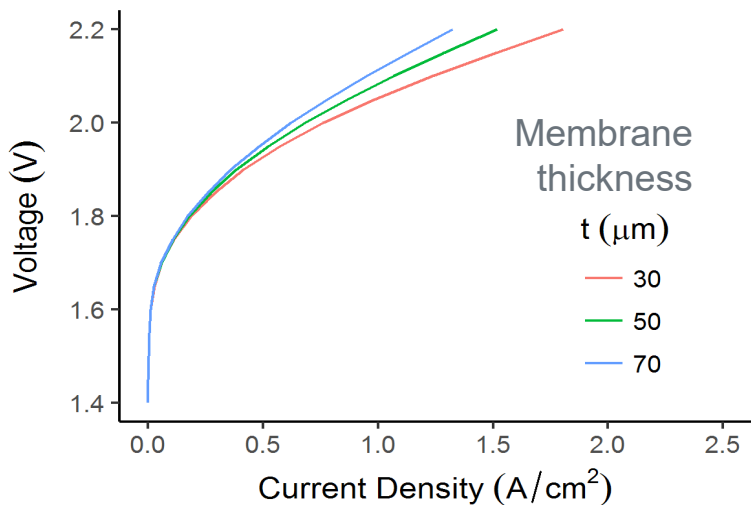
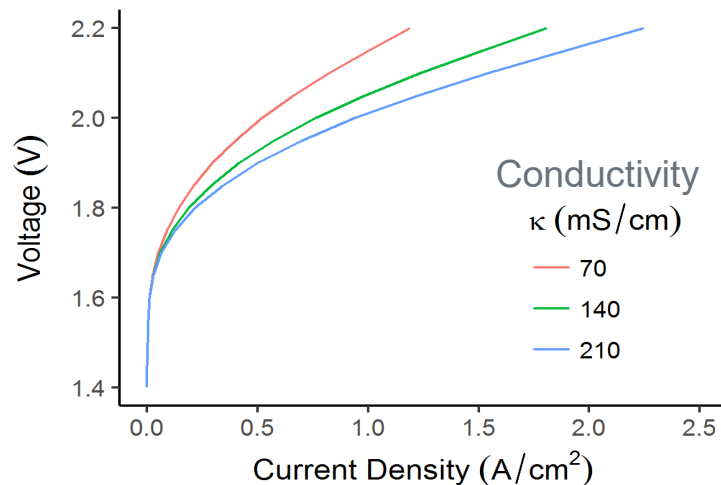


# Collaboration: EMN node: LBNL

Water electrolysis modeling provides the insight on AEM design.

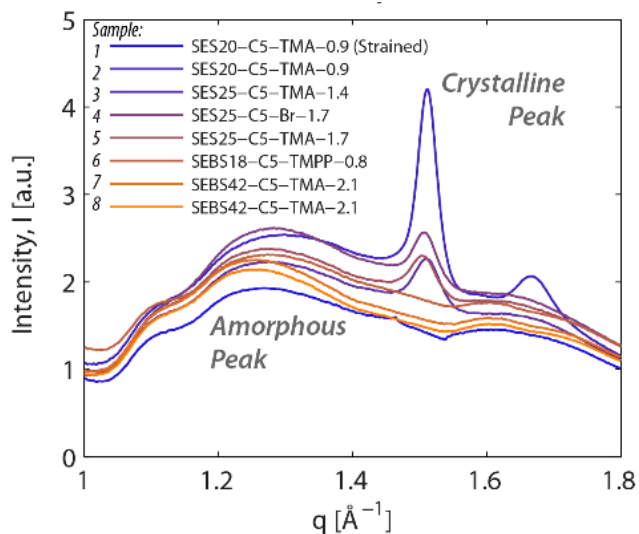
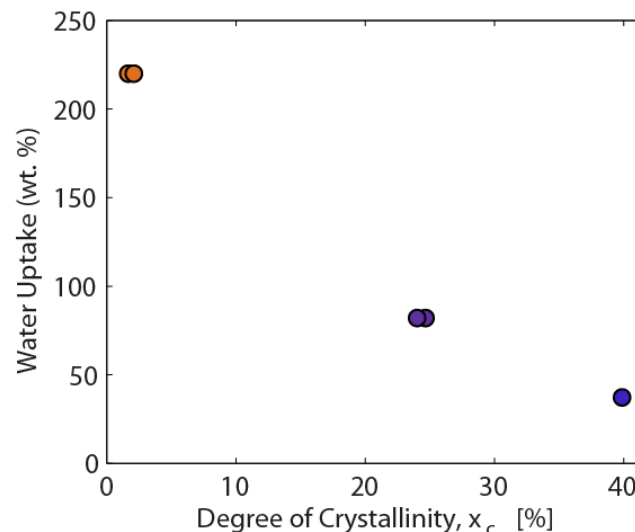
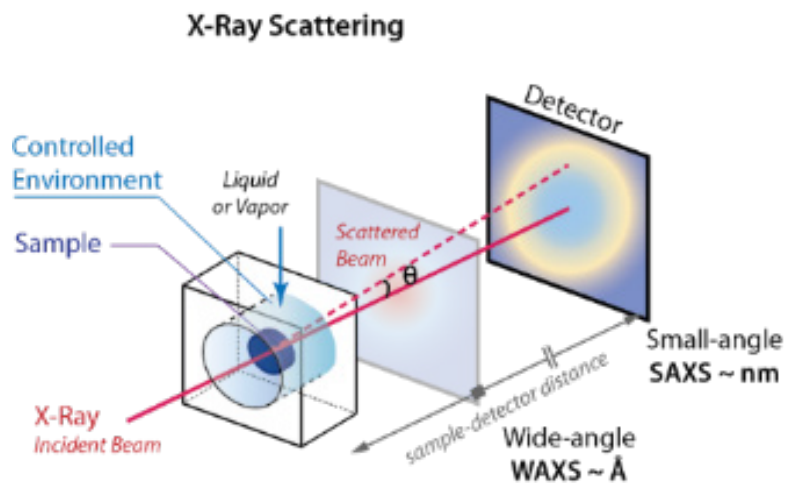


- ▶ Thinner membranes result in improved performance
- ▶ Membrane conductivity  $\kappa$  significantly impacts performance
- ▶ Avoiding a factor of 10 reduction in water transport coefficient  $\alpha$  is advised





# Collaboration: EMN node: LBNL



- ▶ WAXS data indicates that the crystallinity of membrane increases with PS content.
- ▶ Degree of crystallinity impacts membrane water uptake.
- ▶ Increasing PS content may lead better mechanical properties.



# Collaboration: Interactions with broader HydroGEN research community

- LANL and RPI have provided membrane benchmarking/protocol suggestions to Proton Onsite including conductivity and membrane stability data.
- LANL has worked closely with Sandia National Laboratories in order to improve chemical stability of benchmark anion exchange membranes.
- LANL, RPI and Proton Onsite participated the ARPA-E IONICS review meeting on April 10, 2018 to discuss AEM benchmark membrane production and test protocols for water electrolyzers.
- LANL has discussed a possible collaboration with NREL team for testing membrane based water electrolyzers.





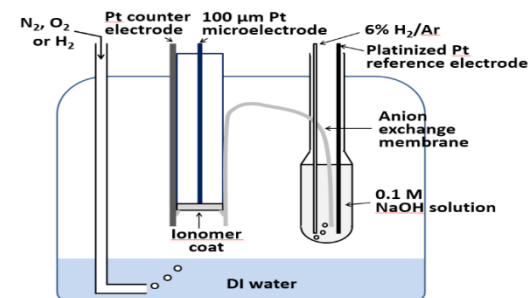
# Proposed Future Work

- Optimize the chemical structures of SEBS to balance conductivity and mechanical properties.
- Complete the alkaline stability of SEBS assessment.
- Down select alkaline ionomers based on microelectrode measurement.
- *In-situ* ASR measurement and stability test under electrolyzer mode.

Alkaline  
membrane  
electrolyzer  
setup  
(3/30/18)



## AEM microelectrode





# Project Summary

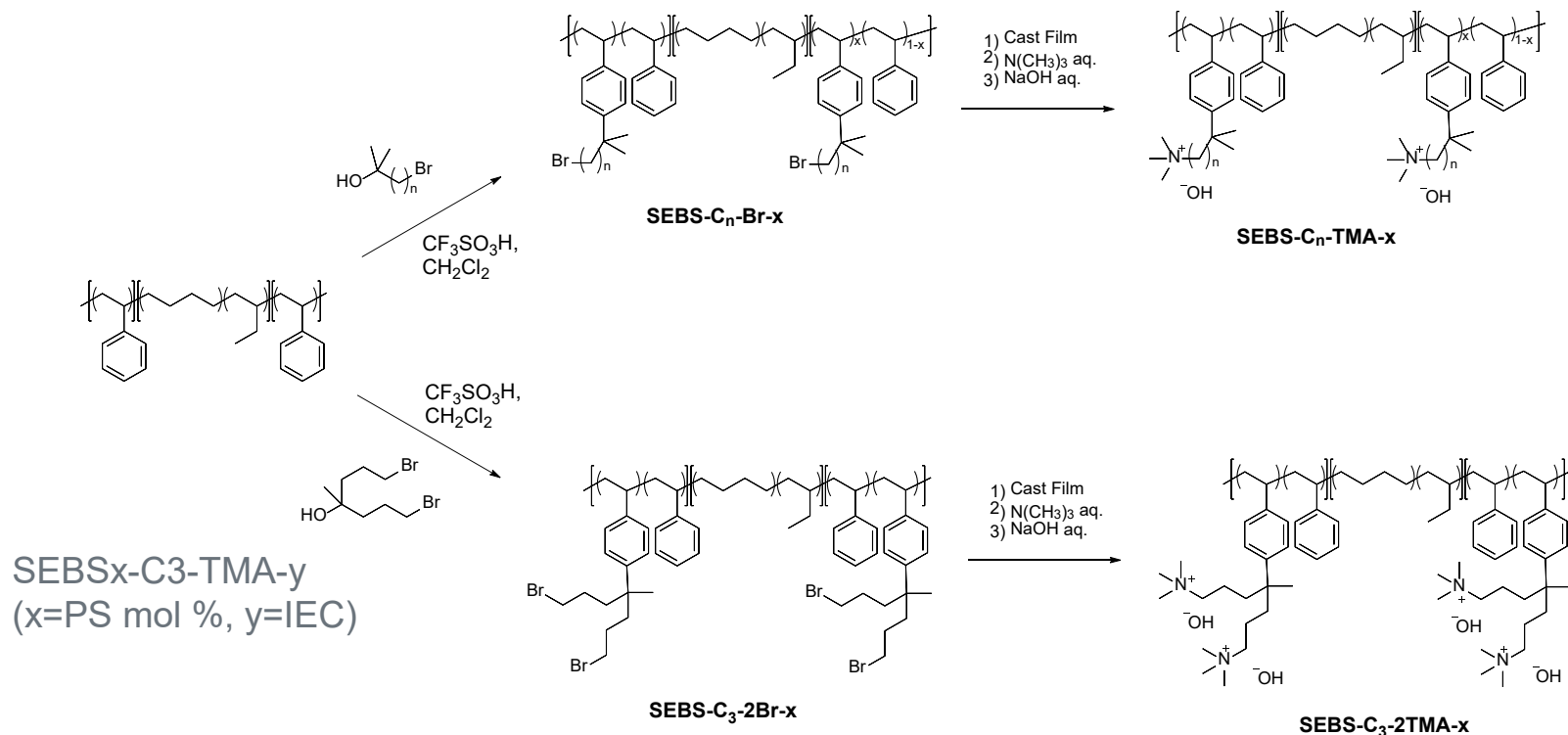
- Elastomeric, alkaline-stable SEBS anion exchange membranes for water electrolysis have been successfully synthesized via acid catalyzed polymerization (without using metal catalyst).
- The newly synthesized SEBS membranes possess excellent hydroxide conductivity, good alkaline stability and promising mechanical properties.
- Soluble polystyrene-based ionomeric dispersion have been successfully prepared for MEA fabrication.
- Further structural optimization of these membranes and ionomers is on going.



# Technical Back-Up Slides



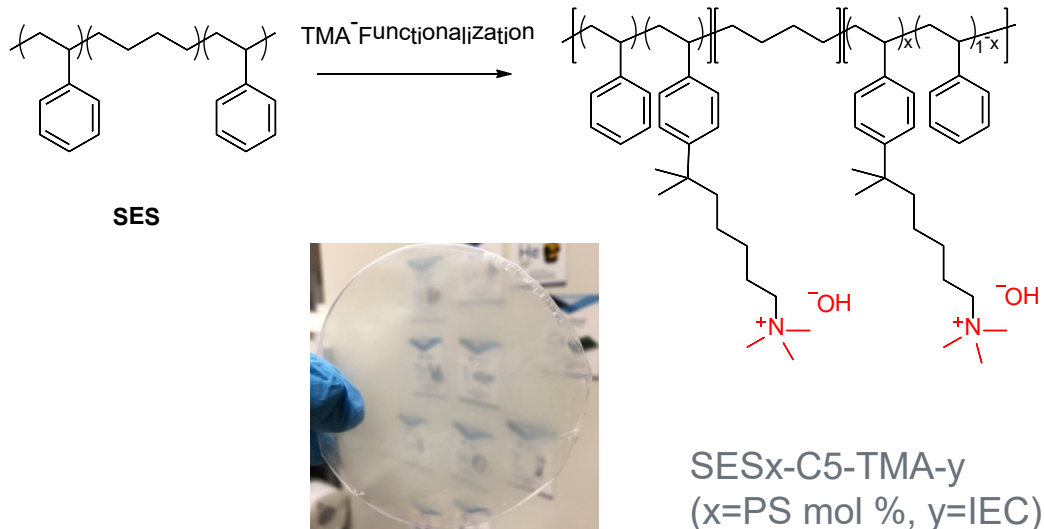
# Synthesize Acid Catalyzed SEBS



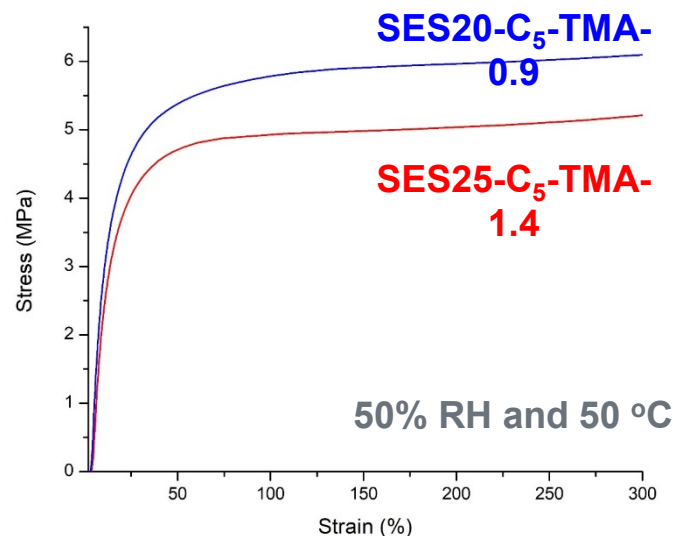
Samples	IEC (meq./g)		OH <sup>-</sup> WU (wt %)	In-plane swelling OH <sup>-</sup> (%)	OH <sup>-</sup> σ (mS/cm)		
	<sup>1</sup> H NMR	Titration			30 °C	60 °C	80 °C
SEBS18-C <sub>3</sub> -TMA-0.8	1.62	1.55	150	31	47	72	93
SEBS18-C <sub>3</sub> -2TMA-0.4	1.72	1.55	173	27	40	56	70



# Synthesis of Semi-crystalline SEBS



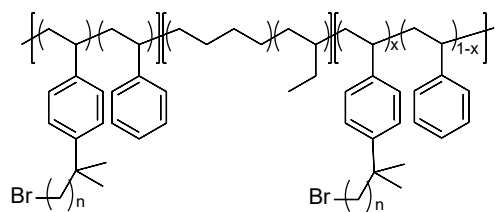
## Mechanical properties



Samples	IEC (meq./g)		OH <sup>-</sup> WU (wt %)	In-plane swelling OH <sup>-</sup> (%)	Cl <sup>-</sup> σ (mS/cm)			OH <sup>-</sup> σ (mS/cm)		
	<sup>1</sup> H NMR	Titration			30°C	60°C	80°C	30°C	60°C	80°C
SES20-C <sub>5</sub> -TMA-0.9	0.89	0.87	35	17	8	14	20	25	42	53
SES25-C <sub>5</sub> -TMA-1.4	1.37	1.41	80	23	12	21	24	36	56	70

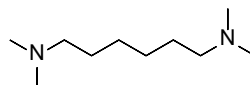


# Synthesis Cross-linked SEBS



**SEBS-C<sub>n</sub>-Br-x**

+ Tetrahydrofuran +



**TMHDA**

IEC : 1.36 mequiv/g,

Thickness : 50  $\mu$ m,

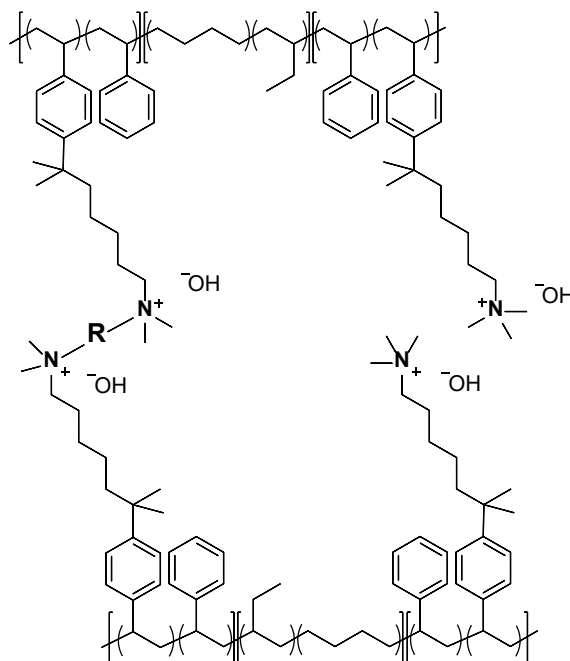
Water uptake (OH<sup>-</sup>) : 30 %

1. Rxn 1-3hr

2. Casting solution

3. dry

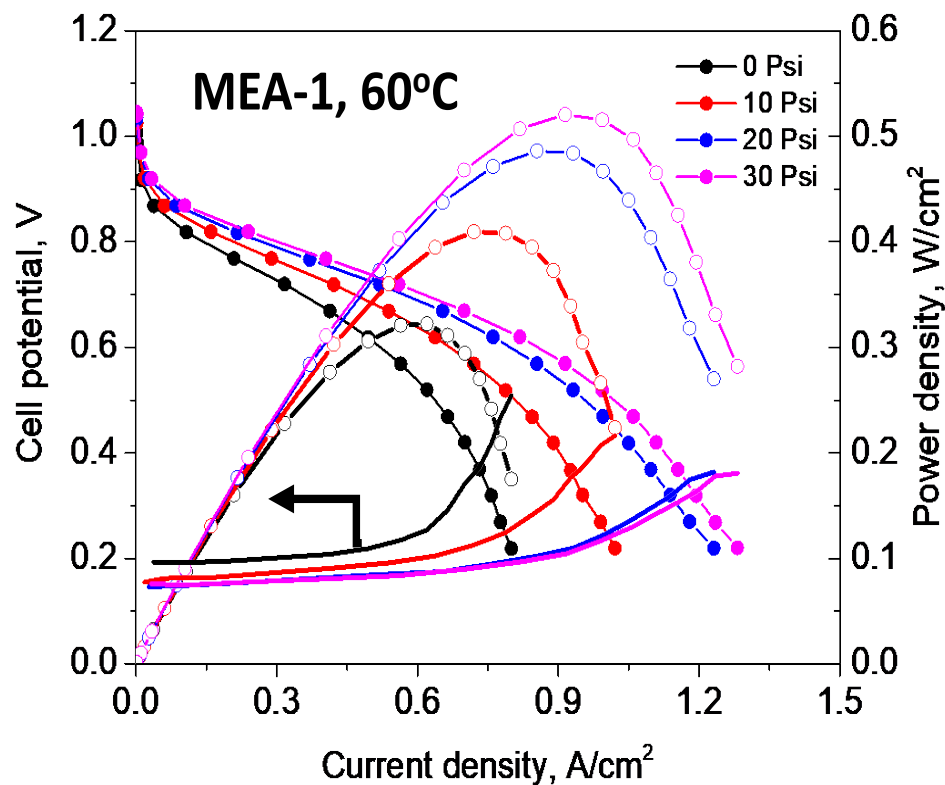
**N(CH<sub>3</sub>)<sub>3</sub>**



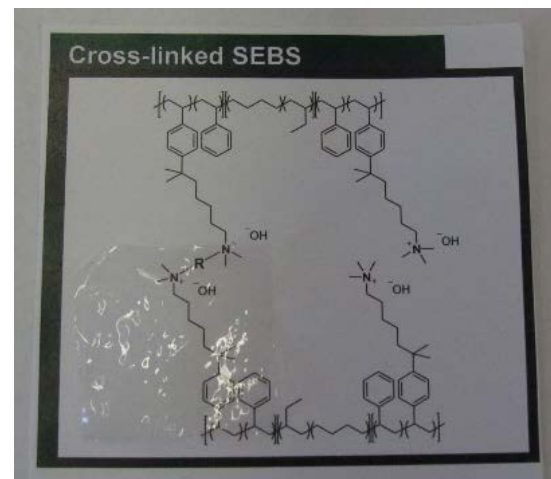
**XL100-SEBS18-C<sub>5</sub>-TMA-0.7**  
(R = C<sub>6</sub>H<sub>12</sub>)



# Device Performance (Fuel Cell Mode)



membrane



- SEBS AEM holds backpressure to 30 psi at 60 °C.
- Cell HFR is  $\sim 0.15 \Omega \text{ cm}^2$  for 50 micron thick membrane (equivalent to 33 mS/cm)  $\rightarrow$  *ex situ* measurement: 33 mS/cm at 60 °C.
- AEM dehydration occurred at high current density in fuel cell mode.