V.F.16 High Conductivity Durable Anion Conducting Membranes

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Project Start Date: September 1, 2014
Project End Date: 2015

Overall and Fiscal Year (FY) 2015 Objectives

The goal of this one-year project is the development of highly conducting durable anion exchange membranes (AEMs) and their demonstration in alkaline fuel cells (AFCs). Outcomes include:

- Synthesizing two classes of anion conducting membranes for use in fuel cells.
- Demonstrating the high conductivity of these membranes.
- Preparing and testing durable membrane electrode assemblies (MEAs) constructed from these new materials.

Technical Barriers

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

(A) Durability

(B) Cost

(C) Performance

Technical Targets

Second quarter 2017 milestone: Develop AEMs with an area specific resistance (ASR) <0.1 ohm-cm^2 that is maintained for 500 h during testing at 600 mA/cm^2 and at T > 60°C.

FY 2015 Accomplishments

- Produced two classes of highly conductive AEM materials: cross-linked, loaded anion-conducting membranes (CLAMs) and AEMs
- Prepared CLAMs that meet targets for conductivity (>100 mS/cm) at a lower relative humidity (RH) of 50% (**Milestone met)**
- Improved film formation methods for CLAM-type membranes
- Prepared AEMs that meet the conductivity target of >60 mS/cm (**Milestone met)**
- Demonstrated a CLAM-based MEA (>200 µm thick membrane) with an ASR of ~0.09 ohm-cm^2 at 50% RH, exceeding the target of <0.1 ohm-cm^2 (**Milestone met)**
- Prepared and tested first new AEM-based MEA in a fuel cell (FC) with an ASR less than 0.1 ohm-cm^2 and with no precious metal in the cathode
- Demonstrated an AEM lasting >2,500 h at 60°C during ex situ testing

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INTRODUCTION

This project, initiated in August 2014, focuses on improving materials for AFCs. AFCs are a promising technology that can operate without precious metal catalysts on pure hydrogen and CO_2-scrubbed air. To date, the development of high performance AFCs has been somewhat limited by the availability of various materials with suitable performance characteristics as polymer electrolyte binders for electrodes and especially as membranes. Improved conductivity of AEMs and chemical stability of the cationic functional group in hydroxide ion conductors are both areas in which development is lagging.

APPROACH

The project combined several elements for the development of highly conducting, durable membranes and their use in FCs: (i) high-throughput synthesis and physical property evaluation of new materials and processing into AEMs with the key aims of manipulating molecular polarity to aid in OH^- conduction and limit OH^- reactivity and of protecting cationic groups to limit degradation pathways; (ii) accelerated membrane life testing; (iii) 'ink' formulation and catalyst-coated membrane (CCM) preparation; and (iv) FC testing.

RESULTS

We prepared more than a dozen different polymers that were one of two types of membranes. First, we prepared CLAMs from conserved polymer backbones modified with cationic moieties and cross-linking agents. Cross-linking agents were chosen to provide the highest possible conductivity. The cross-linking process was carried out during film formation. This approach required substantial effort devoted to optimizing processing conditions such as temperature, concentration of polymer and cross-linker, and casting medium. A second stream of work was devoted to preparing more conventional AEMs.

In the context of this work, we demonstrated that many CLAM compositions possessed excellent conductivity. One remaining goal lay in showing that this conductivity could be maintained at lower RH. As shown in Figures 1 and 2, conductivity was maintained at >100 mS/cm at reduced RH at both 30ºC and 60ºC. Note that the results were obtained in air; thus, we can assume that the films are saturated with CO_2. Since CO_2 lowers the conductivity of hydroxide conductors, CO_2-free air testing may result in higher values.

One aspect of the CLAMs is the availability of chemical diversity within this class of membranes via modifications of both the cation type and the cross-linker. Given the large number of properties that require optimization beyond conductivity, our current work on the CLAMs is focused on identifying the best compositions for a variety of purposes, including mechanical property optimization and CCM formation. We are also pursuing work to improve film processing to enable us to make thinner films.

AEM-type films, which contain only water in the pores of the membrane, are more conventional than CLAMs. Our synthetic approaches allow us to prepare many different

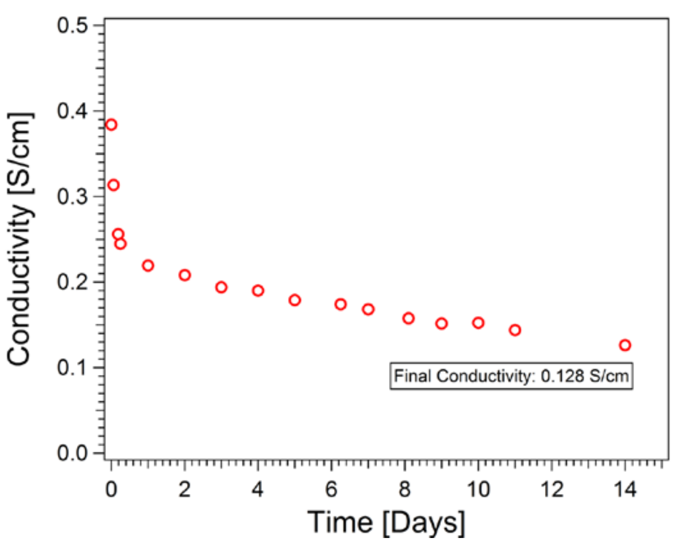

FIGURE 1. CLAM conductivity at 30°C during equilibration at 50% RH

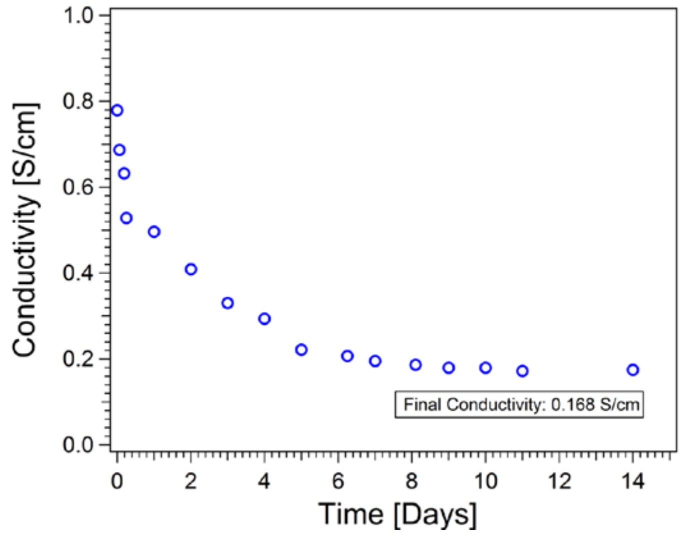

FIGURE 2. Conductivity of CLAM membrane at 50% RH at 60°C

versions of these materials as well. We have varied the backbone polymer chemistry used and have found some compositions that meet the benchmark of 60 mS/cm at 60°C that was set for our milestone.

The CLAMs were used to prepare MEAs for testing. An ASR of 0.09 ohm-cm^2 was observed in the fuel cell. Electrode performance, especially anode performance, was rather poor in initial tests. This poor performance necessitated the development of improved materials that are currently being tested.

CONCLUSIONS AND FUTURE DIRECTIONS

- CLAMs can be suitable electrolytes for use in FCs, particularly if RH of 50% or higher is available.
- We are able to readily prepare conventional AEMs with conductivities >60 S/cm.
- Key issues that remain include the development of high performance electrodes for AFCs and the demonstration of significant tolerance to CO_2.
- Water management issues are not adequately defined for AFCs.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Patent application in process.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Presented poster at the June 2015 U.S. DOE Annual Merit Review and Peer Evaluation.