Scalable Elastomeric Membranes for Alkaline Water Electrolysis

Yu Seung Kim
Los Alamos National Laboratory
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Project Overview

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

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

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Expected Advance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxide conductivity (mS/cm)</td>
<td>30-40</td>
<td>40</td>
</tr>
<tr>
<td>% Loss conductivity after 300 h, 1 M NaOH, 80 °C</td>
<td>30</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Tensile toughness (MPa × % elongation)</td>
<td>2000</td>
<td>3000</td>
</tr>
</tbody>
</table>

Partnerships
- 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

HydroGEN: Advanced Water Splitting Materials
Benefits of AEM electrolyzer over PEM electrolyzer

Technical challenges of AEM electrolyzers
- Low performance and durability are two technical challenges for AEM electrolyzers. 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).
## Milestone progress

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

## 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)

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>IEC (mequiv./g)</th>
<th>WU (OH⁻, wt.%)</th>
<th>OH⁻ σ (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS-C₃-TMA-0.8 (QA)</td>
<td>1.55</td>
<td>150 (±10)</td>
<td>47 72 93</td>
</tr>
<tr>
<td>SEBS-C₃-2TMA-0.4 (Di-QA)</td>
<td>1.55</td>
<td>173 (±13)</td>
<td>40 56 70</td>
</tr>
</tbody>
</table>

\( a \) 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

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)
Alkaline Stability and Mechanical Properties of Semi-Crystalline SES

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

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Titration IEC (meq./g)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>OH⁻ σ (mS/cm) at 80 °C&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SES25-TMA-1.7</td>
<td>1.71</td>
<td>63</td>
<td>0</td>
</tr>
<tr>
<td>SES25-C5-TMA-1.4</td>
<td>1.52</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>SES25-C5-TMA-1.7</td>
<td>1.70</td>
<td>63</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Titration IEC values from Mohr titration method. <sup>b</sup>All OH⁻ σ were measured in water under argon atmosphere. <sup>c</sup>After alkaline test in 1 M NaOH Solution at 80 °C for 300 h

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

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Strength (MPa)</th>
<th>Strain (%)</th>
<th>Toughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SES20-TMA-0.9</td>
<td>6.1</td>
<td>300</td>
<td>1830</td>
</tr>
<tr>
<td>SES25-TMA-1.4</td>
<td>5.2</td>
<td>300</td>
<td>1560</td>
</tr>
<tr>
<td>SES25-TMA-1.7</td>
<td>5.1</td>
<td>410</td>
<td>2091</td>
</tr>
</tbody>
</table>

- 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

**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
    - \(i_{0,\text{HER}}\): 0.7 mA/cm\(^2\)
    - \(i_{0,\text{OER}}\): \(1 \times 10^{-4}\) mA/cm\(^2\)
    - Specific surface area: \(10^5\) cm\(^2\)/cm\(^3\)

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• 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, IrO2 anode)

- **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

- 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)

<table>
<thead>
<tr>
<th>Ionic group (x)*</th>
<th>100%</th>
<th>75%</th>
<th>50%</th>
<th>25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>5.18</td>
<td>3.60</td>
<td>2.23</td>
<td>1.04</td>
</tr>
<tr>
<td>TEA</td>
<td>4.26</td>
<td>3.13</td>
<td>2.04</td>
<td>1.00</td>
</tr>
<tr>
<td>N2</td>
<td>5.92</td>
<td>4.73</td>
<td>3.37</td>
<td>1.81</td>
</tr>
</tbody>
</table>

* The rest of the percentage (y) is FPEA

Solubility Chart (mmol/g)

<table>
<thead>
<tr>
<th>Solubility (Cl-form)</th>
<th>Polymer</th>
<th>IEC (mmol/g)</th>
<th>H2O</th>
<th>MeOH</th>
<th>EtOH</th>
<th>IPA</th>
<th>Ethylene glycol</th>
<th>CH3CN</th>
<th>Acetone</th>
<th>THF</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA-75</td>
<td>3.60</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>TMA-50</td>
<td>2.23</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>TEA-75</td>
<td>3.13</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>TEA-50</td>
<td>2.04</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>+Δ</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>N2-50</td>
<td>3.37</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+Δ</td>
<td></td>
</tr>
<tr>
<td>N2-25</td>
<td>1.81</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+Δ</td>
<td></td>
</tr>
</tbody>
</table>

Ion exchange using dialysis membranes and 1M NaOH, washed with DI water and dried under vacuum at room temperature

<table>
<thead>
<tr>
<th>Solubility (OH-form)</th>
<th>TMA-50</th>
<th>2.23</th>
<th>-</th>
<th>±</th>
<th>±</th>
<th>±</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA-50</td>
<td>2.04</td>
<td>-</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>-</td>
</tr>
<tr>
<td>N2-25</td>
<td>1.81</td>
<td>-</td>
<td>+Δ</td>
<td>+Δ</td>
<td>+Δ</td>
<td>+Δ</td>
<td>+Δ</td>
</tr>
</tbody>
</table>

++: soluble instantly; +: soluble at rt; -: insoluble; ±: partially soluble/swollen; +Δ: 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

• Ionomer thin film study indicates that within thin-film $\lambda$ increased with increasing film thickness.

• For a similar thickness 936 nm, significant higher water uptake was obtained with multi-cation group functionalized ionomer.
**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)

**Task 4: AEM performance and durability validation**

**Collaborator: NREL (Guido Bender)**
- AEM performance evaluation (started from 2nd year)
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/cm² 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.

Accomplishments (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:


Presentation:


Technical Back-Up Slides
Mono-QA and di-QA Functionalized SEBS AEMs

1) Cast Film, 2) N(CH$_3$)$_3$, 3) NaOH aq.
**Stress-strain Curves of Crystalline SES AEMs**

**50 °C and 90% RH**

![Stress-strain Curves](image)

(a) XL100-SES25-TMA-1.7

17.5 MPa, 346%  
17.5 x 346 = 6055

(b) SES25-TMA-1.7

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