V.C.3 Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Overall Objectives

- Synthesize highly conductive and stable perfluorinated anion exchange membranes.
- Prepare perfluorinated ionomer dispersions for the fabrication of fuel cell electrodes.
- Develop non-precious metal electro-catalysts for the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR).
- Demonstrate the single-cell performance of alkaline membrane fuel cells (AMFCs).
- Demonstrate the long-term AMFC performance under steady and accelerated stress conditions.

Fiscal Year (FY) 2014 Objectives

- Prepare tough and thin perfluorinated anion exchange membranes by new chemistry.
- Evaluate chemical stability of resonance stabilized perfluorinated membranes under high pH conditions.
- Characterize HOR and ORR behaviors at the Pt-perfluorinated polymer interface using a thin film-coated microelectrode.
- Demonstrate AMFC performance using the perfluorinated anion exchange ionomers.

Technical Barriers

This project addresses the following technical barriers from Section 3.4.4 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability (polymer electrolytes)

(B) Cost (non-precious metal catalysts)

(C) Performance (AMFCs)

Technical Targets

The purpose of this project is to investigate practical aspects of AMFCs for practical use in intermediate (10-50 kW) power applications. Insights gained from this project will be applied toward the next stage of advanced AMFC systems. Since there are no specific technical targets for AMFCs in the current U.S. DOE Fuel Cells Program, we modified technical targets for proton exchange membrane fuel cell (PEMFC) membranes from the DOE Multi-Year RD&D Plan [1] based on appropriate AMFC operating conditions (Table 1).

TABLE 1. DOE Membrane Targets for Transportation Applications

Technical Targets: Membrane for Transportation Applications				
Characteristics	**Units**	**2012 Status[a]**	**2017 Targets**	**LANL Status**
Area specific resistance at maximum operating temperature	Ohm cm^2	0.086	0.02	0.05
Hydroxide conductivity (σ)	mS/cm	70	100[b]	50
Membrane formation ability	μm	60	20[b]	25
Chemical stability after immersion in 0.5 M, NaOH at 80°C for 100 h	% σ decrease	75	0	33

[a] From our previous project: poly(phenylene) membrane (ATM-PP) [1]

[b] Based on PEMFC transportation application target; Corresponding areal resistance: <0.02 Ohm cm^2

FY 2014 Accomplishments

- Developed synthetic route to produce thin and tough perfluorinated anion exchange membranes with the thickness range from 20 to 50 μm and the elongation at break >200%.
- Demonstrated good hydroxide conductivity (30–80 mS/cm) at low water uptake <15% by introducing hydrophobic perfluorinated polymer backbone and guanidinium functional group.
- Improved chemical stability of perfluorinated membranes, ca. 3.3% conductivity loss after 120 hours 0.5 M NaOH treatment at 80°C by introducing more stable amide linkages between the perfluorinated polymer side chain and guanidinium functional group.
- Discovered superior HOR behaviors of Pt with perfluorinated ionomers to Pt with hydrocarbon ionomers from alkaline microelectrode experiments.

- Achieved excellent AMFC performance at 80°C using a perfluorinated anion exchange ionomer, ca. peak power density: 580 mW/cm^2.

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INTRODUCTION

AMFCs are currently drawing tremendous attention because non-precious metal catalysts have shown good ORR activities under high pH environments. However, current AMFC performance using nonprecious metal catalyst is much inferior to their PEMFC counterparts. One of the reasons for this inferior performance is the unavailability of anion-conducting perfluorinated ionomers for AMFC systems. Perfluorinated ionomers have many desired properties for the use in fuel cell applications including good ionic conductivity, chemical stability, high oxygen permeability, hydrophobicity, less anion adsorption onto the catalyst, facile polymer chain mobility, the ability to create porous electrode structures. In the previous project (2008-2011), we first demonstrated stable perfluorinated hydroxide conducting ionomers from sequential reactions of Nafion® precursors. In the continuation of this effort, we report several updated research achievements to produce a series of perfluorinated hydroxide conducting polymers.

APPROACH

Our approach to achieve high performance AMFCs is to develop new hydroxide conducting perfluorinated membranes which have improved stability and conductivity compared to state-of-the-art benzyl ammonium-hydrocarbon based anion exchange membranes. The degradation of anion exchange membranes occurs not only at the cationic functional group and its linkage to the polymer but also at the polymer backbone itself [2]. In order to improve the polymer backbone stability, perfluorinated polymers are used. The hydrophobicity of the polymer backbone structure prevents the access of solubilized hydroxide ion and improves the alkaline stability. Resonance stabilized phenyl guanidinium is used for the cationic functional group. In order to enhance the stability of the functional group-polymer linkage, amide groups are used. The amide linkages are stable in both acid and base conditions. The general polymer structure is shown in Figure 1.

RESULTS

Synthesis: The synthesis of guanidinium functionalized perfluorinated polymers was accomplished with a three-step procedure: (i) attachment of tetramethyl guanidinium to Nafion®-COOH, (ii) functionalization of tetramethyl guanidinium, and (iii) methylation. We prepared a series of guanidinium functionalized perfluorinated polymers, PF-Amide-G1 to -G6, which have different amide and phenyl guanidinium groups. Cast membranes with thickness range from 20 to 50 µm were converted to hydroxide form. These cast membranes prepared from the reactions had excellent mechanical properties, e.g., tensile toughness is 19 MPa and elongation at break is >200% at 0% relative humidity and 50°C.

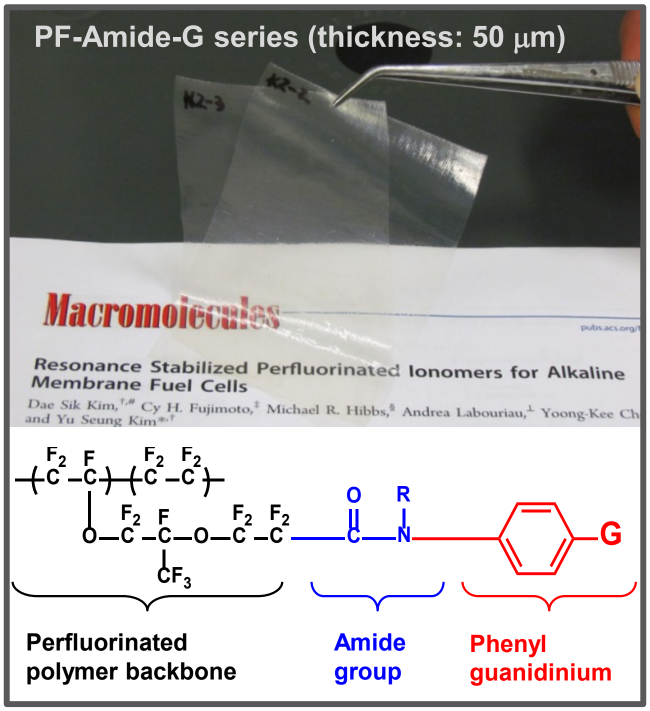

FIGURE 1. The Chemical Structure of PF-Amide-G Series Membranes

Hydroxide conductivity and water uptake: The hydroxide conductivity of the PF-Amide-G membranes was measured as a function of temperature. In order to avoid the possible (bi)carbonate formation, the hydroxide conductivity was measured in hydroxide-rich environment as described in the previous report [3]. Figure 2 shows the hydroxide conductivity of the PF-Amide-G membranes. The conductivity of PF-Amide-G membranes increases approximately 2-fold as the temperature increases from 30 to 80°C. The hydroxide conductivity of PF-Amide-G1 to G4 is comparable to that of the state-of-the-art benzyl trimethyl ammonium functionalized poly(phenylene) anion exchange membrane (ATM-PP). Improved conductivity was observed with for the PF-Amide-G5 and G6 membranes (40-60% higher than that of the reference ATM-PP polymer).

The water uptake of the PF-Amide-G membranes were less than 15 wt%, which was much lower than ATM-PP (~100 wt%). These extremely low water uptakes of the PF-Amide-G membranes were due to the hydrophobicity of perfluorinated polymer backbone and low hydration energy of guanidinium functional group. The low water uptake of the PF-Amide-G

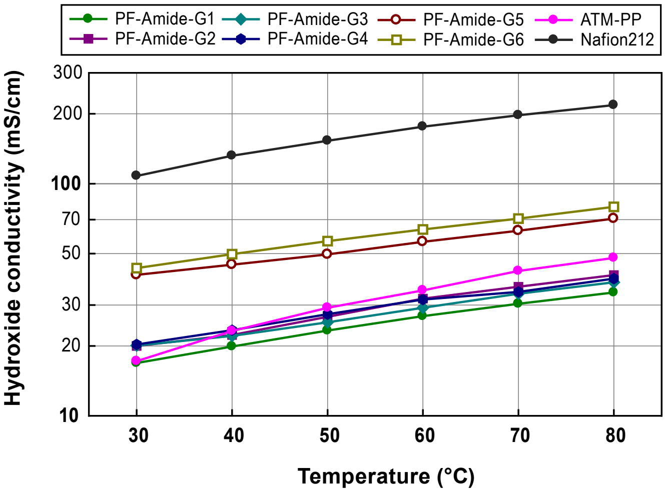

FIGURE 2. Hydroxide conductivity of PF-Amide-G series membranes as a function of temperature; proton conductivity of Nafion® 212 is drawn for comparison purpose.

membranes are desirable because (i) hydroxide conductivity can be further increased by increasing the ion exchange capacity of the membranes and (ii) the dimensional and membrane-electrode interfacial stability are better with low water swollen membranes.

Stabilities: The acid and alkaline stabilities of the PF-Amide-G membranes were investigated. The PF-Amide-G membranes exhibited excellent acid stability as we observed no chemical structural change of the membranes after acid treatment, 0.5 M H_2SO_4, 80°C for 24 h. The alkaline stability of the PF-Amide-G membranes was measured after alkaline treatment, 0.5 M NaOH, 80°C. The alkaline stability of the PF-Amide-G membranes strongly depends on the chemical structure of the amide linkage group since amide hydrolysis occurs before guanidinium cation degradation. The PF-Amide-G4 membrane showed 12.5% and 30.3% loss of the amide linkage after 120-h and 300-h NaOH treatments, respectively. The conductivity loss after stability test was 3.3% and 19.0% after 120 h and 300 h test, exceeding the FY 2014 milestone (<10% conductivity loss after 100 h in 0.5 M NaOH at 80°C).

Electrochemical activities: The electrochemical activity of an electro-catalyst in contact with the perfluorinated ionomer was examined using Pt microelectrode setup. We found that chain flexibility of ionomers is critically important for HOR behavior. The facile chain mobility of the perfluorinated ionomers allows diffusing the guanidinium cation group away from the Pt surface while the polymer stiffness of ATM-PP prevents the cation diffusion which brings quick readsorption upon applying low cell potential. As a result, the HOR current density of the PF-Amide-G2 ionomer coated with Pt is approximately 40% greater than that of ATM-PP coated with Pt (Figure 3). The microelectrode experiments also exhibited that the oxygen permeability of PF-Amide-G2 was 2.3×10^{12} mol s^{-1} cm^{-1} which was 2.5-fold greater than that of ATM-PP.

The AMFC performance and durability using PF-Amide-G2 was investigated. Figure 4 shows the hydrogen/oxygen AMFC performance of membrane electrode assemblies (MEAs) using PF-Amide-G2 and ATM-PP as an ionomeric binder in the AMFC electrodes at 80°C. The

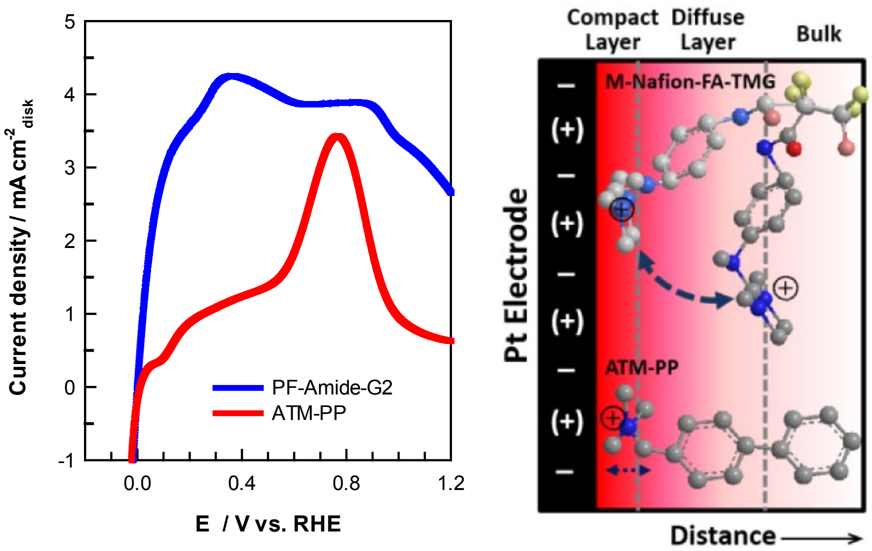

FIGURE 3. Hydrogen oxidation reaction of platinum in contact with PF-Amide-G2 and ATM-PP alkaline polymer electrolytes at 40°C after pre-conditioning at 1.4 V for 10s. Right figure: schematic diagram of ionomer relaxation on platinum surface during potential change.

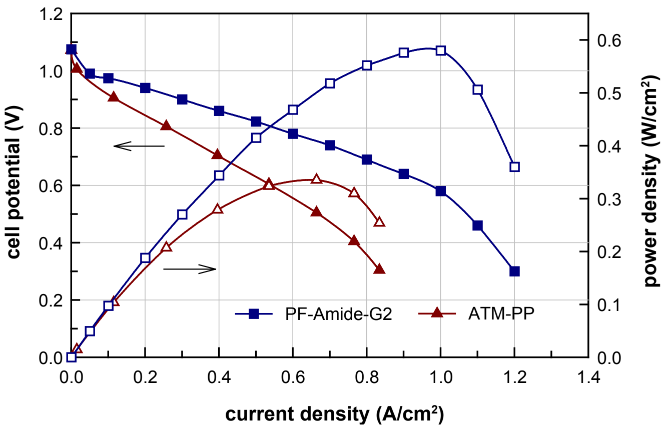

FIGURE 4. AMFC performance using ATM-PP and PF-Amide-G2 as the ionomeric binder for the electrode at 80°C; membrane: ATM-PP (50 μm thick); gas supply: H_2/O_2.

MEA using PF-Amide-G2 shows a maximum power density = 577 mW/cm^2 under H_2/O_2 conditions which is 172% of the maximum power density of a MEA using ATM-PP as an ionomeric binder under H_2/O_2 conditions. Higher oxygen permeability and lower cation adsorption potential of PF-Amide-G2 are the reasons for the better AMFC performance.

CONCLUSIONS AND FUTURE DIRECTIONS

- A series of perfluorinated anion exchange membranes (PF-Amide-G) were successfully prepared from Nafion®-COOH precursors and multi-step condensation reactions. The membranes prepared from newly developed chemistry have tough and ductile properties, e.g., the elongation at break of the membranes: >200% at 0% relative humidity, which is 10 times greater than that of the state-of-the-art ATM-PP.
- The hydroxide conductivity of the PF-Amide-G membranes ranged from 32 to 80 mS/cm at 80°C. The PF-Amide-G membranes had low water uptake, ca. six times lower water uptake at 30°C relative to the ATM-PP membranes having comparable hydroxide conductivity.
- The acid and alkaline stabilities of the PF-Amide-G membranes are excellent; no chemical degradation was observed after 0.5 M H_2SO_4 treatment at 80°C for 24 h. Only 3.4% hydroxide conductivity decreased after 0.5 M NaOH treatment at 80°C for 120 h, which exceeded the FY 2014 milestone.
- Excellent AMFC performance using PF-Amide-G2 ionomer was demonstrated. The Pt microelectrode experiments elucidated that the improved HOR kinetics and higher oxygen permeability of PF-Amide-G2 compared to ATM-PP.
- Further development of perfluorinated membranes having better stability and hydroxide conductivity and their performance and durability in AMFCs as a membrane as well as an ionomeric binder for the electrodes.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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2. Anion Exchange Polymer Electrolytes, USP 8,530,109 B2 (2013)

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