V.F.18 DOE's High Acid Content Diels-Alder Poly(Phenylene)s for High Temperature and Low Humidity Applications

Cy Fujimoto

Sandia National Laboratories (SNL)
Organic Materials Group
Albuquerque, NM 87123
Phone: (505) 844-6432
Email: chfujim@sandia.gov

DOE Manager

Gregory Kleen
Phone: (720) 356-1672
Email: Gregory.Kleen@ee.doe.gov

Subcontractor

Tom Zawodzinski, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN

Project Start Date: August 1, 2014
Project End Date: July 31, 2015

Overall Objectives

- Synthesize polymer exchange membrane block copolymer membranes employing DOE's highly phenylated motif
- Measure proton conductivity of the films at 80°C and 120°C at various relative humidities
- Fabricate membrane electrode assemblies (MEAs) of the block copolymer membranes
- Demonstrate single-cell proton exchange membrane fuel cell (PEMFC) performance of the block copolymer membranes
- Demonstrate long-term PEMFC performance

Fiscal Year (FY) 2015 Objectives

- Synthesize highly conductive, high temperature block copolymers
- Measure performance of new architectures through proton conductivity measurements and fuel cell testing

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance (over a range of temperatures and humidities)

Technical Targets

The objective of this program is to develop high performance, low cost, durable membranes that will meet the DOE's 120°C membrane technical targets for transportation applications. Insights gained from this project will be applied towards the next generation PEMFC systems. The technical targets are listed below.

- Demonstrate area specific resistance (ASR) of 0.05 ohm cm^2 at 120°C and 50% relative humidity (RH) (or 25 μm film 50 mS/cm)
- Demonstrate 100 h of fuel cell performance under load at 120°C

FY 2015 Accomplishments

- Demonstrated nearly double the conductivity of NRE211 211 at 120°C at approximately 30% RH
- Demonstrated significant fuel cell performance of hydrocarbon block copolymer
  - 85°C at 50% RH 0.6 V–2 A/cm^2, at 25% RH 0.6 V–1 A/cm^2
  - 100°C at 50% RH 0.6 V nearly 1 A/cm^2, at 25% RH 0.6 V–500 A/cm^2
  - 120°C at 35% RH 0.6 V–500 mA/cm^2
- Developed and demonstrated improved wet-dry cycling mechanical properties of a highly conductive hydrocarbon block copolymer
- Developed new intellectual property (IP) that SNL is securing to patent

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INTRODUCTION

Although the current state-of-the-art perfluorinated sulfonic acid (PFSA) membranes, such as Nafion® 211, have shown both good durability and performance, cost still remains an issue. Moreover, transient temperature excursions at or above 120°C can be detrimental to PFSAs due to their low glass transition temperature (90–110°C). The objective of this program is to develop high performance, low cost, durable membranes that will meet the DOE 120°C membrane

technical targets for transportation applications [1]. This program consists of three partners that will be responsible for specific tasks. SNL will perform materials testing, ORNL will perform materials characterization and fuel cell testing, and Automotive Fuel Cell Corporation (AFCC) will act as an industrial consultant.

APPROACH

SNL has developed and patented (U.S. 12/425,413) a first generation, block copolymer structure built by pendant aryl sulfonated Diels-Alder poly(phenylene) as the hydrophilic domain, with a highly fluorinated hydrophobic domain (Figure 1a) [2]. The resultant block copolymer was found to possess conductivities and fuel cell performance similar to PFSAs (Figures 1b and 1c). However, under cyclic humidity conditions, these membranes, mechanically failed after only a short time. It was believed that the high water uptakes of these films (+100%) led to high swelling and deswelling under cyclic humidity. Borrowing innovation strategies from our vanadium redox flow battery work (patent submitted 2014), we have discovered that the phenylene backbone can also be functionalized (Figure 2). In this program, we synthesized block copolymers that contain acid moieties on the pendant and backbone segments of the hydrophilic domain (Figure 3a). We initially focused on employing a hydrophobic domain that did not contain any fluorine to reduce cost and eliminate possible hydrogen fluoride formation. However, in response to a request by the United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) team and feedback from the DOE Annual Merit Review, we did ultimately examine a fluorine containing hydrophobic domain (Figure 3b).

Through our unique polymer architecture we hoped to gain both high conductivity at low RH and improved mechanical properties. Our hypothesis is based on recent work by Zawodzinski [3], who has determined that PFSAs

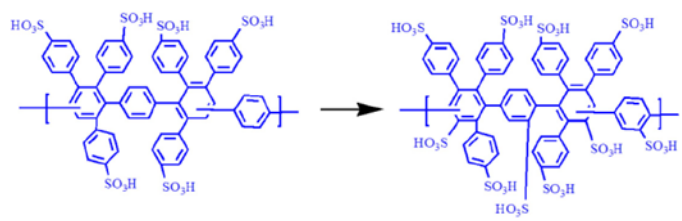

FIGURE 2. High density sulfonation

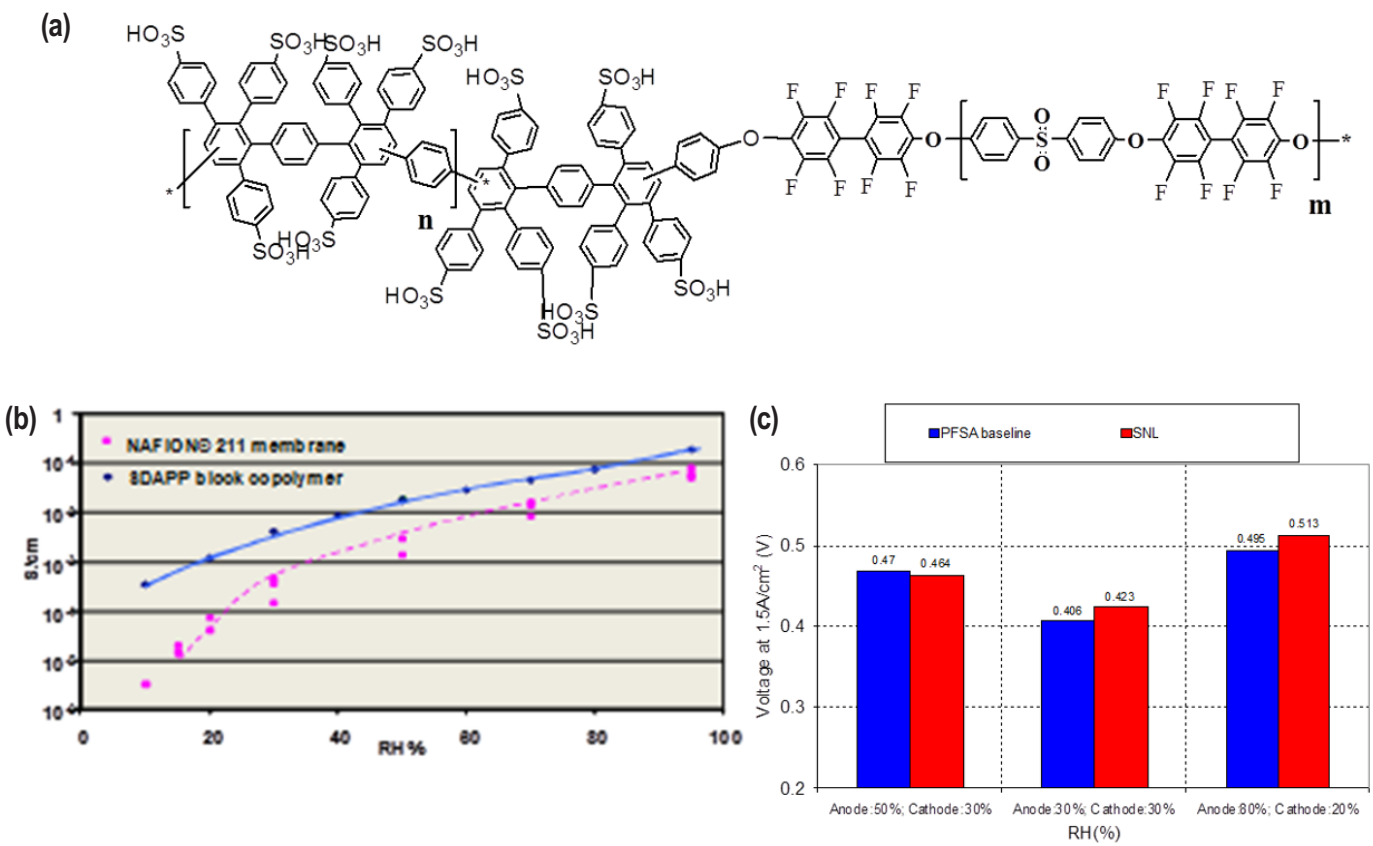

FIGURE 1. First generation block structures: (a) structure of proof of concept block with AFCC; (b) conductivity of first generation vs. Nafion® 211 at 85°C; (c) fuel cell performance of PFSA vs. first generation at 80°C at 1 A/cm²

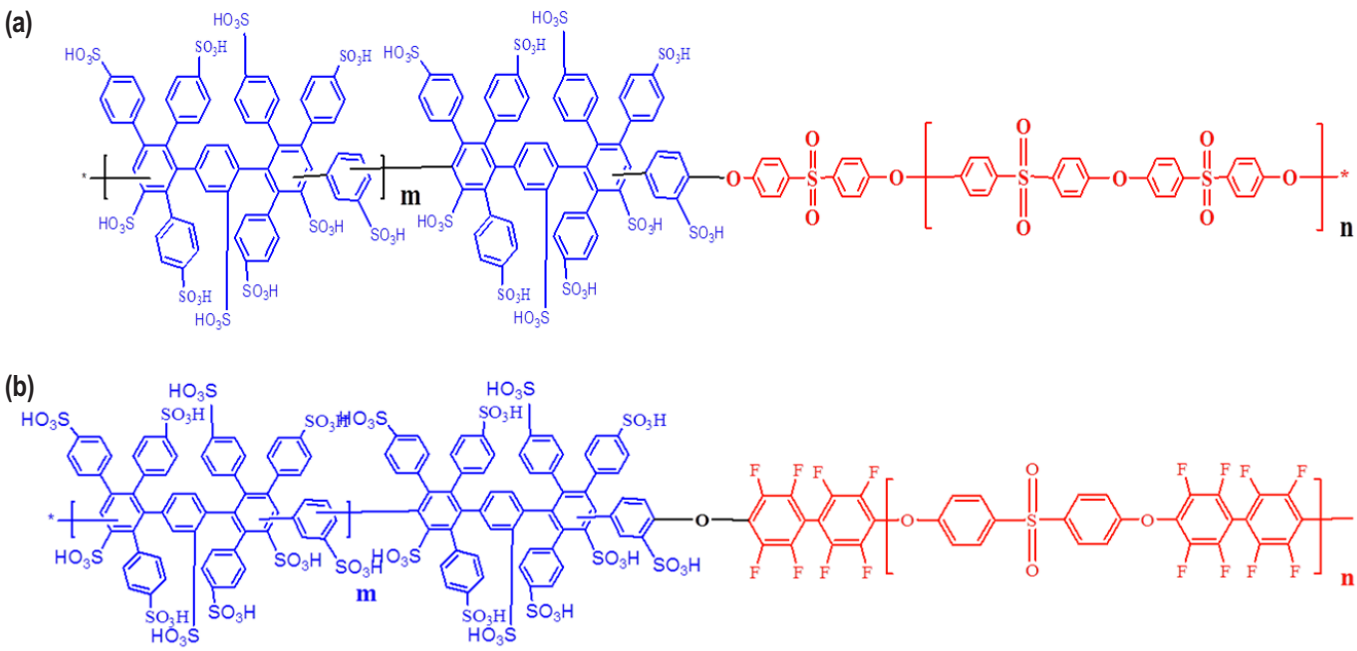

FIGURE 3. (a) Non-fluorinated sulfonic acid FS-DAPP-block copolymer; (b) fluorinated sulfonic acid FS-DAPP-block copolymer

with closely spaced acid moieties enable higher proton mobility at low water content compared to PFSAs of similar equivalent weight that possess longer distances between acid functional groups. We hope to see the same trend in our hydrocarbon block copolymer. Also, by nearly doubling the acid content in the hydrophilic domain we can shorten the hydrophilic segment length relative to the hydrophobic segment; a longer (dominant) hydrophobic segment should strongly influence and improve the mechanical properties of the membranes.

RESULTS

Conductivity of DOE's Block Copolymers

Two of the most critical variables that dictate the physical properties of ionomers in block copolymers are segmental chain length and ion content (ion exchange capacity [IEC] or equivalent weight). From our work with AFCC we have found that an intermediate hydrophilic chain length of m = 10–15 gave promising performance (Figure 1). Therefore, at the start of this project we focused on an intermediate hydrophilic chain length and explored varying the hydrophobic segment length to fine tune the proper ion content for optimal conductivity at high temperatures. Table 1 summarizes the segment lengths tested, resultant ion content, and conductivity of the films.

With exception of the lowest IEC(2.0), all of the block copolymer prepared displayed similar conductivities compared to Nafion® at both low RH and high temperature. Data taken from IEC(3.0) are highlighted in yellow to further emphasize that under all RH and temperature this sample provided the highest conductivities. Moreover, this sample surpassed the first milestone of the program (demonstrate ASR 0.05 ohm cm^2 at 120°C and 50% RH [or 25 µm film 50 mS/cm]); with an average film thickness of 20 µm the ASR for IEC(3.0) is 0.04 ohm cm^2, which is a lower ASR at more aggressive RH conditions (33% instead of 50%)!

TABLE 1. Conductivity of DOE's Block Copolymer vs. Nafion® 211 at Various Temperatures and RH

m Hydrophilic Domain Length	n Hydrophobic Domain Length	IEC meq/g	Conductivity 85°C 95% RH S/cm	Conductivity 85°C 50% RH S/cm	Conductivity 85°C 30% RH S/cm	Conductivity 120°C 33% RH S/cm
15	91	2.0	8.8×10^{-2}	3.7×10^{-3}	8.2×10^{-4}	1.1×10^{-3}
15	72	2.5	2.9×10^{-1}	2.7×10^{-2}	5.0×10^{-3}	2.1×10^{-2}
15	47	3.0	5.8×10^{-1}	5.1×10^{-2}	9.9×10^{-3}	4.7×10^{-2}
Nafion® 211		0.97	1.7×10^{-1}	3.7×10^{-2}	8.5×10^{-3}	2.5×10^{-2}

Fuel Cell Performance of DOE's Block Copolymers

Membrane electrode assembly (MEA) fabrication and testing of IEC(3.0) was performed by Tom Zawodzinski's group at ORNL. Figure 4 displays the polarization curves of both Nafion® 212 (baseline) and IEC(3.0) at 85°C at various RH with H_2/O_2. Oxygen was used initially instead of air to eliminate possible losses from the catalyst layer (e.g., non-optimized catalysts composition/layer) and solely evaluate membrane performance. At 0.6 V IEC(3.0) has a current output of nearly 2 A/cm^2 under all RH conditions! Nafion® 212 however, shows a drop in current density to 1 A/cm^2 at both 50% and 25% RH. Another promising feature of IEC(3.0) is the low ASR under all RH conditions (0.05 ohm cm^2). However, there is also a notable drop in cell voltage at 25% RH at low current density (kinetic region). This loss does not stem from the membrane however, and is instead caused by the dehydration of the catalyst layer. We believe through further optimization of the catalyst layer composition this initial loss can be mitigated.

Since IEC(3.0) outperformed the baseline at 85°C with oxygen, testing under more aggressive real world conditions was initiated. In Figure 5a, IEC(3.0) under H_2/air at 100°C with various RH is plotted. The 75% and 50% RH curves almost overlap and can maintain nearly 1 A/cm^2 at 0.6 V. At 25% RH, the membrane does experience a slight increase in ASR, due to drying of the membrane; however significant loss is again seen in the kinetic region at 25% RH, due to an unoptimized catalyst layer. At 120°C (Figure 5), the data were not as stable as 100°C since the membrane began to self-humidify (by the water product) and dehumidify simultaneously. This makes it difficult for the water content of the membrane to equilibrate. However, in conversations with advisors from General Motors, they expect short temperature excursions up to 120°C that do not necessarily hold at this temperature. At 0.6 V IEC(3.0) can reach a current density of 500 mA/cm^2. Moreover, it is interesting to note that both the infrared (IR) raw and IR free curves are almost identical and may suggest the catalyst layer has water management issues. In this case, further improvements to the catalyst layer composition will further improve performance at these higher temperatures.

We decided not to run IEC(3.0) at 120°C overnight (for durability) since the data were unstable (see water management issue mentioned above) and we were unsure if the carbon gas diffusion layer (GDL) would degrade-combust at 120°C with long term exposure. This brought up safety concerns that will need to be addressed before overnight runs are performed under these conditions. However, we have demonstrated significant fuel cell performance of a hydrocarbon block copolymer ([85°C at 50% RH 0.6 V, 2 A/cm^2, at 25% RH 0.6 V, 1 A/cm^2]; [100°C at 50% RH 0.6 V nearly 1 A/cm^2, at 25% RH 0.6 V, 500 A/cm^2]; [120°C at 35% RH 0.6 V, 500 mA/cm^2]).

Although IEC(3.0) exhibits high conductivity under both high temperature and low relative humidity, its mechanical properties are still an issue. During MEA fabrication, the researchers commented on the large degree of swelling observed when the membrane was exposed to water and the brittleness of the film once it was fully dried. In order to address these concerns we began to develop membranes that would better resist water uptake and mechanical fatigue.

Improved Dimensional Stability of DOE's Block Copolymer

In order to improve the mechanical properties of the block copolymer and reduce water uptake, we modified

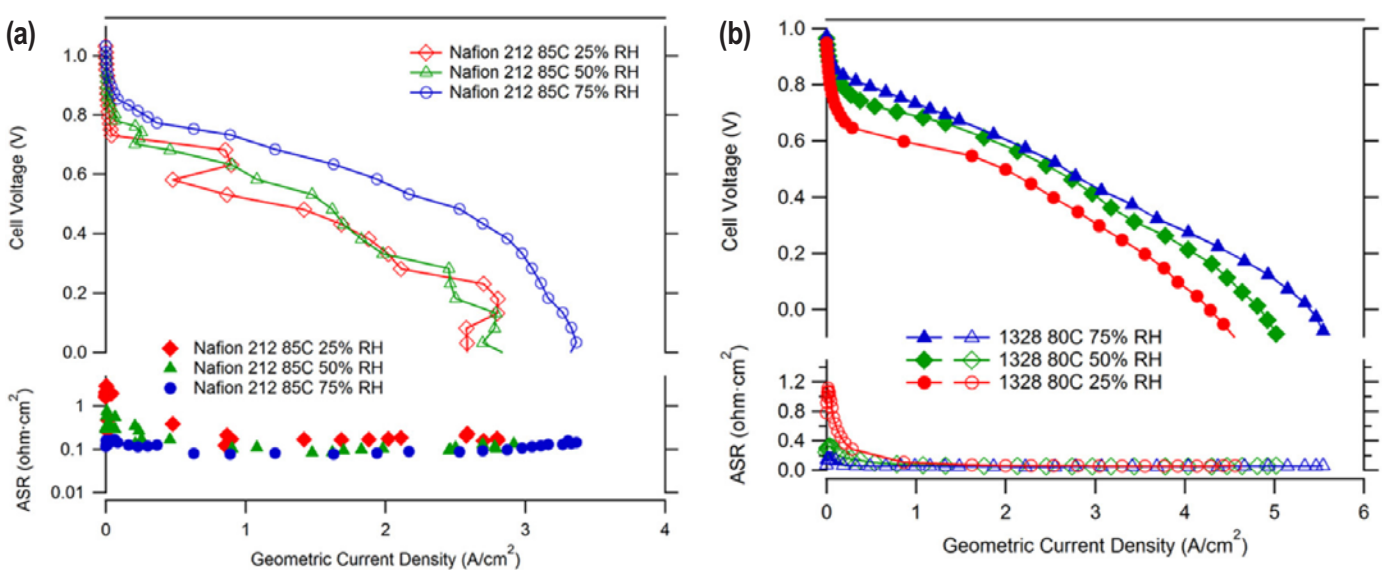

FIGURE 4. Fuel cell polarization H_2/O_2 at 85°C at various RH: (a) Nafion® 212; (b) IEC(3.0)

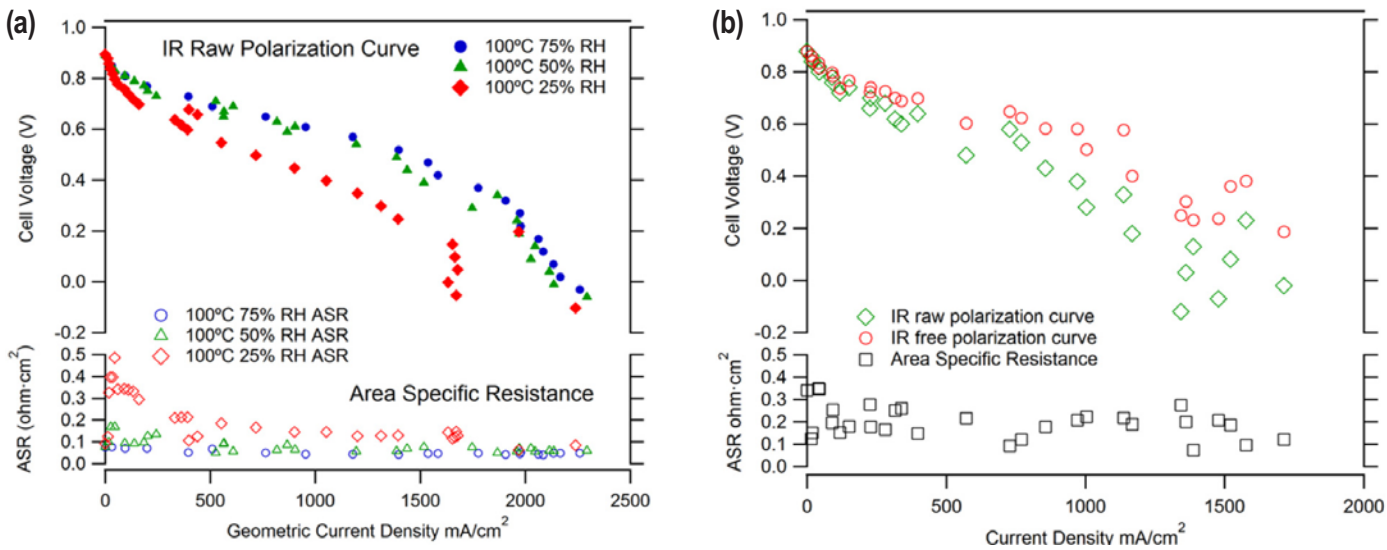

FIGURE 5. Fuel cell polarization H_2/O_2 at 85°C of IEC(3.0): (a) 100°C, various RH; (b) 120°C at 35% RH

the hydrophobic domain to incorporate fluorine. Figure 3b displays the structure of the second block copolymer investigated in this program. The fluorinated block copolymer had a very similar structure to the materials that we previously examined with AFCC (Figure 1a). The main difference between the current and previous materials is that the updated hydrophilic domain has both backbone and pendant sulfonic acid groups. The conductivity data of the fluorinated and non-fluorinated block copolymers and of the Nafion® are summarized Table 2.

Although the conductivity values of the fluorinated block copolymer were slightly lower than both the non-fluorinated block and Nafion® 211, the fluorinated block is promising in that it does not demonstrate a large water uptake (48% compared to 150% between the fluorinated and non-fluorinated). Also, the conductivity drop from 95% RH to 30% RH in the non-fluorinated block is substantial, while the same drop in the fluorinated block is similar to that of Nafion® 211, as shown in Figure 6. This difference is due to the improved water resistance of the fluorinated material and also the more effective water partitioning (water mainly resides in the hydrophilic domain while the hydrophobic domain is better able to resist water). Figure 7 shows the physical expansion of the membranes from dry to wet; the non-fluorinated membrane increased in diameter by 30% while the fluorinated membrane demonstrated a diameter expansion of only 8%.

MEA fabrication and testing of the fluorinated block copolymer was also completed and the results were compared to the non-fluorinated IEC(3.0) membrane in Figure 8. Although the conductivity of the fluorinated membrane

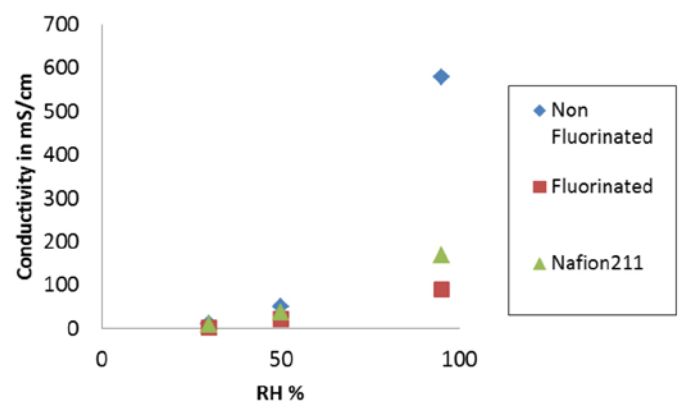

FIGURE 6. Conductivity of the non-fluorinated, fluorinated, and Nafion® 211 at various RH values

TABLE 2. Conductivity of DOE's Fluorinated, Non-Fluorinated Block Copolymer and Nafion® 211 at Various Temperatures and RH

IEC meq/g	Water uptake % RT	Conductivity 85°C 95% RH S/cm	Conductivity 85°C 50% RH S/cm	Conductivity 85°C 30% RH S/cm	Conductivity 120°C 33% RH S/cm
Non-Fluorinated (IEC[3.0])	150%	5.8×10^{-1}	5.1×10^{-2}	9.9×10^{-3}	4.7×10^{-2}
Fluorinated	48%	8.9×10^{-2}	2.1×10^{-2}	2.2×10^{-3}	2.1×10^{-2}
Nafion® 211	34%	1.7×10^{-1}	3.7×10^{-2}	8.5×10^{-3}	2.5×10^{-2}

RT – room temperature

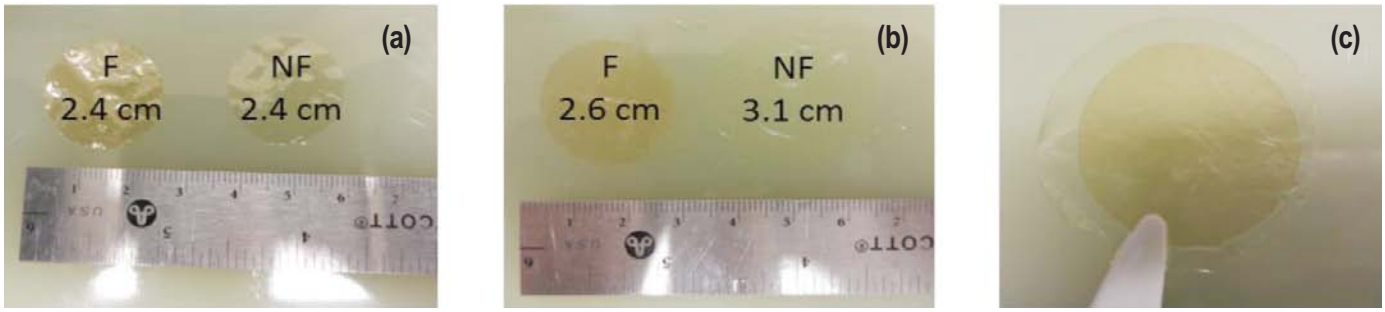

FIGURE 7. Wet-dry dimensional changes of the fluorinated (F) and non-fluorinated (NF) block copolymers: (a) films dry; (b) films wet; (c) overlay of N and NF

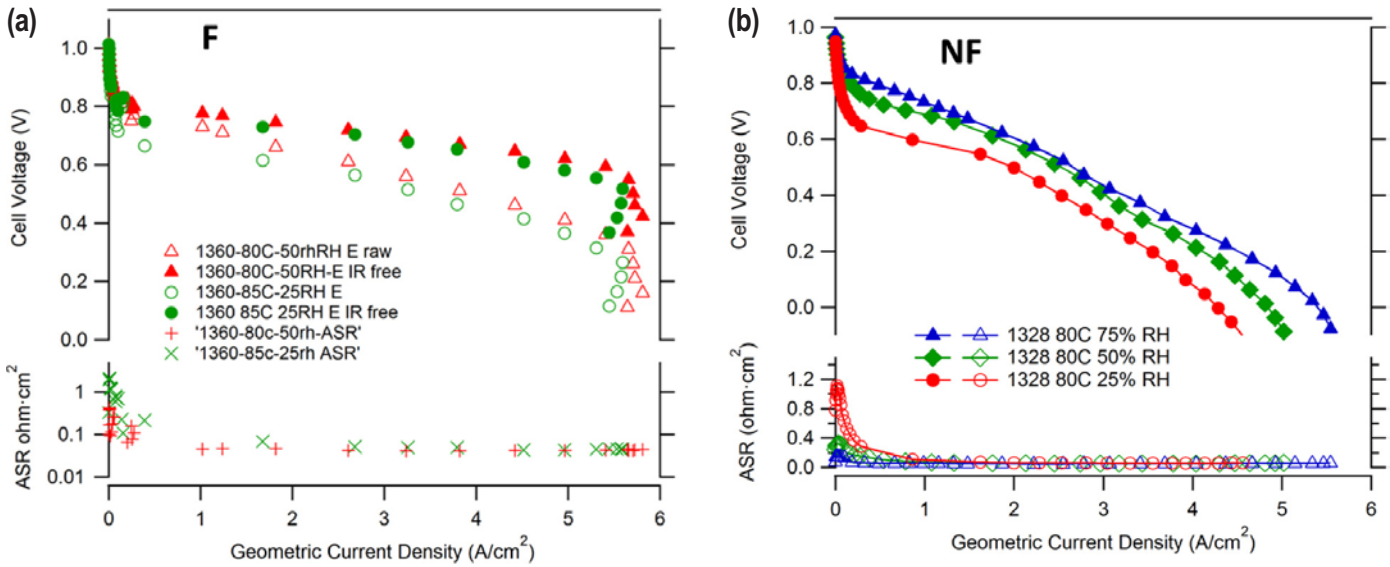

FIGURE 8. Fuel cell polarization H_2/O_2: (a) fluorinated at 80°C at 50% and 25% RH; (b) non fluorinated at 80°C at 50% and 25% RH

was slightly lower than that of the IEC(3.0), the fuel cell performance at both 50% and 25% RH at 80°C was nearly identical, with very similar ASRs.

These results are very encouraging since the fluorinated block copolymer is a rare example of a hydrocarbon displaying high conductivity and low water swelling. We are currently optimizing the hydrophilic-hydrophobic segment length and ion content for transportation use. We believe that this improvement will lead to significant improvement in the durability of the DOE's block copolymer, which was a hurdle in earlier work with AFCC. Finally, Sandia is currently pursuing to patent the fluorinated block copolymer as an improvement over (U.S. 12/425,413).

CONCLUSIONS AND FUTURE DIRECTIONS

- A series of DOE owned, hydrocarbon block copolymers have been synthesized. These materials have shown outstanding conductivities at high temperatures/low RH and achieved the program's initial milestone of 0.05 ohm cm^2 at 120°C at 50% RH.
- The DOE block copolymers were readily fabricated into MEAs. Single cell fuel cell tests of the block copolymers outperformed Nafion® 212, especially in the lower RH regions (50% and 25%). Although the fuel cell tests were very promising, further work in optimizing the catalyst layer composition for the hydrocarbon block copolymers is expected to further improve its performance under these aggressive conditions.
- With concerns about the high degree of water uptake and swelling of the initially tested materials, we modified the polymer architecture to reduce water affinity. The new polymer morphologies showed very promising properties of high conductivities at low RH and low water uptake. SNL is currently securing the IP for this new set of materials.

- We were unable to perform long term durability testing at 120°C with the initial materials that were investigated due to concerns of film brittleness and unstable fuel cell output. However, with the new materials developed within this program and further optimization of the catalyst layer composition, stable fuel cell output and long term testing will become viable.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

We are currently working on submitting a patent on the fluorinated hydrocarbon membrane discussed in this report shortly. We have held off on publishing the new findings of this report until the patent has been submitted.

FY 2015 PUBLICATIONS & PRESENTATIONS

1. High Temperature and Low Humidity Membranes. Fujimoto, C.; Zawodzinski, T; Tang, Z.; Nelson, J. Oral Presentation at the U.S. DRIVE Fuel Cell Meeting. February 2015, Detroit, MI.

2. High Temperature and Low Humidity Membranes. Fujimoto, C.; Zawodzinski, T; Tang, Z.; Nelson, J. Poster Presentation at DOE Hydrogen and Fuel Cell AMR. June 2015, Washington, DC.

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2. Fujimoto, C.; Hibbs, M.; Ambrosini, Andrea. Multi-block sulfonated poly(phenylene) copolymer proton exchange membranes. U.S. (2012), US 8110636 B1 20120207.

3. Maalouf, M.; Sun, C.N.; Pyle, B.; Emery, M.; Haugen, G.; Hamrock, S.; Zawodzinski, T. Factors enabling high mobility of protons and water in perfluorosulfonate membranes under low hydration conditions. International Journal of Hydrogen Energy (2014), 39(6), 2795–2800.