V.C.7 Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells

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Project Start Date: October 1, 2015
Project End Date: September 30, 2018

Overall Objectives

- Improve novel perfluoro (PF) anion exchange membrane (AEM) properties and stability.
- Employ high performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells (AMFCs). Apply models and diagnostics to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate related).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability (of membranes and membrane electrode assemblies)

(B) Cost (of membranes and membrane electrode assemblies)

(C) Performance (of membranes and membrane electrode assemblies)

Technical Targets

This project will synthesize novel PF AEMs and ionomers and incorporate these into membrane electrode assemblies (MEAs) for fuel cell testing. The project generally supports targets outlined in the Multi-Year Research, Development, and Demonstration Plan in application specific areas (portable, stationary, transportation). However, as AMFCs are at an earlier stage of development, specific target tables have not yet been developed. There are four tasks presented by Dimitrios Papageorgopoulos at the AMFC Workshop, April 1, 2016 [1].

TABLE 1. Targets for AMFCs Presented at the April 2016 AMFC Workshop

	Task
Q2, 2017	Develop anion-exchange membranes with an area specific resistance ≤0.1 ohm cm^2, maintained for 500 hours during testing at 600 mA/cm^2 at T >60°C.
Q4, 2017	Demonstrate AMFC peak power performance >600 mW/cm^2 on H_2/O_2 (maximum pressure of 1.5 atm$_a$) in MEA with a total loading of ≤0.125 mg$_{PGM}$/cm^2.
Q2, 2019	Demonstrate AMFC initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atm$_a$) in MEA a total loading of <0.1 mg$_{PGM}$/cm^2, and less than 10% voltage degradation over 2,000-hour hold test at 600 mA/cm^2 at T > 60°C. Cell may be reconditioned during test to remove recoverable performance losses.
Q2, 2020	Develop non-PGM catalysts demonstrating AMFC peak power performance >600 mW/cm^2 under H_2/air (maximum pressure of 1.5 atm$_a$) in PGM-free MEA.

T – temperature; PGM – platinum group metal

FY 2017 Accomplishments

- The project has successfully improved performance, durability, and processing of Generation (Gen) 2 PF AEMs.
- Implementing PF AEMs into devices plus University of Connecticut gas diffusion electrodes (GDEs) has allowed us to demonstrate performance ~1 W/cm^2 and durability beyond 500 hours (demonstrating a 2017 second quarter DOE milestone).
- Model development is providing insight into the role of water and carbon dioxide in these systems, allowing the performance potential and limitations of AMFCs to be better understood.

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INTRODUCTION

AMFCs are of interest primarily because they enable the use of non-Pt catalysts, the main cost/supply limitation of proton exchange membrane fuel cells. AMFCs, therefore, offer the potential of greatly decreased polymer electrolyte fuel cell cost. Operating AMFCs under ambient conditions where carbon dioxide is present remains a challenge due to carbonate formation. An approach that has shown promise for carbon dioxide tolerance is increased operating temperature. Unfortunately, the stability of the cation side chains on the membrane polymer and water management within the membrane both become more difficult as temperature rises.

The use of perfluorinated ionomers, similar to those used in proton exchange membrane systems, with tethered cation head groups that allow hydroxide conduction should help improve water transport properties and offer exceptional chemical durability of the backbone. The significant advances demonstrated in AMFC systems have been accomplished primarily through improving water management and the bonding between membrane and electrode. Both issues can be tackled much more effectively when employing PF AEMs and ionomers. The project consists of three sub-tasks: synthesis of novel perfluorinated alkaline ionomers (NREL); characterization of PF AEMs (NREL, Oak Ridge National Laboratory/University of Tennessee, Colorado School of Mines); and fuel cell performance and modeling optimization (NREL, Lawrence Berkeley National Laboratory).

APPROACH

The team has focused on achieving higher-temperature, higher-power-density AMFC operation through implementation of novel alkaline PF membranes and ionomeric dispersions. PF materials are expected to enhance water transport capabilities and electrode performance and durability significantly, thereby enabling higher temperature and power density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO_2 and potentially enabling tolerance to these conditions. Starting with the sulfonyl fluoride form of current perfluoro ionomers we have identified, and in several cases verified, the ability to convert commercially available precursors into anion exchange polymers and membranes. The synthesized PF ionomers have been cast into membranes, made into polymeric dispersions, and characterized in fuel cell tests. Modeling efforts have been made in parallel to better understand cell performance, loss mechanisms, and mitigation approaches.

RESULTS

While PF chemistry improves PF sulfonic acid acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available perfluoro sulfonyl fluoride precursor, different strategies can be employed to tether cations to the polymer backbone. We have focused on an amide linkage as shown in Figure 1 for our Gen 1 and Gen 2 PF AEMs. We have improved our processing of Gen 2 PF AEM and have demonstrated 90% of theoretical ion exchange capacity with hydroxide conductivity as high as 52 mS/cm (liquid equilibrated at room temperature). These materials have demonstrated reasonable water uptake and conductivity as a function of relative humidity (RH). They behave essentially as PF AEM analogues to perfluorosulfonic acids with many of the envisioned benefits of a perfluorinated system (high conductivity and water mobility) being maintained. While our Gen 1 materials have shown greater than 90% loss of ion exchange capacity (IEC) after two days in 2 M KOH at 80°C, our Gen 2 materials have shown >50x improvement in chemical stability and have allowed us to significantly increase our fuel cell durability testing, as shown in Figure 2. Following optimization of reaction and processing conditions, tough, ductile films and ionomeric solutions and dispersions have been obtained. We have synthesized over 200 g of Gen 2 PF AEM and have shared this material with more than 10 collaborating institutions.

Our Gen 2 PF AEM materials have been tested in AMFCs under a range of conditions. When used as an ionomer solution in electrode inks, performance has achieved up to 300 mw/cm^2 on H_2/O_2. Through collaboration with the Prof. Bill Mustain (University of Connecticut [UConn]) we also tested electrodes (UConn GDE) based on ionomer supplied by Prof. John Varcoe (University of Surrey). These electrodes were applied to our PF AEM materials and demonstrated performance approaching 1 W/cm^2. These two PF AEM AMFCs tests show significantly different performance and durability, as shown in Figure 3. The performance benefits of the UConn GDE are significant and cannot be fully explained by the improved high frequency resistance. Additionally, the UConn GDE was found to have a lower catalyst surface area (29 m^2/g Pt vs. 71 m^2/g Pt) in spite of its higher performance. The UConn GDE also showed a high sensitivity to water balance, achieving stable, high
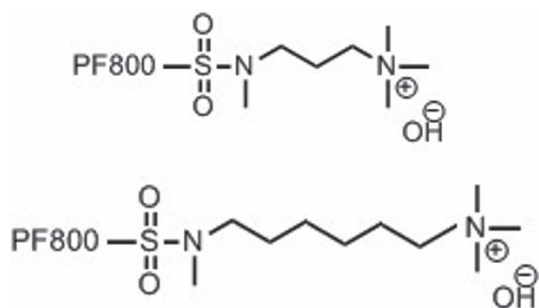

FIGURE 1. Chemical structures of Gen 1 and Gen 2 PF AEMs

current density within a narrow range of anode and cathode humidification. This AMFC also showed significantly improved durability compared to the PF AEM catalyst coated membrane. Unlike the PF AEM catalyst coated membrane which lost all performance within 15 h, the UConn GDE retained reasonable performance after 500 h of testing at

600 mA/cm^2 at 60°C. The high frequency resistance of this cell showed a slight increase over time, but demonstrated the ability to meet the DOE second quarter 2017 milestone of an area specific resistance ≤0.1 ohm cm^2, maintained for 500 h during testing at 600 mA/cm^2 at temperature >60°C.

The areas of modeling and advanced diagnostics have both been lacking in the AMFC area, and we have been addressing these aspects in this project. In last year's report we highlighted efforts to develop AMFC models. This year we expanded our use of models to study additional aspects of AMFC performance. Shown in Figure 4 are model results that investigate the impact of RH and oxygen content. These studies highlight the tremendous impact that RH has on AMFC performance. Additionally, we have been investigating carbonate formation due to the presence of carbon dioxide through models and experimental studies. In order to enable widespread commercialization of AMFCs, tolerance to atmospheric CO$_2$ levels will likely be required.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has successfully synthesized PF AEM sulfonamide-linked chemistries for highly OH-conductive AEMs. Extensive characterization has been performed on the polymer. Implementing this polymer into devices yields reasonable AMFC power densities. Modeling and diagnostic techniques are being performed to advance/optimize AMFC architecture. Upcoming activities focus on:
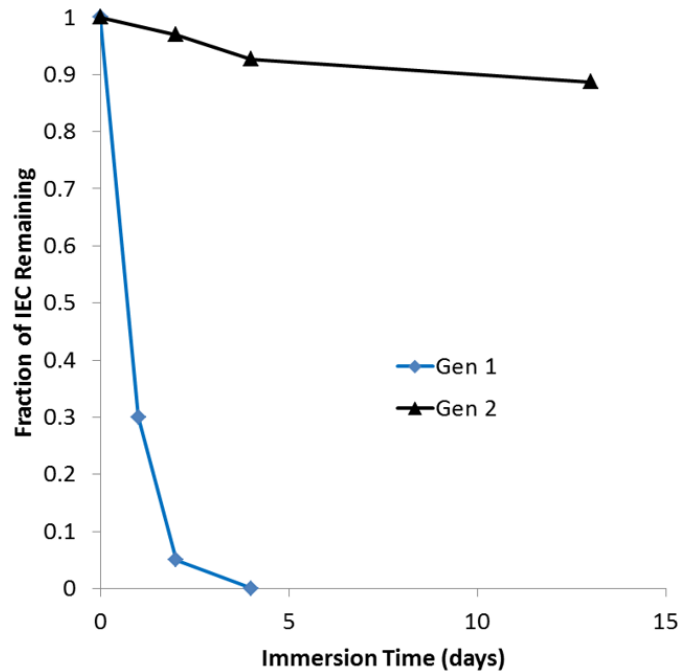
- Polymer synthesis:

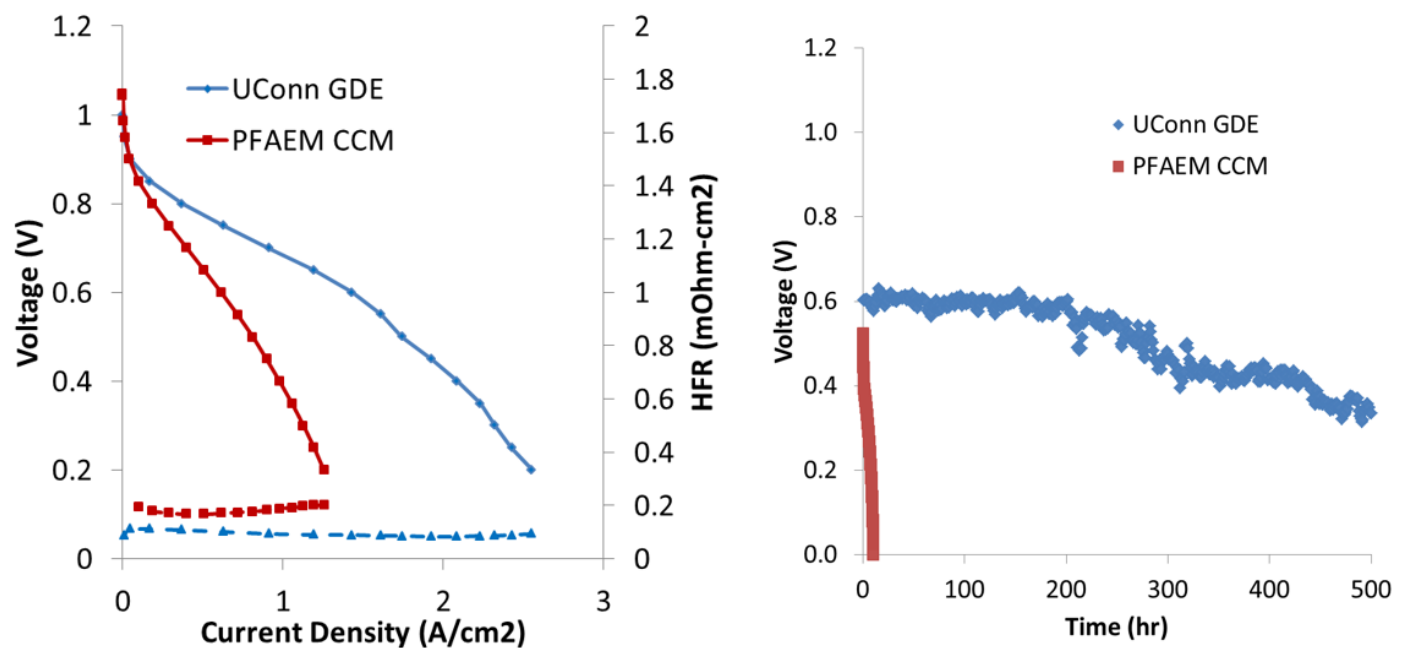**FIGURE 2.** Chemical durability of Gen 1 and Gen 2 PF AEMs

FIGURE 3. AMFC performance and durability of PF AEM membranes with standard PF AEM ink electrodes and UConn GDEs
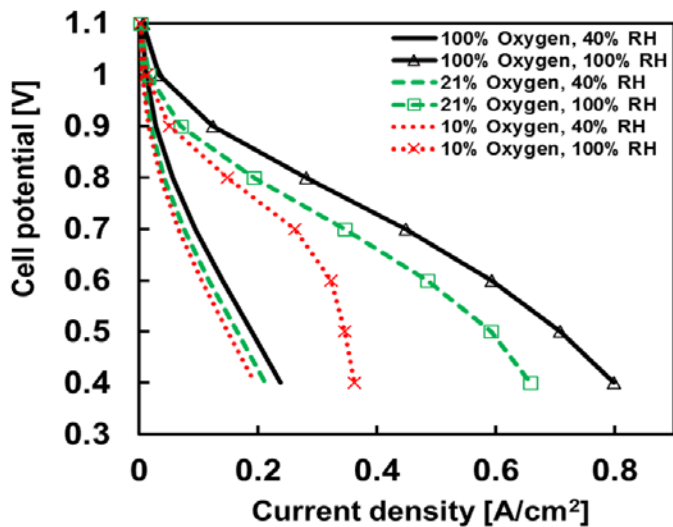
FIGURE 4. Modeling of AMFC performance as a function of oxygen concentration and RH

- – Avoid sulfonamide linkage.
- – Focus on Gen 3 polymer development.
- • Characterization:
  - – Conductivity, stability, water transport, carbonate formation and resulting effects.
- • AMFC implementation, modeling, and diagnostics:
  - – Electrode optimization and diagnostic studies focused on further characterization of electrodes and elucidating performance loss and durability.
    - - In situ: limiting current, RH studies, cyclic voltammetry, and impedance (and water management).
    - - Ex situ: microscopic, electrochemical, and spectroscopic analysis.
  - – Integration of modeling efforts with cell testing.
    - - Further elucidation of the impact of operating conditions (temperature, RH, current density, CO_2 concentration).

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Adam Z. Weber, Lalit Pant, Tobias Schuler, Haui-Suen Shiau, Anna Freiberg, Michael C. Tucker, Anamika Chowdhury, K.C. Neyerlin, Shyam Kocha, Iryna Zenyuk, "Elucidating and Understanding Transport Phenomena in Polymer-Electrolyte Fuel Cells," CARISMA, Newcastle, UK, April 11, 2017.

2. B. Pivovar, "Status of AMFC Technology and Advances in NREL's Perfluorinated Anion Exchange Membranes (PFAEM)," Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 26, 2017.

3. B. Pivovar, "Development and Implementation of Perfluoro Anion Exchange Membranes (PF AEMs)," 21st International Solid State Ionics Meeting, June 21, 2017, Padua, Italy.

4. A.M. Park, Z.R. Owczarczyk, L.E. Garner, A.C. Yang-Neyerlin, H. Long, C.M. Antunes, M.R. Sturgeon, M. Lindell, S.J. Hamrock, M.A. Yandrasits, B.S. Pivovar, "Synthesis and Characterization of Perfluorinated Anion Exchange Membranes," submitted to ECS Transactions.

5. H-S. Shiau, I.V. Zenyuk, and A.Z. Weber, J. Electrochem. Soc., submitted (2017).

REFERENCES

1. D. Papageorgopoulos presentation AMFC Workshop, Phoenix, AZ, April 1, 2016.