
HydroGEN Seedling: Scalable Elastomeric Membranes for Alkaline Water Electrolysis

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Overall Objectives

- Prepare durable and economically affordable hydroxide-conducting materials based on poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (SEBS) as anion exchange membranes (AEMs).
- Prepare high-performing ionomeric electrode binders for alkaline water electrolyzers.
- Demonstrate high-performance alkaline water electrolyzers.
- Demonstrate alkaline water electrolyzer durability under steady and accelerated stress conditions.

Fiscal Year (FY) 2018 Objectives

- Synthesize quaternized SEBS via acid-catalyzed Friedel-Crafts alkylation.
- Prepare soluble styrene-based ionomers for the electrode binder.
- Down-select the SEBS membrane for the membrane electrode assemblies of alkaline water electrolyzer.

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 Plan¹:

- Stability of polymer electrolytes
- Low cost and efficient hydrogen generation system
- Understanding the performance- and durability-limiting factors of alkaline membrane electrolyzers.

Technical Targets

Metric	Target	Status
Hydroxide conductivity (mS/cm)	40	42
% loss conductivity after 300 h, 1 M NaOH, 80 °C	<5	~0
Tensile toughness (MPa × % elongation) at 50 °C, 90% relative humidity	1,400	2,091

FY 2018 Accomplishments

- Quaternary ammonium (QA)-crosslinked SEBS AEMs were prepared and investigated.
- Semi-crystalline poly(styrene-*b*-ethylene-*b*-styrene) (SES)-based AEMs were synthesized and investigated.
- Soluble styrene-based ionomers were prepared.

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

INTRODUCTION

Our approach is to prepare a quaternized polystyrene block of SEBS by acid-catalyzed Friedel-Crafts bromoalkylation with brominated tertiary alcohol (SEBS- C_n -Br- x , where $n = 3-5$ and x is the degree of functionalization of the polystyrene block) (Figure 1). The properties of the quaternized SEBS are further optimized by incorporating di-QA groups per functionalization site for high ion exchange capacity (IEC) by the Friedel-Crafts bromoalkylation process (SEBS- C_3 -2Br- x) and the utilization of the semi-crystallinity of polyethylene block in the SES precursor polymer.

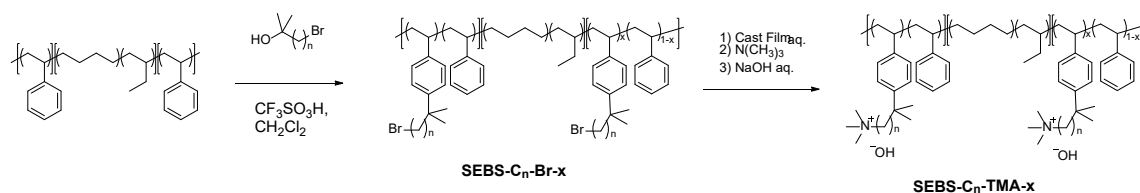


Figure 1. General synthetic procedure of acid-catalyzed SEBS

RESULTS

Preparation of Quaternized SEBS Membranes

Mono- and di-bromoalkyl side chains ($n=3$) were incorporated to the aromatic ring of the polystyrene unit of SEBS using acid-catalyzed Friedel-Crafts alkylation followed by quaternization with trimethylamine (TMA). The degree of functionalization of the polymer was 40 mol%, and the IEC of the membrane after amination of the bromoalkyl groups was 1.72 mequiv./g. Compared to a SEBS AEM with mono-QA side chain in similar IEC (i.e., SEBS- C_3 -TMA-0.8), the di-QA SEBS AEM (i.e., SEBS- C_3 -2TMA-0.4) showed slightly higher water uptake and lower hydroxide conductivities. We also found that the maximum degree of functionalization was limited around 40%, which gives an IEC of 1.72 mequiv./g. Because the di-QA SEBS AEM did not show significantly better membrane property in swelling and hydroxide conductivity, we decided to hold the direction of di-QA synthetic strategy.

Crosslinking is a representative approach to control the mechanical stability of membranes against large water uptakes [1-2]. We synthesized a crosslinked SEBS AEM using bromoalkylated SEBS and 1,6-hexanediamine. The crosslinked SEBS AEM, XL100-SEBS- C_5 -TMA-0.7 (degree of crosslinking = 100%, IEC = 1.36 mequiv./g), showed significantly lower water uptake than a non-crosslinked SEBS AEM (e.g., 30 vs. 150 wt% at room temperature in OH^- form, respectively).

To increase mechanical stability of the elastomeric AEMs, semi-crystalline SES precursor polymers were used as a backbone polymer. Because SESs are composed of crystalline polyethylene domains in the middle block, the tensile strength of the SES-based AEMs was higher than that of the SEBS-based AEMs in the similar IEC range. The mechanical properties of quaternized SEBS were further improved by reinforcing the membrane with polytetrafluoroethylene.

Properties of Quaternized SEBS Membranes

Table 1 shows the physical and electrochemical properties of the synthesized SEBS. The SEBS AEMs with mono-QA side chain (control) and di-QA side chain have high hydroxide conductivity, $\sim 45 \text{ mS cm}^{-1}$. However, the water uptake of the membranes is over 100%. Crosslinked, semi-crystalline, and reinforced SEBS membranes have much lower water uptake, $< 50\%$ with some reduction of hydroxide conductivity. The semi-crystalline SEBS meets the conductivity and water uptake milestones.

Table 1. Properties of the Synthesized SEBS

Samples	Code	IEC (mequiv./g)	Water Uptake (%)	Hydroxide Conductivity (mS cm ⁻¹)
Mono-QA-control	SEBS18-C3-TMA-0.8	1.55	150	47
Di-QA	SEBS18-C3-2TMA-0.4	1.55	173	40
Crosslinked	XL100-SEBS18-TMA-1.4	1.42	28	29
Semi-crystalline	SES25-TMA-1.7	1.71	30	42
Reinforced	RXL100-SEBS18-TMA-1.7	0.77	7	26

The chemical stability of the crosslinked (SES25-TMA-1.7) and reinforced SEBS (RXL100-SEBS18-TMA-1.7) was evaluated in 1 M NaOH at 80°C for 300 h. Table 2 shows the change of IEC and hydroxide conductivity after the test. Both AEMs showed excellent alkaline stability with less than 5% degradation. Table 2 also shows the mechanical properties of the AEMs. The crosslinked AEM showed 5.1 MPa ultimate tensile stress at 410% elongation, which is the limitation of the instrument, under 50°C and 90% relative humidity condition. Although the membrane did not break at 410% elongation, mechanical toughness (mechanical strength [MPa] × % elongation) was higher than the target value of 1,400. The mechanical properties of the reinforced AEM showed even higher mechanical toughness, ca. 4820.

Table 2. Chemical Stability and Mechanical Properties of the Synthesized SEBS

Samples	Code	Hydroxide Conductivity (mS/cm) at 80°C ^a		Tensile Properties		
		Before	After	Stress (MPa)	Elongation (%)	Toughness (stress × % elongation)
Semi-crystalline	SES25-TMA-1.7	63	64	5.1	174	4,820
Reinforced	RXL100-SEBS18-TMA-1.7	67	65	27.7	410	2,091

^a Alkaline stability test was conducted in 1 M NaOH at 80°C for 300 h.

Ionomer Synthesis

Figure 2 shows the synthetic procedure of quaternized polystyrene for the use of ionomeric binder for alkaline membrane water electrolysis. The quaternized polystyrene was synthesized using chloromethylated polystyrene and subsequent quaternization. The solubility of the ionomer was controlled by the ratio of hydrophilic and hydrophobic blocks of the ionomer. Different cationic functional groups including trimethyl ammonium, triethylammonium, and di-ammonium were incorporated into the polymer. The synthesized ionomers have the IEC range of 1.81 to 3.60 mmol/g and are soluble in alcoholic solvents including methanol, ethanol, and ethylene glycol. The ionomers are insoluble in most aprotic solvents including acetonitrile, acetone, and tetrahydrofuran but soluble in some highly polar solvents such as dimethylsulfoxide.

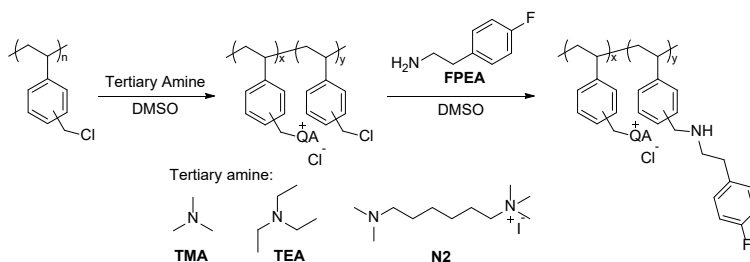


Figure 2. General synthetic procedure of quaternized polystyrene ionomer

CONCLUSIONS AND FUTURE DIRECTIONS

- Synthesized quaternized SEBS via acid-catalyzed Friedel-Craft reactions.
- Achieved the balanced hydroxide conductivity and water uptake properties through the crosslinking, semi-crystalline structure, and reinforced AEM strategies.
- Met all the project milestones (hydroxide conductivity, mechanical properties, and alkaline stability) using the semi-crystalline SEBS
- Synthesized styrene-based soluble ionomers for the electrolyzer electrode.
- Planned to conduct larger-scale synthesis of alkaline membrane and ionomers for the membrane electrode assembly testing
- Plan to investigate the performance- and durability-limiting factors for alkaline membrane-based water electrolysis.

PUBLICATIONS/PRESENTATIONS

1. 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, “Efficient Synthesis of Aromatic Anion Exchange Membranes by Friedel-Crafts Bromoalkylation and Crosslinking of Polystyrene Block Copolymers,” *Macromolecules* (submitted 2018).

REFERENCES

1. P. Dai, Z.-H. Mo, R.-W. Xu, S. Zhang, and Y.-X. Wu, “Cross-Linked Quaternized Poly(styrene-b-(ethylene-co-butylene)-b-styrene) for Anion Exchange Membrane: Synthesis, Characterization and Properties.” *ACS Appl. Mater. Interfaces* 8 (2016): 20329–20341.
2. J. Hao, X. Gao, Y. Jiang, H. Zhang, J. Luo, Z. Shao, and B. Yi, “Crosslinked High-Performance Anion Exchange Membranes Based on poly(styrene-b-(ethylene-co-butylene)-b-styrene).” *J. Membr. Sci.* 551 (2018): 66–75.