HydroGEN Seedling: Scalable Elastomeric Membranes for Alkaline Water Electrolysis

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Subcontractors:
- Rensselaer Polytechnic Institute, Troy, NY
- Proton Onsite, Wallingford, CT

Project Start Date: October 1, 2017
Project End Date: September 30, 2020

Overall Objectives

- Prepare durable and economically affordable hydroxide-conducting materials based on poly(styrene-*b*-ethylene-*b*-styrene) (SES) as anion exchange membranes (AEMs).

- Prepare high-performing ionomeric electrode binders for alkaline water electrolyzers.

- Demonstrate high-performance alkaline water electrolyzers using PGM-free catalysts.

- Demonstrate alkaline water electrolyzer durability under steady and accelerated stress conditions.

Fiscal Year (FY) 2019 Objectives

- Synthesize a quaternized SES AEM that meets all AEM technical targets.

- Down select an AEM for alkaline membrane electrolyzer testing.

- Prepare soluble styrene-based ionomers for electrode binders.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Low production cost for polymer electrolytes

- High mechanical properties of AEMs

- Understanding the performance-and durability-limiting factors of AEM electrolyzers.

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Prepared acid-catalyzed SES AEMs that met conductivity, stability, and mechanical property targets required for operation with a 78% decrease in reagent cost.

- Prepared a series of uncrosslinked and crosslinked SES AEMs by a facile and more environmentally benign synthetic route.

- Demonstrated the performance of the down-selected SES AEMs in terms of hydroxide conductivity, chemical stability, and mechanical properties.

- Initiated ionomer development for high-performance AEM electrolyzers.

- Identified the alkaline electrolyzer durability-limiting factor as phenyl oxidation of the membrane.

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

Table 1. Technical Targets

Metric	Target	Status	Comment
Conductivity	40 mS cm^{-1} at 30°C	42 mS cm^{-1} at 30°C	Met all technical targets with SEM25-trimethylamine(TMA)-1.7 AEM. Conductivity target: 3/31/18 Stability target: 9/30/18 Mechanical property target: 9/30/18
Chemical stability	<5% hydroxide conductivity loss after 300 h, 1 M NaOH, 80°C	No conductivity change after 300 h, 1 M NaOH, 80°C	
Mechanical property	Mechanical strength (MPa) × % elongation >1,400 at 50°C, 90% RH	2,091 at 50°C, 90% RH	

INTRODUCTION

Alkaline exchange membrane electrolysis could significantly reduce the cost of hydrogen production without sacrificing efficiency as inexpensive catalysts, and hardware materials are usable in alkaline media. Despite the significant benefits of AEM-based devices, no high-performance AEM electrolyzers have demonstrated the full potential because of the absence of advanced anion exchange polymers for use as membrane and catalyst layers. In this project, the Los Alamos National Laboratory (LANL) team aims to develop alkaline anion exchange polymers with economically viable synthetic pathways. Rensselaer Polytechnic Institute (RPI) will produce scalable SES-based AEMs via acid-catalyzed Friedel-Crafts alkylation, using commercially available polymer precursors. LANL will develop high-performance styrene-based electrode binders that have minimum interactions with hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) electrocatalysts. Proton Onsite will test the membrane electrode assembly (MEA) using the SES-based AEM and styrene-based ionomers under ambient and differential pressurized conditions.

APPROACH

AEM Preparation

The most popular approach to the preparation of AEMs is chloromethylation, followed by amination with trimethylamine. However, the chloromethylation is unreliable and frequently causes polymer gelation. Furthermore, the reagent used for the process, $ClCH_2OCH_3$, is carcinogenic and hazardous [1]. The undesirable properties of AEM from the chloromethylation may be avoided by a metal-catalyzed coupling reaction. For example, quaternized styrene-ethylene-styrene (SES) polymers can be produced via iridium-catalyzed C-H borylation followed by palladium-catalyzed Suzuki coupling with amine-containing phenyl bromides [2]. However, the need to use expensive transition metal catalysts for the post-functionalization reactions has been a significant barrier to the broader adoption of this method. Therefore, in this project, we are pursuing the development of a new synthetic way, "Friedel-Crafts bromoalkylation" to functionalize polymer without using expensive metal catalysts.

Electrode Binder Preparation and Electrode Study

Polymeric electrode binders play a significant role in the performance and durability of AEM electrolyzers. Nonetheless, the interactions of the ionomer with catalysts used in alkaline AEM electrolyzers have not been studied much. In our previous studies, cation-hydroxide-water coadsorption and phenyl group adsorptions possibly impact the performance and durability of AEM electrolyzers [3, 4]. In this project, we further expand the electrode study to understand the ionomer effects on AEM performance and durability. Based on the results, we will synthesize polystyrene-based ionomers to maximize the performance and longevity of AEM electrolyzers.

The performance- and durability-limiting factors of AEM electrolyzers are investigated by rotating disk electrode (RDE) experiments using commercial IrO_2 catalysts. In this experiment, we used benzyltrimethyl ammonium hydroxide (BTMAOH) as the electrolyte. After 100 h run at OER potentials, we characterized the structural change of the electrolyte. We also performed the MEA test to confirm the possible ionomer-catalyst interaction. In this experiment, we analyzed the electrode ionomer of an MEA after a 100 h test at 2.1 V by ^{1}H NMR.

RESULTS

We synthesized quaternized SES block copolymers using by acid-catalyzed Friedel-Crafts alkylation using bromoalkylated tertiary alcohols followed by amination (Scheme 1). As the tertiary alcohol is protonated by a Brønsted acid, it loses water as a byproduct and forms a tertiary carbocation intermediate, which can readily react with the π electrons of the aromatic rings to generate bromoalkylated SES. We found that the triflic acid is the most effective acid catalyst for this reaction. Slightly more than 1 equivalent of acid (1.1–1.2) relative to the *tert*-alcohol reagent was required because the reaction byproduct water is also readily protonated by triflic acid, thus reducing its reactivity. Excessive addition of triflic acid caused gelation of the polymer. Because the reaction is exothermic, the reaction was conducted at 0°C. The degree of functionalization of the polystyrene block was controlled by changing the molar ratio of the *tert*-alcohol reagent to the aromatic ring of the polystyrene block. The bromoalkylated polymers were quaternized using trimethylamine for the preparation of uncrosslinked membranes or hexanediamine for crosslinked membranes. The degree of crosslinking was controlled by adjusting the stoichiometric ratio of the hexanediamine to the bromoalkyl groups in the bromofunctionalized SES.
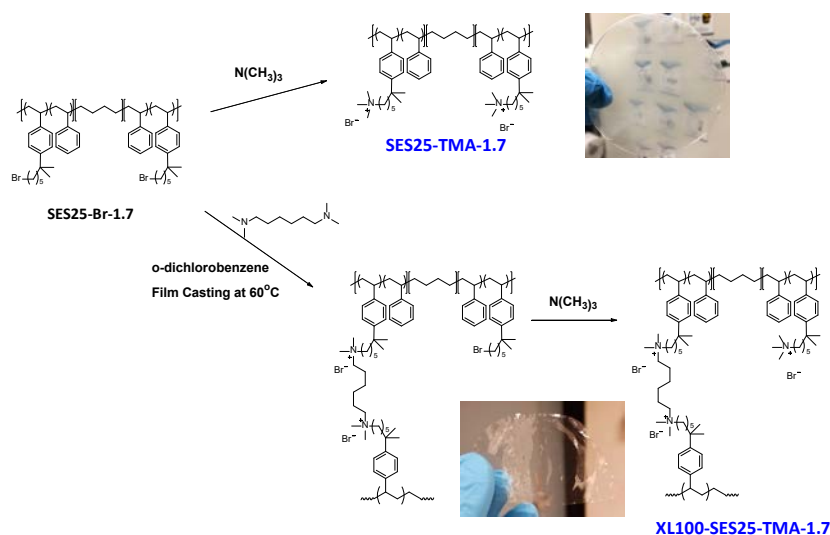
Scheme 1. Synthetic Route for quaternary ammonum-functionalized SES via Friedel-Crafts Bromoalkylation (x = ion exchange capacity, y = degree of crosslinking)

A series of quaternized SES block copolymers were prepared. The AEMs were evaluated in terms of hydroxide conductivity, alkaline stability, and mechanical toughness. The SES copolymers with 25% of polystyrene block and ion exchange capacity (IEC) of 1.7 meq.g^{-1} (SES25-TMA-1.7) met all the technical targets (**Table 2**). SES25-TMA-1.7 AEM and crosslinked version (XL100-SES25-TMA-1.7) were down-selected for further study.

Table 2. The properties of down-selected SES AEM

Sample	IEC[a] (meq./g)	σ at 30°C[b] (mS/cm)	σ at 80°C[c] (mS/cm)			Toughness[d]
			0 h	300 h	% loss	
SES25-TMA-1.7	1.71	42	63	64	~0	2091
XL100-SES18-TMA-1.7	1.50	43	82	80	2	6055

[a]IEC values were measured by Mohr titration method (average of two experiments). [b]All OH⁻ σ were measured in water under argon atomosphere. [c]After alkaline test in 1 M NaOH Solution at 80°C. [d]Mechanical toughness (strength (MPA) % elongation) measured at 50°C, 90% RH.

The cost of the SES AEM prepared by acid-catalyzed Friedel-Crafts bromoalkylation was compared with the one prepared by a metal-catalyzed route (**Table 3**). For the SES-TMA via Suzuki coupling reaction, the lab-scale cost to produce the 6" × 6" × 45 μm thickness of AEM is $25.61, while the cost for the same size SES-TMA via Friedel-Crafts alkylation reaction is only $5.62. This cost-estimation is based on the pricing of

laboratory chemical suppliers, which is often at least several times higher than the pricing of large quantities. The cost analysis indicates that the acid-catalyzed SEBS AEMs have a significant cost benefit over the metal-catalyzed AEMs. We expect the large-scale production of SES membranes to further reduce the production cost, *ca.* <$1/gram of the membrane.

Table 3. Approximate total chemical cost for a 6 in x 6 in of the membrane (45 micrometer thickness) based on the laboratory chemical sources

SEBS-TMA via Suzuki Coupling (metal-catalyzed)			SEBS-TMA via Friedel-Crafts Alkylation		
Reagent	Quantity (g or mL)	USD	Reagent	Quantity (g or mL)	USD
4-bromobenzyl bromide	1.63 g	$1.71	6-bromohexanoic acid	0.935 g	$1.81
$HNMe_2$ aq. solution	1.32 mL	$0.04	Sulfuric acid	0.0751 mL	<$0.01
dioxane	3.25 mL	$0.17	methanol	5.67 mL	$0.09
diethyl ether	26.0 mL	$0.25	ethyl acetate	4.25 mL	$0.05
SEBS	0.86 g	$0.21	MeMgBr_ether solu.	4.25 mL	$0.37
B_2Pin_2	2.14 g	$2.51	THF anhydrous	4.25 mL	$0.22
[IrCl(COD)]$_2$	0.0845 g	$13.6	diethyl ether	11.3 mL	$0.11
dtbpy	0.0672 g	$0.58	SEBS	0.838 g	$0.20
THF anhydrous	8.62 mL	$0.44	triflic acid	0.585 g	$1.73
$CHCl_3$	4.31 mL	$0.17	CH_2Cl_2 anhydrous	16.8 mL	$0.63
K_2CO_3	0.683 g	$0.01	Toluene	16.8 mL	$0.29
Pd(dppf)Cl$_2$-CH_2Cl_2	0.0414 g	$0.90	TMA-water solution	2.96 mL	$0.13
THF anhydrous	8.27 mL	$0.42			
$CHCl_3$	31.0 mL	$1.25			
Dimethyl sulfate	1.05 mL	$0.08			
N,N-Dimethylacetamide	83.9 mL	$3.22			
Total cost for 1 g polymer		$25.61	Total cost for 1 g polymer		$5.62

We studied the ionomer degradation mechanism under alkaline water electrolyzer operating conditions. A possible distinctive degradation mechanism, which is uncommon in alkaline membrane fuel cells, is ionomer oxidation at high oxygen evolution potentials. We suspected that phenyl group adsorption on electrocatalyst might promote electro-oxidation of the phenyl group [4]. In order to investigate, we designed a RDE experiment where we put RDE in dilute BTMAOH solution at 1.6 V vs. RHE for 5 hours and analyzed the BTMAOH solution. **Figure 1** shows the ^{1}H NMR analysis indicating that the aryl protons gradually oxidize at the OER potential. At the end of chronoamperometry, ~17% of BTMAOH was oxidized. This result indicates that phenyl group may be oxidized at OER potentials.
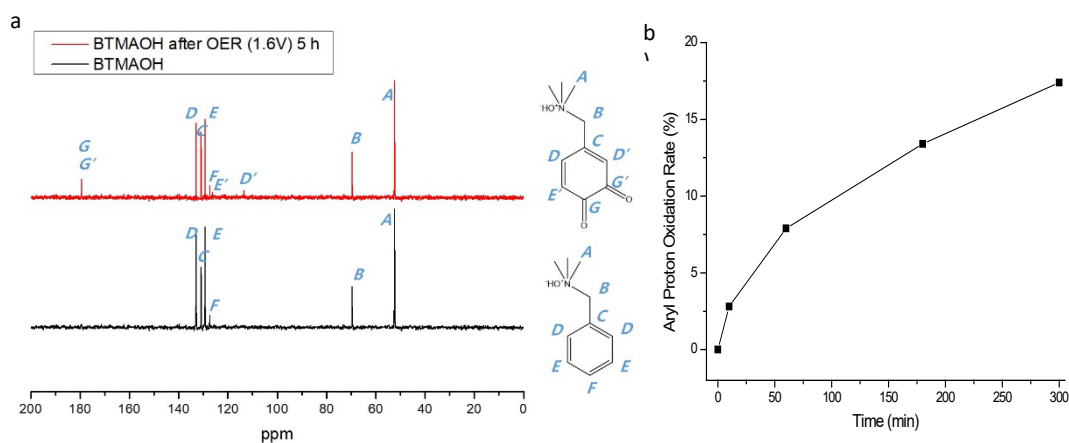

Figure 1. (a) ^{1}H NMR change of the BTMAOH electrolyte before and after 5-hour IrO_2 RDE test at 1.6 V vs. RHE (b) Aryl proton oxidation rate of BTMAOH as a function of time

To confirm the phenyl oxidation, we fabricated an MEA using the IrO_2 anode catalyst and a soluble quaternized polybiphenylene (BPN) ionomer. After testing the MEA at 2.1 V, we analyzed the structural change of the ionomer by ^{1}H NMR (**Figure 2**). The ^{1}H NMR spectrum of the BPN ionomer obtained from the postmortem anode catalyst layer after the test showed no changes in the characteristic peaks except for a small and broad new peak centered at 5.75 ppm, which was assigned to the phenolic proton. From this experiment, we identified that quaternized ionomer may be oxidized during the operation of alkaline AEM electrolyzer and produces acidic phenols. This result sets a base for our high-performance MEA fabrication using the down-selected SES-based AEMs.
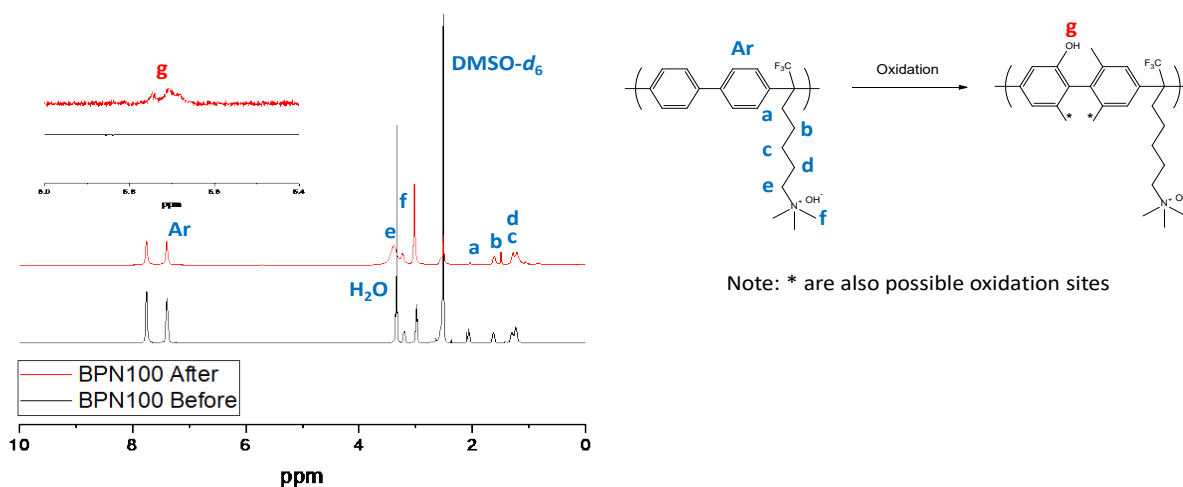

Note: * are also possible oxidation sites

Figure 2. ^{1}H NMR change of the BPN ionomer before and after 100-hour MEA test at 2.1 V vs. RHE

CONCLUSIONS AND UPCOMING ACTIVITIES

- We have successfully prepared the acid-catalyzed SES AEMs that met the conductivity, stability, and mechanical property targets.

- We developed the acid-catalyzed SES AEMs that can be produced much less cost compared to the metal-catalyzed AEMs.

- RDE experiments indicated that phenyl oxidation may limit the AEM electrolyzer performance and durability.

- We plan to develop durable ionomers for electrode binders.

- We plan to evaluate AEM electrolyzer performance and durability in MEAs.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. Li, I. Matanovic, A.S. Lee, E.J. Park, C. Fujimoto, H.T. Chung, Y.S. Kim. "Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer," *ACS Applied Materials & Interfaces* 11 (2019): 9696-9701.

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3. S. Noh, J.Y. Jeon, S. Adhikari, Y.S. Kim, C. Bae. "Molecular Engineering of Hydroxide Conducting Polymers for Anion Exchange Membranes in Electrochemical Energy Conversion Technology." *Acc. Chem. Res.* 52 (2019): 2745-2755.

4. Y.S. Kim, D. Li, I. Matanovic, A.S. Lee, H.T. Chung, "Electrolyte Oxidation Limits the Life of Alkaline Membrane Water Electrolyzer." I01-1406, 235th ECS Meeting, May 26-30, 2019, Dallas, TX, USA.

5. E.J. Park, S. Maurya, M. Hibbs, C. Fujimoto, Y.S. Kim, "Caveat of High Temperature Accelerated Stability Test for Anion Exchange Membranes," I02-1575, 235th ECS Meeting, May 26-30, 2019, Dallas, TX, USA.

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2. A.D. Mohanty, C.Y. Ryu, Y.S. Kim, C. Bae. "Stable Elastomeric Anion Exchange Membranes based on Quaternary Ammonium-tethered Polystyrene-*b*-Poly(ethylene-co-butylene)-*b*-Polystyrene Triblock Copolymers," *Macromolecules* 48 (2015): 7085-7095.

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4. I. Matanovic, H.T. Chung, Y.S. Kim. "Benzene Adsorption: A Significant Inhibitor for the Hydrogen Oxidation Reaction in Alkaline Conditions," *J. Phys. Chem. Lett.* 8 (2017): 4918-4924.