High-Temperature Membranes

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Objectives

Develop new membranes and membrane electrode assemblies (MEAs) for operation at temperatures substantially in excess of 120°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

Simultaneously carry out R&D on:

- Physical chemistry of polymer electrolytes
- New polymeric electrolytes
- New approaches to proton transport in polymer electrolytes

Develop MEAs based on new polymer electrolytes

Accomplishments

<u>New Membranes</u>

- Synthesized new hybrid organic/inorganic membranes
- Synthesized new materials to implement strategies targeting 'water replacements'

<u>Catalyst Coated Membranes (CCMs)/Electrodes</u>

- Showed performance limitation associated with low humidity operation relying on water
- Elucidated effect of imidazole adsorption on electrode reactions

<u>Industrial and Other Collaborative Interactions</u>

- Evolved team model for project

- Completed Roadmap for High Temperature Polymer Membranes
- High-Temperature Polymer Membrane Working Group continues to expand with increased industrial interaction

Future Directions

Computational Studies

- Perform more extensive work on novel systems designed to identify approaches to maintain water content at 120oC

Membrane Development

- Provide new materials from each partner
- Implement battery of methods for screening membranes; new electrolytes to be tested in 4-month cycle starting in fall

CCMs/Electrodes

- Start developing MEAs from new materials (CWRU)
- Expand initial tests on oxygen reduction reaction (ORR) at high temperature/low humidity and on adsorption of imidazole, with intent to provide solutions
- Develop understanding of interactions at buried interfaces within electrodes
- Provide means for scale-up of polymers, film-making and CCM production to modest scale

Industry and Other Collaborations

- Next round of new start funding: increased emphasis on 120oC solutions
- Begin to distribute 'lessons learned' info via website

Introduction

The need to operate at temperatures exceeding 100°C presents difficult new challenges for the electrolytes used in fuel cells. This difficulty stems from the decrease in water content of the polymer electrolytes in the desired temperature range. There is a need for detailed understanding of the impact of poor or zero hydration on membrane and electrode processes in the fuel cell. Water plays a key facilitating role in proton transport, and lower water content thus leads to lower conductivity. Lack of water also has important negative consequences for electrode behavior.

Approach

At this point, we do not know which of several approaches is most promising. Thus, our membrane development efforts include: (1) a full-fledged effort to explore approaches involving polymer synthesis and development, as well as implementation of new "carrier" media to replace the function of water in Nafion; and (2) a study of proton transfer dynamics to inform the synthetic efforts. We are using theory to explore specific possibilities for new acid group types or for acid-base interactions that could lead to progress in proton transfer media and to assess the possibility of holding useful water in electrolytes at high temperature. We are increasing our understanding of the energetics of proton transfer to inform synthetic efforts. We are working to incorporate new polymers in fuel cells by developing catalyst-coated membranes from new materials. Finally, we also have extended our range of polymer electrolyte development efforts by including several different universities and significant industrial input. Our goal is to engage the polymer community to the

maximum extent possible, harvesting the best new ideas for development.

Results

Physical Chemistry. We are extending our computational studies to provide insight into the following processes: (i) tailoring bases to mimic water using substituted imidazoles or other proton carriers; and (ii) continuous water transport pathways at low relative humidity. This work augments experimental studies on water uptake by polymers and additives of various types.

New Membranes. Many new materials are presently being prepared and tested. These are: (i) polymers and inorganic materials with controlled pore size modified with acid groups lining pores or by inclusion of proton conducting subunits; (ii) polymer matrices filled with surface-modified inorganic particles; (iii) polymeric systems with intrinsically stronger acid groups; and (iv) polymer systems swollen or imbibed with tailored proton acceptors including imidazole and ionic liquids. These are useful both intrinsically and as test or model systems. Summarized below are approaches being explored by some of the partners in the High Temperature Membrane project:

CWRU: inorganic/organic hybrid systems; new polymers; strong acid groups; electrode studies at high temperature; making MEAs; polymer scale-up and film processing; computational studies; and fuel cell testing (working on both temperature ranges).

University of Texas/Dallas: inorganic scaffolds with added conducting polymers (primarily high temperature range)

Arizona State University: molten salts (primarily high temperature range)

NASA Jet Propulsion Laboratory: proton conducting salts (primarily high temperature range)

Virginia Commonwealth University: strong acid groups; advanced MEA processing method (low temperature range)

CCMs. In work this year, we focused on basic studies of the problems that arise in the high temperature regime. Specifically, we used impedance spectroscopy on fuel cells operating under conditions of subsaturation. We found additional features in the spectrum under these conditions. This is illustrated in Figure 1. We are presently working to understand the precise mechanistic reasons for existence of these features.

Several approaches to high temperature conduction involve the use of imidazole or modified imidazoles. In Figure 2, a cyclic voltammogram shows the impact of imidazole on basic electrochemistry at Pt. It appears that the oxide

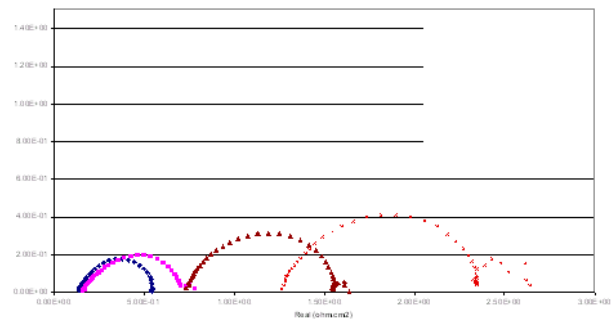

Figure 1. Impedance Spectrum of Fuel Cell Under Sub-Saturation Conditions (Operating conditions: Current density: 0.1 A/cm^2; Pressure: ambient; Fuel: H_2; Oxidant: oxygen; Gas utilization: 10%; Cell temperature: 70°C to 100°C; Dew point: 70°C)

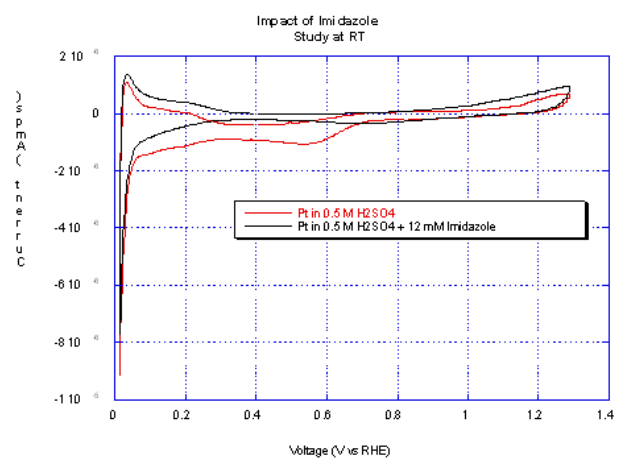

Figure 2. Cyclic Voltammogram of Pt Electrode Exposed to Imidazole

formation region is strongly impacted by the presence of imidazole in solution.

Industrial and Other Collaborative Interactions. We are engaged in a series of collaborative efforts with industry, national laboratories, and universities to facilitate efforts to achieve the targets for high-temperature polymer membranes. We have organized the High-Temperature Polymer Membrane Working Group, which has met four times to date. Bi-annual meetings allow us to assess progress and to communicate issues and needs to the high-temperature membrane community.

Conclusions

The development of new polymer electrolytes for operation at elevated temperature is under way. However, this is a long-term project. Replacement of water is the most difficult problem, but adequate stability and cathode activity are not trivial objectives to achieve. We have developed several different approaches to address this problem. Fundamental work is guiding the process via useful insights into the conduction process to guide synthetic efforts. The first polymers geared for temperatures in excess of 100°C are emerging, and testing is showing that, although promising, there are definite shortcomings. Work on making viable new materials continues.