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RPPR Final Report
as of 12-Oct-2017

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STEM Degrees: 11 **STEM Participants:** 13

Major Goals: This project aimed at the synthesis and characterization of block copolymers with multiple ionic domains for direct methanol fuel cell applications. The specific objectives for the project were:

1. To synthesize sulfonated polyether and sulfonated polyester based block copolymers using ATRP.
2. To create proton exchange membranes for direct methanol fuel cell applications and compare their selectivity against state-of-the-art membranes.
3. To perform a comprehensive materials characterization to fully understand the chemical, thermal, mechanical, morphology, and transport properties of the membranes in their dry and hydrated state.
4. To elucidate the transport mechanism for protons and methanol as a function of chemistry, morphology and hydration levels.

Accomplishments: This section is included in the "upload" section.

Training Opportunities: Nothing to Report

RPPR Final Report
as of 12-Oct-2017

Results Dissemination: Research Publications:

1. E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. "Synthesis and Characterization of Sulfonated Fluorinated Block Copolymer Membranes with Different Esterified Initiators for DMFC Applications." Journal of Applied Polymer Science, 132, 42046, 2015.
2. M. Pérez-Pérez and D. Suleiman. "Transport Properties of Sulfonated Poly(ether ketone) with Counter-Ion Substitution." Journal of Membrane Science, 493, 414-427, 2015.
3. M. Pérez-Pérez and D. Suleiman. "Effect of Block Composition on the Morphology, Hydration and Transport Properties of Sulfonated PS-b-PEGPEM-b-PS Membranes." Journal of Applied Polymer Science, 133, 48, 2016.
4. E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. "Morphology and Transport Properties of Sulfonated Fluoroblock Copolymer Blend Membranes." In Press, Polymer Engineering and Science, DOI: 10.1002 /pen.24508, 2017.
5. M. Pérez-Pérez and D. Suleiman. "Synthesis and Characterization of Poly(styrene-2-ethoxyethyl methacrylate-styrene) (PS-b-PMEEM-b-PS) for Direct Methanol Fuel Cell Applications." In Preparation, to be Submitted to the Journal of Applied Polymer Science,2017.
6. M. Pérez-Pérez and D. Suleiman. "Solubility Parameters, Phase Equilibria and Solvation Effects for Novel Block Copolymer Ionomers." In Preparation, to be Submitted to the Journal of Chemical Thermodynamics, 2017.
7. K. Barrios and D. Suleiman. "Effect of Amine Block on the Morphology, Hydration and Transport Properties of Sulfonated Poly(styrene-isobutylene-styrene) Membranes." In Preparation, to be Submitted to the Journal of Applied Polymer Science,2017.

Research Presentations
1. M. Pérez and D. Suleiman. "Solubility Parameters, Water Activity Coefficients and Proton Mobility of Sulfonated Poly (styrene-isobutylene-styrene), Sulfonated Poly (ether ether ketone), and Sulfonated Poly (2-ethoxyethyl methacrylate) Membranes." Oral Presentation at the 2017 AIChE National Meeting, Minneapolis, MN, November, 2017.
2. M. Pérez and D. Suleiman. "Synergy Between the Ether and the Sulfonic Group of Sulfonated Block Copolymer Membranes for Direct Methanol Fuel Cell Applications." Oral Presentation at the 2017 AIChE National Meeting, Minneapolis, MN, November, 2017.
3. D. Suleiman. "Polymer Nanocomposite Membranes: Contemporary and Emerging Applications." University of Puerto Rico,2017 NSF-CREST Nanoland Expo, March, 2017.
4. K. Barrios and D. Suleiman. "Synthesis and Characterization of Sulfonated Amine Block Copolymers for Energy Efficient Applications". Chemical Engineering Symposium, University of Puerto Rico at Mayaguez, 2016.
5. M. Pérez and D. Suleiman. "Effect of Block Composition on the Morphology, Hydration and Transport Properties of Sulfonated PS-b-PEGPEM-b-PS." Oral Presentation at the 2016 AIChE National Meeting, San Francisco CA, November, 2016.
6. D. Suleiman. "Polymer Nanocomposite Membranes for Energy, Environmental and Biomedical Applications." Colegio de Ingenieros y Agrimensores de Puerto Rico (CIAPR), Expo Cumbre 2016, San Juan, PR, May, 2016.
7. D. Suleiman. "Nanostructured Polymers: From Contemporary to Emerging Applications, CREST 2016 NanoDaysKeynote, University of Puerto Rico, Mayaguez, PR, April, 2016.
8. A. Millet, and D. Suleiman. "The Role of Water in Multi-Ionic Polymer Membranes)".ACS Jr. Technical Meeting, Ponce, PR, 2016.
9. M. Pérez and D. Suleiman. "Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution." Oral Presentation at the 2015AIChENational Meeting, Salt Lake City, UT, November, 2015.
10. M. Pérez and D. Suleiman. "Chemical and morphological changes of sulfonated Poly(styrene-2-phenoxyethyl methacrylate): Effect of block composition." Oral Presentation at the 250thACS National Meeting, Boston, MA, August, 2015.
11. A. Millet and D. Suleiman "Sulfonation and Characterization of Poly(1,4-phenylene ether-ether-sulfone) (PEES) and Polyphenylsulfone (PPSF) for Fuel Cells and Specialty Separation Applications." Poster Presentation at the 2015 ACS PRISM Meeting San Juan, PR March, 2015.
12. D. Suleiman"Polymer Nanocomposites: Technology for the XXI Century" Oral Key Note Presentation at the 2014 Science & Materials Assembly. Mayaguez, PR, November, 2014.
13. M. Pérez and D. SuleimanTransport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution". Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA, November, 2014.
14. M. Pérez and D. Suleiman. "Synthesis and Characterization of Poly(styrene-isobutylene-methyl vinyl ether) for Direct Methanol Fuel Cell Applications". Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA,

November, 2014.
15. D. Suleiman. "Functionalized Nanostructured Block Copolymer Ionomers for Fuel Cells and Specialty Separations" Oral Presentation during the 2014 Chemical Engineering Department Symposium (Key Note Speaker), University of Puerto Rico, Mayaguez, PR, May, 2014.
16. M. Pérez and D. Suleiman. "Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution". Poster Presentation at the 2014 AIChE Southern Regional Meeting, San Juan, PR, March, 2014.
17. A. Millet, M. Pérez and D. Suleiman. "Effect of the Ether Block Position on Novel Copolymers for Fuel Cells and Specialty Separation Applications" Poster Presentation at the 2014 AIChE Southern Regional Meeting, San Juan, PR, March, 2014.
18. A. Millet, M. Pérez and D. Suleiman. "Novel Block Copolymers as Proton Exchange Membranes for Fuel Cells and Specialty Separation Applications". Poster Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.
19. E.M.A. Guerrero and D. Suleiman. "Nanostructure of a Novel Fluoroblock Copolymer using Atom Transfer Polymerization: Poly(styrene)-b-poly(2,3,4,5,6-Pentafluorostyrene)-b-poly(2,2,3,4,4,4-Hexafluorobutyl methacrylate)" Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.
20. E.M.A. Guerrero and D. Suleiman. "Influence of initiator's chemical composition during Atom Transfer Radical Polymerization of poly(styrene)-b-poly(2,2,3,4,4,4-hexafluorobutyl-methacrylate)".Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, 2013.

Honors and Awards: 1. Life Achievement Award, Local Community of Buenaventura, Mayaguez, Puerto Rico, December, 2015.
2. Leadership Award in the College of Engineering of the University of Puerto Rico, May, 2015.
3. Distinguished Professor of Chemical Engineering, University of Puerto Rico, May, 2013.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: David Suleiman
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Faculty
Participant: Lilo D Pozzo
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Edward M Guerrero-Gutiérrez
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Maritza Pérez-Pérez
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Karen Barrios
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Synthesis and Characterization of Block Copolymers with Unique Chemical Functionalities and Entropically-Hindering Moieties

Final Progress Report: Scientific Progress and Accomplishments,
06 May 2013 – 31 July 2017, David Suleiman, PI
University of Puerto Rico at Mayaguez, W911NF-13-10166

Abstract

This report describes the technical accomplishments obtained for the project entitled Synthesis and Characterization of Block Copolymers with Unique Chemical Functionalities and Entropically-Hindering Moieties. Novel ionic block block copolymers (ionomers) with multiple ionic domains were synthesized using atom transfer radical polymerization (ATRP). The resulting ionomer membranes were extensively characterized to understand the chemical (EA, FT-IR, NMR), thermal (TGA, DSC), morphological (AFM, SAXS, SANS), and transport properties for direct methanol fuel cell applications (*e.g.,* proton conductivity and methanol permeability). Unique synergistic effects were observed due to the different ionic domains (*e.g.,* sulfonic, ether, ketone, etc.). In addition, water (bound to ionic domains with a coordination number close to 20) was identified as critically important in the transport mechanism of protons for direct methanol fuel cell (DMFC) applications. Larger coordination numbers allow methanol to permeate loosing the selectivity of the membranes. In addition, counter-ion substitution in different ionic domains created unique alternative mechanisms for protons over methanol for DMFC applications.

Three Hispanic graduate students and ten Hispanic undergraduate students worked in this investigation (84.6% females) during this period. Two PhD in Chemical Engineering were awarded as a result of this investigation. Twenty technical presentations were presented at local and National Conferences (*e.g.,* ACS*,* AIChE). Four technical manuscripts were published, while three additional manuscripts will be submitted for publication in the following months.

1.0 Introduction

Block copolymers are an interesting class of polymers that can exhibit macroscopic homogeneous behavior and microscopic phase segregation.[1-3] One of the blocks often includes an elastomer (*e.g.,* polyisobutylene, polyisoprene, or polybutadiene) that can provide excellent barrier properties, while the other block is a glassy polymer like polystyrene.The latter can be selectively sulfonated to produce high ion exchange capacity (IEC), while providing mechanical strength and thermal stability. Upon ionic functionalization (*e.g.,* sulfonation), these are called ionomers, and the ionic segments can get interconnected to create unique nanostructured domains that can be useful for several applications such asfuel cells, chemical and biological protective clothing, gas sensors, etc.[2-3]

Although block copolymer ionomers have been studied for several decades and significant advances have been made towards understanding their morphology as well

as the limitations in their transport properties,[4] it is evident that both, chemical functionality and morphology play a major role in the transport properties of the polymers. Numerous studies have been performed to compare the behavior of block copolymer ionomers, but the focus has primarily been on different ionic domains.[5-8] In general, ionomers containing both, hydrogen bonding donor and acceptor ionic sites (*e.g.,* sulfonated ionomers), have similar transport mechanisms (*i.e.,* hoping from sulfonic group to sulfonic group in the presence of water). For these ionomers, chemical functionality and morphology can limit their performance regardless of similarities in ionic content. Ionomers only containing hydrogen bonding acceptor sites (*e.g.,* polyether ether ketone, PEEK), are usually less sensitive to hydration levels[9-10] and are often considered for high temperature applications, where the water content can be low. However, the overall selectivity (proton conductivity/methanol permeability) for direct methanol fuel cells (DMFC) is often lower as compared to hydrogen bonding donor sites, primarily because the IEC is lower.

Nafion®, which is an ionomer composed of a tetrafluoroethylene (TFE) block and sulfonated perfluorinated vinyl ether, has been the market standard for DMFC, gas sensors, and many other ionomer applications for several decades.[11-12] Although part of its success is due to the excellent barrier properties and chemical stability of the TFE block, another important quality is the high proton conductivity thatis provided by the unique combination of sulfonic groups with the perfluoroether chains. Unfortunately, high methanol permeation rates limit its performance and therefore, alternative proton exchange membranes (PEM's) must be considered and evaluated.

This investigation studied novel block copolymer ionomers with improved materials and transport properties over Nafion®. The objective was to further the understanding of the transport mechanism of protons and methanol with membranes containing different ionic blocks and morphology. These goals were achieved by synthesizing a unique combination of blocks that contained an elastomeric block with at least two chemically different ionic blocks. One of the blocks contained a hydrogen bonding donor-acceptor site (sulfonic domain), while the other block contained a hydrogen bonding acceptor site (*e.g.,* ether). One of the blocks used was polystyrene (PS), which was easily sulfonated to high IEC,[13] polyethers such as polyether ether ketone (PEEK), polyesters and other ions from ionic liquid domains were studied as the additional ionic block. Polyethers with functional groups that make the ether ionic domain less accessible were also studied to evaluate the effect of adding entropically-hindering moieties to the resulting morphology and the transport properties of the polymer membrane.

Finally, the newly-developed polymers were compared with previously studied block copolymers. For this, a direct comparison with sulfonated poly(styrene-isobutylene-styrene) (SIBS) was conducted. The PI has studied SIBS extensively, since it can be sulfonated to very high IEC (1.9 for 97% sulfonation).[14-22] Therefore, critical comparisons were performed in terms of morphology and transport properties in an attempt to further the understanding of how the structure-property relationship influences the performance of the polymer membranes, including the understanding of the effect of the different types of water on the transport mechanism of protons and methanol.

2.0 Summary of Work Performed

A chronological description of the work performed will be described ahead. During the first year of the project, several block copolymers were synthesized, mainly poly(styrene-methyl vinyl ether-isobutylene) with various block compositions and sulfonation levels. A comprehensive materials characterization study helped to complete a phase equilibria diagram, but suggested limited ionic interconnections for the homogenous membranes at low sulfonation levels; higher sulfonation levels resulted in non-homogenous membranes. In addition, the elastomeric block, polyisobutylene, was difficult to make due to the need to polymerize at -30°C and last in the order of blocks due to block reactivity. To overcome the phase equilibria challenges, we started working with sulfonated poy(ether-ether ketone) (SPEEK). At high sulfonation levels, SPEEK was water soluble; therefore, counter-ion substitution was studied to control its water swelling and phase equilibria behavior. Counter-ion substitution also helped to understand the effect of the different ions (sulfonic, ether and ketone domains) in the direct methanol fuel cell (DMFC) transport properties (*e.g.,* proton conductivity and methanol permeability). DMFC normalized selectivities (proton conductivity divided by methanol permeability normalized with the values of Nafion) for some of the counter-ion substituted SPEEK were up-to-30 times better than the state-of-the-art Nafion.[23] This work also showed unique ionic interconnections, that resulted in improved proton conductivity and enhancing the differences in transport mechanisms between protons and methanol upon the counter-ion substitution of the different ionic domains.[23]

During the second year of the investigation we worked on the synthesis and characterization of sulfonated poly(styrene-ethylene glycol ethyl methacrylate-styrene) (PS-b-PEGPEM-b-PS). The work evaluated the effect of block composition and sulfonation level on PS-b-PEGPEM-b-PS. The synergism of the different ionic domains and the entropic limitations were evaluated for DMFC applications.[24] During the second year another study on the effect of different esterified initiators was published.[25] Also during the second year of the investigation one PhD student completed his degree and a new graduate student joined the project. She started incorporating amines into SIBS to evaluate the effect of this group into SIBS before starting to polymerize ionic liquids (ILs).

During the third year of the project, a study on morphology and transport properties of multi-ionic block copolymers was published.[26] The work on poly(styrene-ethoxy ethyl methacrylate-styrene) (PS-b-PEEM-b-PS) and poly(styrene-methoxy ethyl methacrylate-styrene) (PS-b-PMEEM-b-PS) was completed. Unfortunately, a fire in the Chemical Engineering department of the University of Puerto Rico delayed the submission of this work. This work will be submitted for publication in the following months.[27] In addition, since phase equilibria has limited the formation of homogeneous membranes with multi-ionic domains, a comprehensive study on polymer thermodynamics was performed with different polymers and solvents. Solubility and chi parameters were obtained and the Flory-Huggins theory has been critically evaluated. This work will also be submitted for publication this year.[28] Also, the work with amine containing polymers will produce a publication this year.[29] Finally, to complete the

report, the work performed by the sub-awardee at the University of Washington on organic-inorganic hybrid membrane structures is included in this report.

Three Hispanic graduate students and ten Hispanic undergraduate students worked in this investigation (84.6% females) during this period. Ten technical presentations were presented at local and National Conferences (*e.g.,* ACS*,* AIChE). Four technical manuscripts were published, while three additional publications are in the final stages of preparation.

3.0 Products from this Work

3.1 Research Publications

1. E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. *"Synthesis and Characterization of Sulfonated Fluorinated Block Copolymer Membranes with Different Esterified Initiators for DMFC Applications." Journal of Applied Polymer Science, 132, 42046,* **2015**.
2. M. Pérez-Pérez and D. Suleiman. *"Transport Properties of Sulfonated Poly(ether ketone) with Counter-Ion Substitution." Journal of Membrane Science, 493, 414-427,* **2015**.
3. M. Pérez-Pérez and D. Suleiman. "*Effect of Block Composition on the Morphology, Hydration and Transport Properties of Sulfonated PS-b-PEGPEM-b-PS Membranes." Journal of Applied Polymer Science,* 133, 48, **2016**.
4. E.M.A. Guerrero-Gutiérrez, M. Pérez-Pérez and D. Suleiman. *"Morphology and Transport Properties of Sulfonated Fluoroblock Copolymer Blend Membranes." In Press, Polymer Engineering and Science,* DOI: 10.1002/pen.24508, **2017**.
5. M. Pérez-Pérez and D. Suleiman. "Synthesis and Characterization of Poly(styrene-2-ethoxyethyl methacrylate-styrene) (PS-b-PMEEM-b-PS) for Direct Methanol Fuel Cell Applications.*" In Preparation, to be Submitted to the Journal of Applied Polymer Science,* **2017**.
6. M. Pérez-Pérez and D. Suleiman. *"Solubility Parameters, Phase Equilibria and Solvation Effects for Novel Block Copolymer Ionomers." In Preparation, to be* Submitted to the *Journal of Chemical Thermodynamics*, **2017**.
7. K. Barrios and D. Suleiman. "*Effect of Amine Block on the Morphology, Hydration and Transport Properties of Sulfonated Poly(styrene-isobutylene-styrene) Membranes." In Preparation, to be Submitted to the Journal of Applied Polymer Science,* **2017**.

In addition, potential additional publications from this investigation include: 1. Effect of Ionic Liquids on Polybenzimidazole for DMFC Applications. 2. Organic-Inorganic Hybrid Membranes for Flow Battery Applications (sub-award work also included in this report).

3.2 Research Presentations

1. M. Pérez and D. Suleiman. *"Solubility Parameters, Water Activity Coefficients and Proton Mobility of Sulfonated Poly (styrene-isobutylene-styrene), Sulfonated Poly (ether ether ketone), and Sulfonated Poly (2-ethoxyethyl methacrylate) Membranes."* Oral Presentation at the 2017 AIChE National Meeting, Minneapolis, MN, November, **2017**.
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4. K. Barrios and D. Suleiman. "*Synthesis and Characterization of Sulfonated Amine Block Copolymers for Energy Efficient Applications". Chemical Engineering Symposium, University of Puerto Rico at Mayaguez,* **2016**.
5. M. Pérez and D. Suleiman. *"*Effect of Block Composition on the Morphology, Hydration and Transport Properties of Sulfonated PS-b-PEGPEM-b-PS." Oral Presentation at the 2016 AIChE National Meeting, San Francisco CA, November, **2016**.
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7. D. Suleiman. "*Nanostructured Polymers: From Contemporary to Emerging Applications*, CREST 2016 Nano Days Keynote, University of Puerto Rico, Mayaguez, PR*, April,* **2016**.
8. A. Millet, and D. Suleiman. "*The Role of Water in Multi-Ionic Polymer Membranes)".ACS Jr. Technical Meeting*, Ponce, PR*,* **2016**.
9. M. Pérez and D. Suleiman. *"*Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution.*"* Oral Presentation at the 2015AIChENational Meeting, Salt Lake City, UT, November, **2015**.
10. M. Pérez and D. Suleiman. *"*Chemical and morphological changes of sulfonated Poly(styrene-2-phenoxyethyl methacrylate): Effect of block composition." Oral Presentation at the 250thACS National Meeting, Boston, MA, August, **2015**.
11. A. Millet and D. Suleiman "Sulfonation and Characterization of Poly(1,4-phenylene ether-ether-sulfone) (PEES) and Polyphenylsulfone (PPSF) for Fuel Cells and Specialty Separation Applications." Poster Presentation at the 2015 ACS PRISM Meeting San Juan, PR March, **2015**.
12. D. Suleiman *"Polymer Nanocomposites: Technology for the XXI Century"* Oral Key Note Presentation at the 2014 Science & Materials Assembly. Mayaguez, PR, November, **2014**.
13. M. Pérez and D. Suleiman Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution". Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA, November, **2014**.
14. M. Pérez and D. Suleiman. *"Synthesis and Characterization of Poly(styrene-isobutylene-methyl vinyl ether) for Direct Methanol Fuel Cell Applications".*

Poster Presentation at the 2014 AIChE National Meeting, Atlanta, GA, November, **2014**.

15. D. Suleiman. *"Functionalized Nanostructured Block Copolymer Ionomers for Fuel Cells and Specialty Separations"* Oral Presentation during the 2014 Chemical Engineering Department Symposium (Key Note Speaker), University of Puerto Rico, Mayaguez, PR, May, **2014**.
16. M. Pérez and D. Suleiman. "Transport Properties of Sulfonated Poly(ether ether ketone) Membranes with Counter-Ion Substitution". Poster Presentation at the 2014 AIChE Southern Regional Meeting, San Juan, PR, March, **2014**.
17. A. Millet, M. Pérez and D. Suleiman. "Effect of the Ether Block Position on Novel Copolymers for Fuel Cells and Specialty Separation Applications" Poster Presentation at the 2014AIChESouthern Regional Meeting, San Juan, PR, March, **2014**.
18. A. Millet, M. Pérez and D. Suleiman. "Novel Block Copolymers as Proton Exchange Membranes for Fuel Cells and Specialty Separation Applications". Poster Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, **2013**.
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20. E.M.A. Guerrero and D. Suleiman. "Influence of initiator's chemical composition during Atom Transfer Radical Polymerization of poly(styrene)-b-poly(2,2,3,4,4,4-hexafluorobutyl-methacrylate)".Oral Presentation at the 2013 AIChE National Meeting, San Francisco, CA, November, **2013**.

3.3 Students

3.3.1 PhD Students

1. Edward M.A. Guerrero, PhD in Chemical Engineering, June, 2015.
2. Maritza Pérez-Pérez, PhD in Chemical Engineering, December, 2016.
3. Karen Barrios, PhD in Chemical Engineering, Expected June, 2018.

3.3.2 BS Students

1. Nataira Pagán, BS in Chemical Engineering, May, 2016.
2. Frances Ruiz, BS in Chemical Engineering, May, 2016.
3. Franchesca Rivera, BS in Chemical Engineering, May, 2016.
4. Alexander Millet, BS in Chemical Engineering, May, 2016. Currently PhD student at the University of Wisconsin-Madison.
5. Claudia Feliciano, BS in Chemical Engineering, Dec., 2016.
6. Lorena Cruz, BS in Chemical Engineering, May, 2017.
7. Olga Ortiz, BS in Chemical Engineering, May, 2017.
8. Stephanie Placeres, BS in Chemical Engineering, May, 2017.
9. Vanessa Torres, BS in Chemical Engineering, May, 2017.
10. Michelle Soto, BS in Chemical Engineering, Expected May, 2018.

3.4 Awards

1. Life Achievement Award, Local Community of Buenaventura, Mayaguez, Puerto Rico, December, 2015.
2. Leadership Award in the College of *Engineering* of the University of Puerto Rico, May, 2015.
3. *Distinguished Professor of Chemical Engineering*, University of Puerto Rico, May, 2013.

4.0 References

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6. Kim, B.; Kim, J.; Jung, B. *J Membr Sci* 250, 175, **2006**
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Technical Report for the Sub-Award to the University of Washington

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Abstract

During the past year we have developed protocols for the synthesis of organic-inorganic hybrid membrane structures for use in flow battery applications. In one example, anodized aluminum oxide (AAO) membranes were filled with polystyrene sulfonate (PSS) and sulfonated styrene-isobutylene-styrene (SIBS) with the intention of creating mechanically robust and efficient proton conducting membranes. In another example, sodium silicate and ionic polymers (e.g., poly(diallyldimethylammonium chloride) or polyDADMAC) were combined and cured via sol-gel processing to create proton conducting membranes with high selectivity and proton conductivity. In addition to developing synthetic procedures, these membranes were characterized with techniques such as: small angle x-ray and neutron scattering (SAXS/SANS), scanning electron microscopy (SEM), galvanodynamic measurements and ion diffusivity measurements.
One post-doctoral researcher worked on this investigation during this period. Additionally, one technical presentation was presented at the American Institute of Chemical Engineering (AIChE) National Conference. A provisional patent was filed with the University of Washington and the startup company Ionic Windows is hoping to commercialize the technology.

1.0 Introduction

Grid-scale power storage remains one of the largest challenges to wide-spread adoption of clean energy technologies with intermittent energy sources (e.g., solar, wind and tidal). Flow batteries are a low cost technology with the potential to meet this need given their adjustable discharge rate and effectively infinite storage potential, which is only limited by the size of electrolyte vessels.[1] Flow batteries operate by circulating soluble redox couples that can be oxidized or reduced to store and discharge energy, as seen in Figure 1. Two tanks are separated by a membrane that selectively transports protons (e.g., H^+) to maintain electroneutrality.[1] Current membrane materials, such as Nafion®, account for 25 - 40% of flow battery capital costs.[2] They also have limited operating temperatures, high resistive losses due to proton transport limitations and lack ion selectivity that causes electrolyte diffusion across the membrane leading to performance instability.[3,4] There is a need for new and inexpensive membrane materials that have excellent ion selectivity, high proton conductivity, good chemical and mechanical stability and a thermally stable nanostructure.[3,5]

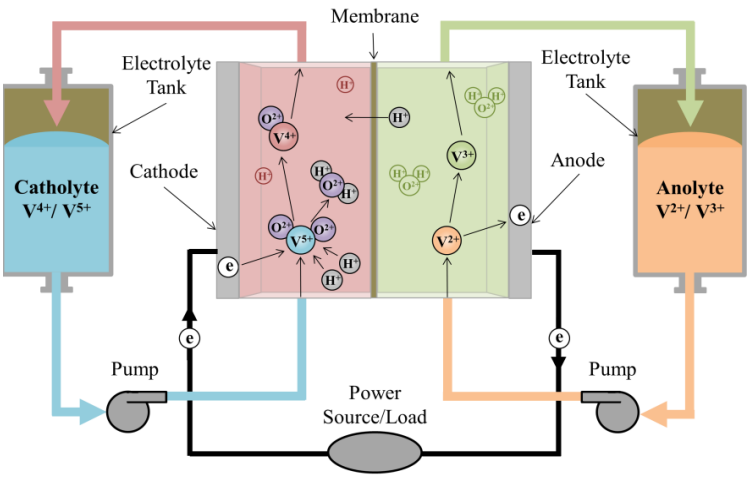

Figure 1. Schematic of an all vanadium flow battery.

Sulfonated block-copolymers made from commercially available elastomers have shown promise as inexpensive membrane replacement materials in fuel cells.[6-7] The sulfonated block has been shown to self-assemble into proton conducting nanochannels while the non-sulfonated block provides mechanical stability for the membrane. These new membrane materials have shown good proton conductivity and the capacity to reduce electrolyte cross-over.[6] However, the purely polymeric nature of these membranes often reduces the potential for long-term mechanical stability and for thermally stable nanostructures. To address these challenges we propose to utilize a hybrid polymeric-metal oxide structure to create thin (< 100 μm) membranes with excellent thermal and mechanical stability.

In one example, anodized aluminum oxide (AAO) membranes with hexagonally packed cylindrical channels were utilized as a template nanostructure. AAO membranes were functionalized with vinyl silanes, filled with styrene and then polymerized before being sulfonated to enhance proton conductivity. Contrastingly, AAO membranes could also be back filled with sulfonated polymers or block copolymers, such as S-SIBS. The sulfonated polymer domain size and orientation were determined by the AAO template, while the ion transport properties resulted from the polymer chemistry, sulfonation level and self-assembled hydration pathways within the pores of the membrane. Unfortunately, these membranes lacked chemical stability in the strongly oxidizing environment of vanadium redox flow batteries.

Silica-based inorganic materials were then proposed as an alternative to improve the chemical stability of hybrid membranes for flow battery applications. A sol-gel process utilizing both silica and polymer was developed to deposit stable mixtures within a macroporous template. Drying and acid curing of the materials resulted in proton conducting membranes with performance attributes similar to Nafion®. These hybrid organic-inorganic membranes are anticipated to have improved stability and transport properties over Nafion®. The objective of the investigation was to elucidate the impact of membrane chemistry and morphological features on stability and transport properties under flow battery operating conditions. In particular, critical parameters such as pore size/structure, polymer chemistry and sulfonation level are expected to influence these properties. Finally, preliminary structure-property relationships are discussed.

2.0 Membrane Synthesis

Hybrid membrane structures can be created using various methods. Capillary action can be utilized to draw polymer solutions (e.g., PSS or S-SIBS) into the membrane structure. However, these un-tethered polymers can also diffuse out of the membrane structure when under flow battery conditions. Instead, a tethering approach similar to that used for silica membranes was employed to ensure that the AAO membrane remained filled with polymer.[8] Figure 2 shows a schematic of this process. Silane chemistry was utilized to functionalize AAO membranes with a vinyl moiety. In the presence of styrene monomer, this linking group can be used to form tethered polystyrene. The polystyrene chains can then be sulfonated utilizing standard chemical methods.[9]

In an alternative method, a solution-phase mixture of an ionic polymer and sodium silicate undergoes a sol-gel transition to form a nanoporous membrane. In this methodology, a macroporous membrane is dipped into the sol and then gelled in an acid bath before drying. This process can be seen in Figure 3.

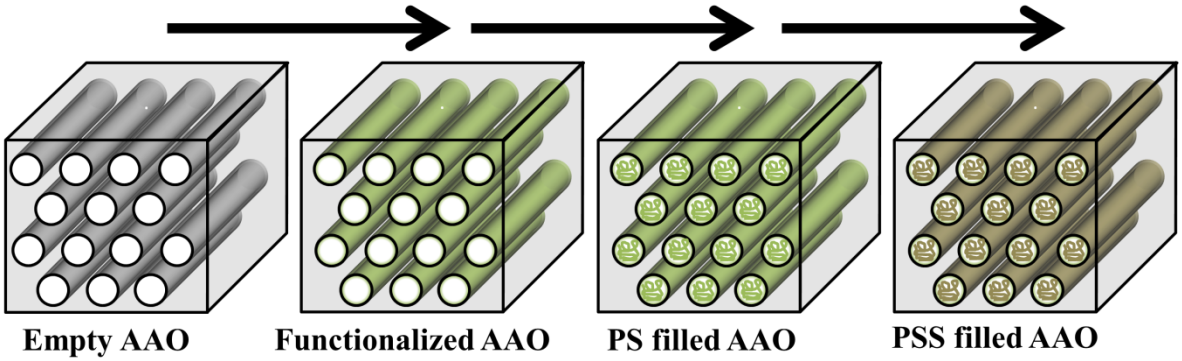

Figure 2. Method for the synthesis of hybrid AAO/polystyrene sulfonate (PSS) membranes.

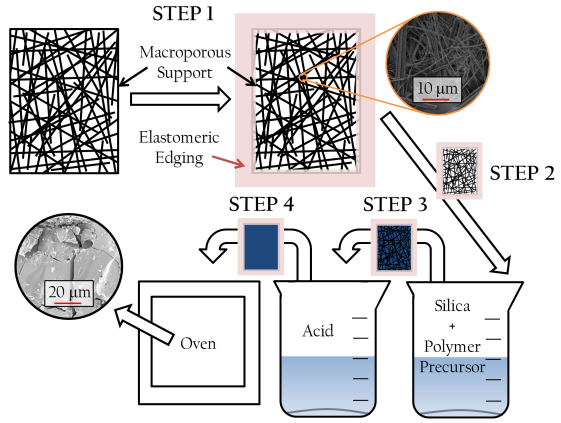

Figure 3. Method for the sol-gel processing of polymer-silica hybrid membranes.

3.0 AAO Membrane Characterization

AAO Membranes were characterized step-wise based on Figure 2. Fourier Transform Infrared (FTIR) Spectroscopy was used to confirm the silane functionalization of AAO (Figure 4). FTIR spectra show the presence of Si-O, Al-O-Si and CH_3 bonding which are indicative of alumina functionalization with either vinyltrimethoxysilane and 3-(trimethoxysilyl)propyl methacrylate. Characterization of AAO hybrid membranes then focused on confirming if the AAO pores were fully filled with polystyrene (PS). PS filled and unfilled AAO membranes were characterized with SEM and SANS, as seen in Figure 5. Cross-sectional SEM (Figure 5 inset) indicates that, under certain conditions, the membrane pores are fully filled with polystyrene. Analysis of membrane with small angle neutron scattering (SANS) further confirms that the pores are filled with polymer since there is increased scattering intensity when compared to water-filled pores at contrast matching conditions for alumina (72%/28% D_2O/H_2O). Figure 6 highlights the FTIR spectrum differences for PS and PSS filled membranes which primarily shows peak broadening due to the hydrophilicity of PSS (e.g., water uptake). These results confirm that the step-by-step methodology in Figure 2 can be used to produce hybrid membranes with polymer-infiltrated pores. Relevant flow battery membrane performance parameters (i.e., proton conductivity and vanadium ion permeability) were then determined and compared to the performance of the industry standard material, Nafion 117 (Figure 7).[10,11] Hybrid AAO-PSS membranes showed a lower proton conductivity and higher vanadium ion permeability (e.g., lower selectivity) when compared to

Nafion®. We believe that this was likely due to incomplete pore filling during the styrene reaction step (Figure 2). Figure 8 shows partially filled pores and, for this application, small pin-hole defects can lead to high vanadium ion cross-over. Unfortunately, AAO is not well suited for flow battery applications because alumina is not stable in the strongly oxidizing environment of flow batteries. The lack of chemical stability led us to pursue more stable chemistries using silica inorganic substrates.

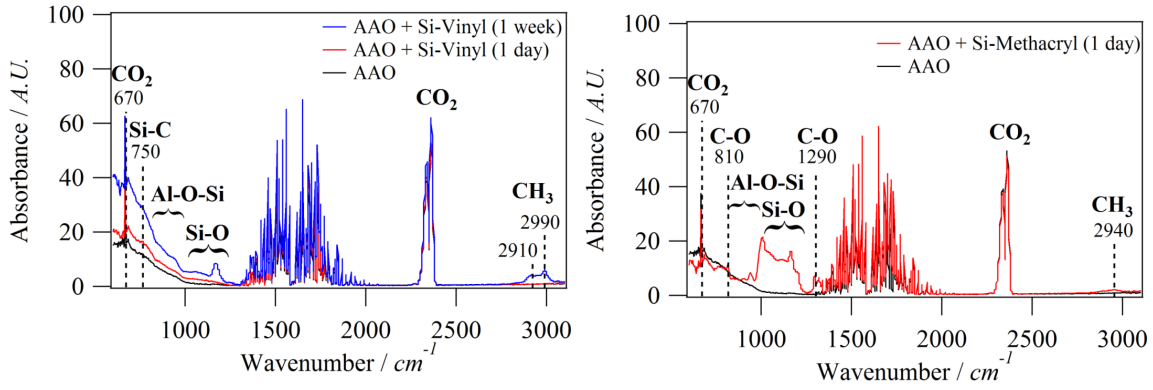

Figure 4. FTIR spectrum for AAO membranes functionalized with vinyltrimethoxysilane (left) or 3-(trimethoxysilyl)propyl methacrylate (right).

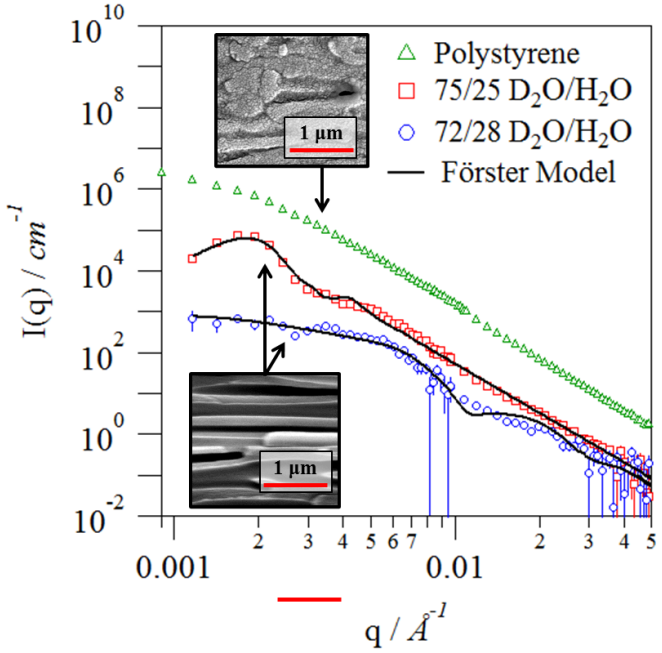

Figure 5. Small angle neutron scattering (SANS) profiles for AAO filled with water at contrast matching conditions and also filled with in-situ polymerized polystyrene. The water-filled membranes are fit with the Förster model for hexagonally packed cylinders.[10]

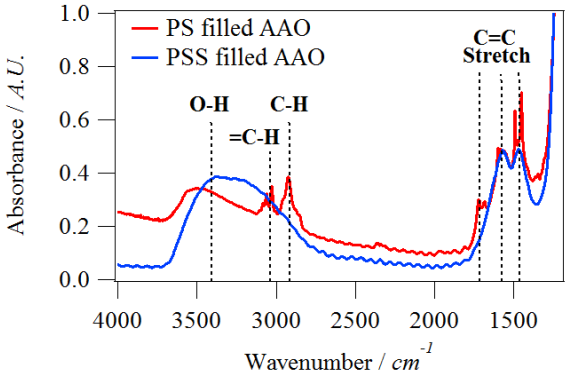

Figure 6. FTIR spectrum for AAO membranes functionalized with vinyltrimethoxysilane and the filled with polystyrene (PS) and polystyrene sulfonate (PSS).

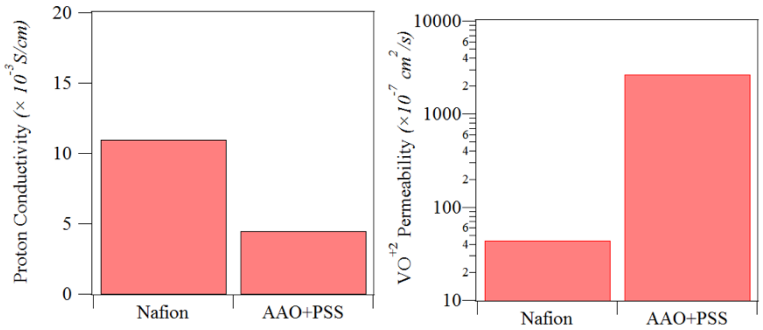

Figure 7. Proton conductivity (left) and vanadium permeability (right) tests for Nafion 117 and AAO-PSS hybrid membranes.

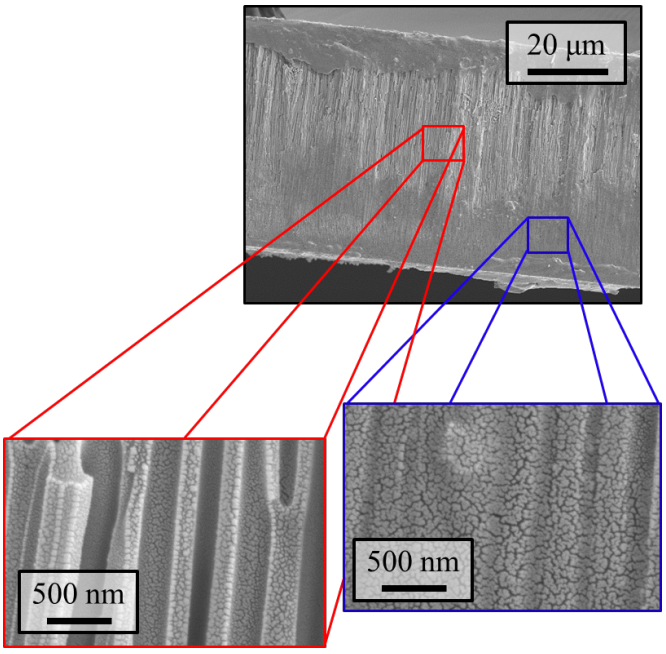

Figure 8. SEM images of PSS filled membranes highlighting filled pores near the edges and unfilled pores (e.g., defects) near the center.

3.1 Sol-Gel Membrane Characterization

Sodium silicate and proton conducting polymer (i.e., polyDADMAC seen in Figure 9) composite membranes were synthesized for this initial study. The curing of sodium silicate in a 3M sulfuric acid solution (Figure 3, Step 3) causes the sodium silicate to form nanopores. These pores were determined to be spherical and approximately 2 nm in radius by fitting of SANS data (Figure 10). Table 1 highlights the potential to tune the porosity (1-10%), pore size (5-17 Å) and fractal dimension (1.6-2.9) through changes in acid type. SEM images in Figure 11 show substantially fewer macroscopic defects in membranes containing polyDADMAC compared to sodium silicate alone. In this case, polyDADMAC can fill-in macroscopic voids to help prevent defects while also enhancing the proton conductivity of the membrane due to the presence of ionic groups. This is demonstrated with proton conductivity and vanadium ion permeability measurements of the membranes (Figure 12). Silica and silica-polyDADMAC membranes show similar proton conductivities to Nafion 117. However, silica-polyDADMAC membranes show substantially lower vanadium ion permeability (similar to Nafion). In fact, the difference in ion selectivity between Nafion 117 and silica-polyDADMAC is only 3:1. Similar results are found in composite membranes containing PSS instead of polyDADMAC (Figure 13). These results highlight the promise for composite membranes under flow battery operating conditions. Preliminary flow battery cycling test have been carried out on 60 cm^2 silica membranes and can be seen in Figure 14. These results demonstrate membrane feasibility under flow battery operating conditions, though further improvements and longer tests are required for commercialization. Initial cost estimates also suggest that silica-polyDADMAC membranes could be fabricated for one tenth the cost of Nafion, which is a great limitation to the adoption of this evolving technology. Further optimization is expected to lead to membranes with improved performance and lower cost than Nafion. A provisional patent has been filed for this membrane innovation which has the potential to dramatically reduce the costs of flow battery technology.

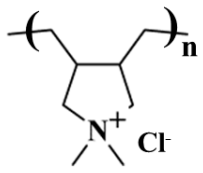

Figure 9. Chemical structure of poly(diallyldimethylammonium chloride) (polyDADMAC).

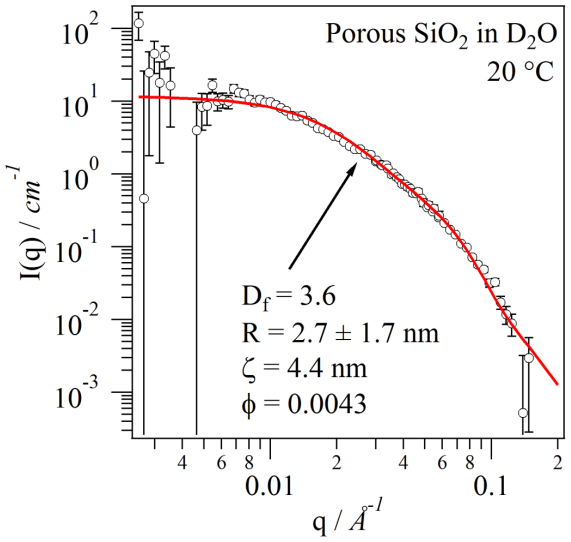

Figure 10. SANS of a sodium silicate membrane cured in 3M sulfuric acid. The membrane is with the fit with a fractal aggregate model and parameters are displayed.[13]

Table 1. Fractal aggregate model fitting results for SANS measurements of silica membranes cured in different types of 3N acid. [13]

Acid Type	Radius (Å)	Fractal Dimension	Porosity (%)
Hydrochloric	5.0	2.4	10.0
Methane Sulfonic	6.0	2.9	1.0
Phosphoric	7.2	1.6	8.3
Nitric	8.1	2.7	8.6
Acetic	4.5	2.9	6.9
Sulfuric	17.4	2.5	6.2

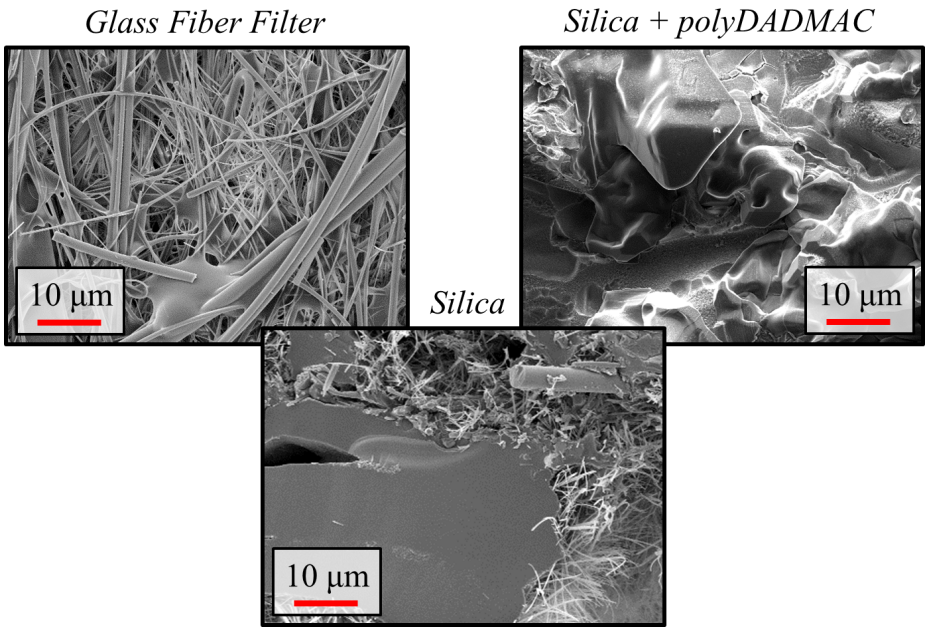

Figure 11. SEM images showing the macroporous filter (left) that can be filled and cured with either silica (bottom) or a silica-polyDADMAC composite (right).

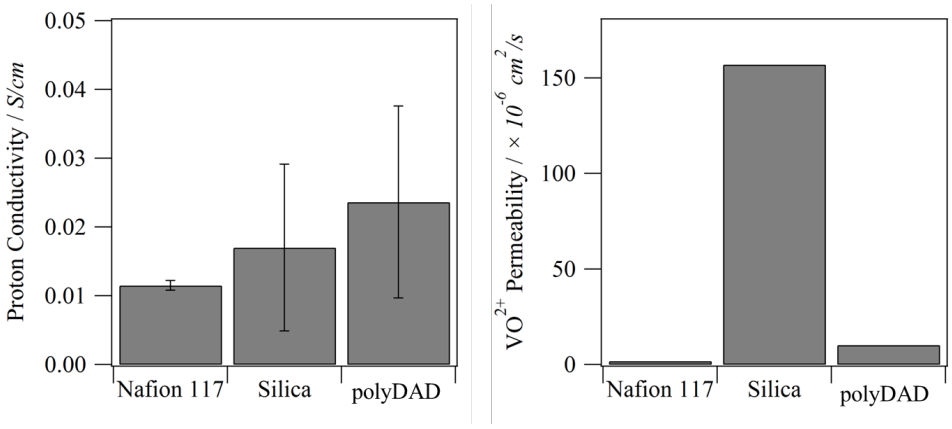

Figure 12. Proton conductivity (left) and vanadium permeability (right) tests for Nafion 117, silica only and silica-polyDADMAC (abbreviated polyDAD) membranes.

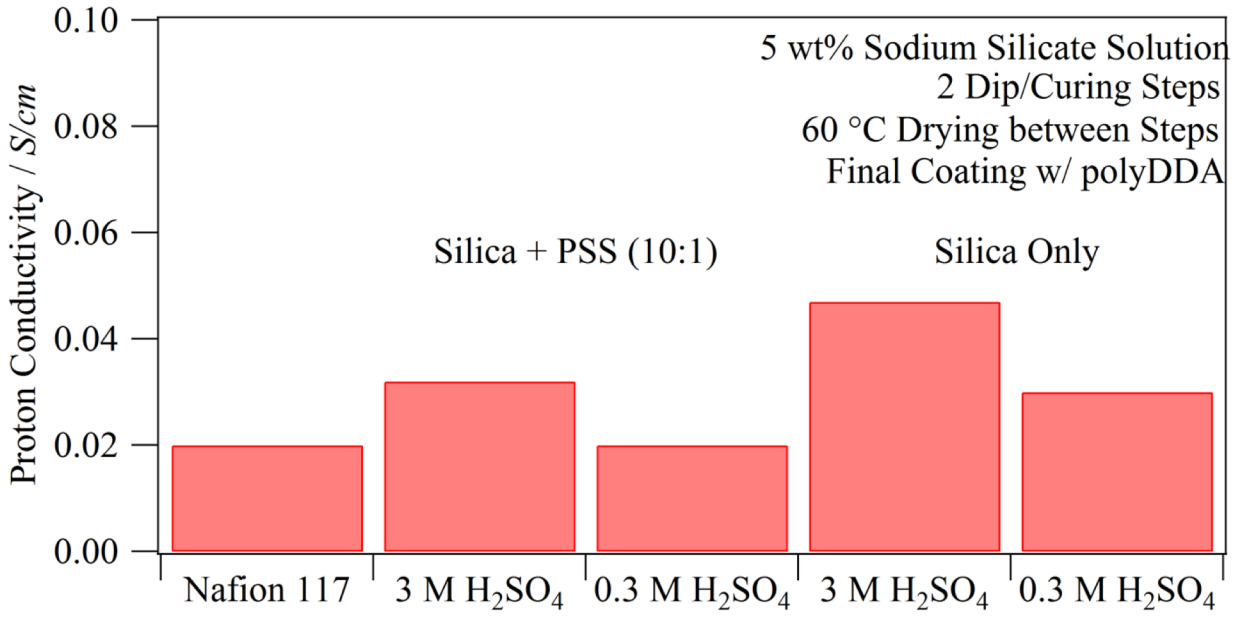

Figure 13. Proton conductivity measurements for membranes with and without PSS and cured in different concentrations of sulfuric acid. All membranes received a final coating of polyDADMAC (abbreviated as polyDDA).

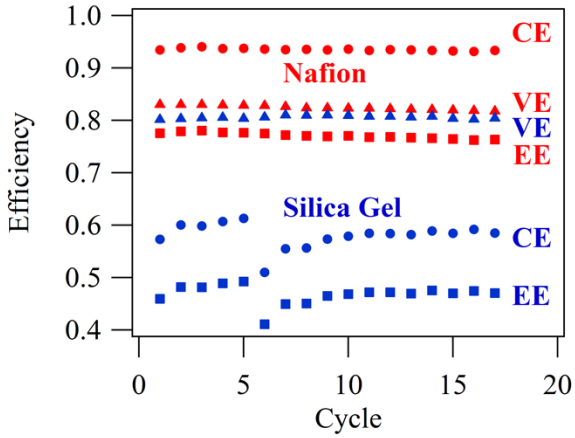

Figure 14. Flow battery cycle testing of Nafion 117 and a silica membrane cured in 3M sulfuric acid. Membranes were run in proprietary vanadium redox flow battery electrolyte provided by UniEnergy Technologies at 50 mA/cm^2.

4.0 Technology Commercialization Efforts

Technology developed under this award is in the early stages of being commercialized. A start-up company (Ionic Windows) has been formed and will obtain an exclusive license for the provisionally patented technology from the University of Washington (UW). Ionic Windows was founded in March 2016 and has made significant progress including winning $20k in cash prizes

for 2nd Place overall and the Clean Energy Prize at the UW Environmental Innovation Challenge as well as the Clean Technology Prize at the UW Business Plan Competition. Ionic Windows has recently joined the competitive UW Jones + Foster Accelerator Program designed to help further business development.

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