

VII.A.3 Development of High-Temperature Membranes and Improved Cathode Catalysts

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Contract Number: DE-FC36-02AL67608

Subcontractors:

Virginia Polytechnic Institute and State University (VaTech), Blacksburg, VA

University of Connecticut (UCONN), Storrs, CT

United Technologies Research Center (UTRC), East Hartford, CT

Northeastern University (NEU), Boston, MA

Start Date: Q1 2002

Projected End Date: Q4 2005

Objectives

- Develop and demonstrate an advanced polymeric membrane able to operate at near ambient pressure (1-1.5 atm) in the temperature range of 100-120°C that is able to meet DOE 2005 targets for performance. Assess and optimize materials that define and influence performance and durability of proton exchange membrane (PEM) fuel cells (FCs) at operating conditions of 100-130°C and 25-50% relative humidity (RH).
- Develop and demonstrate improved Pt cathode catalysts that will enable the reduction of Pt loading and meet DOE 2005 targets [1].

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 Research, Development and Demonstration Plan:

- A. Durability
- C. Electrode Performance
- D. Thermal, Air and Water Management

Approach

- **Phase 1:** High-temperature membranes (HTMs) and improved Pt cathode catalysts were synthesized, characterized and compared with issued specifications. [Completed]

- **Phase 2:** Laboratory-scale catalyst-coated membranes (CCMs) were fabricated, optimized and tested using the Phase 1 down-selected membranes and catalysts. [Completed]
- **Phase 3:** Full-size CCMs with the down-selected and optimized catalysts will be fabricated and tested in multi-cell stacks. In-cell and out-of-cell tests will be carried out to study fundamentals of high-temperature (HT) operation. Advanced membrane for HT operation will be demonstrated on a single-cell level. [In progress]

Accomplishments

- PtCo and PtIrCo cathode catalysts developed at UTC Fuel Cells (UTC FC) showed 1.5-2.5x specific activity improvement in out-of-cell tests. PtCo membrane electrode assemblies (MEAs) were optimized, and the benefit of 20-25 mV was shown in-cell.
- Two-fold reduction of Pt loading was achieved with PtCo cathode catalyst without loss in performance.
- Up to 5x extension of cyclic durability of electrodes was shown with PtIrCo/C cathode systems.
- Cyclic durability improvements at high-temperature operation were shown with use of Pt alloy catalysts.
- Improved Series IV membrane was developed at UCONN. It is shown to be more durable at high temperature than the previous generation Series 2 membrane.
- A high molecular weight biphenyl sulfone (BPSH) membrane was developed by VaTech and showed approximately 5x improvement in HT durability relative to perfluorinated sulfonic acid (PFSA).
- Fundamental studies showed that additional performance benefit can be obtained during HT operation through the use of advanced catalyst (PtCo) and low equivalent weight (EW) ionomer in the electrodes.

Future Directions

- Advanced catalyst development
 - Demonstrate Pt-alloy performance and durability benefits on short stack.
 - Analyze alloy catalyst implications on membrane durability.
- HTM development and HT fundamentals
 - Evaluate temperature and RH effects on membrane durability.
 - Demonstrate endurance of alternative membrane at 100-120°C and 25-50% RH.
 - Demonstrate lessons learned and the best up-to-date technology for HT operation on a single-cell level.

Introduction

Two main challenges in the proton exchange membrane (PEM) fuel cell area are the reduction of Pt loading and development of membranes that can operate at over 100°C. Overcoming these two challenges will directly impact the cost, performance and size of PEM fuel cell stacks. In order to achieve the DOE performance targets, new polymeric membranes with low thermal degradation and acceptable proton conduction at 100°C are needed. At the same time, even if new, capable membranes are developed, other materials that are being used in conventional PEM fuel cells will not last at elevated temperatures [2]. Thus, fundamental understanding

of the current properties of the materials in the application for high-temperature operation is needed.

On the cathode catalyst part of the project, a combination of high-activity alloy catalysts can lead to thinner low-Pt-loading catalyst layers and in such way reach the established performance and cost requirements.

Approach

To develop HTMs and novel cathode catalysts, UTC FC has teamed with research groups that possess competencies in the field of polymer chemistry and electrocatalysis. The subcontractors that participated in the project during this reporting

period together with the description of the approaches for membrane/catalyst synthesis are shown in Table 1 and Table 2.

Table 1. High-Temperature Membrane Project Participants

| Group | Principal Investigator | Approach |
|--------|-----------------------------------|--|
| UCONN | Prof. J. Fenton, Prof. R. Kunz | Hygroscopic solid ion conductor (e.g., zirconium phosphate, etc.) filled Nafion [®] |
| VaTech | Prof. J. McGrath | Sulfonated Poly(arylene ether sulfone), multiblock copolymers |

Table 2. Advanced Cathode Catalyst Project Participants

| Group | Principal Investigator | Approach |
|--------|------------------------|--|
| UTC FC | Dr. L. Protsailo | Carbothermal synthesis of ternary Pt alloys [Pt-Ir-X and Pt-Rh-X, (X =Ni, Co and V)] |
| UTRC | Dr. T. Madden | MEA optimization and fabrication |
| NEU | Prof. S. Mukerjee | Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys. |

Results

This project was initiated in Q1 2002. It consists of three phases: material development, MEA optimization, and cell demonstration of developed technologies. On the catalyst part of the project, the majority of the work during the current reporting period was dedicated to the optimization of the MEAs of down-selected cathode catalysts. The HTM part of the project was preplanned in August 2004 with a focus on the fundamental understanding of high-temperature operation of PEM fuel cells.

Cathode Catalyst Development

For the development of Pt alloy catalysts, UTC FC has applied its past experience with the carbothermal synthesis technique for alloy synthesis. The carbothermal synthesis process involves precipitation of metal salts onto pre-platinized carbon and heat treatment to form alloys [3, 4]. To achieve

combined activation and mass transport benefits, UTC FC has adopted a strategy to develop higher activity and concentration (40-50 wt%) of Pt alloy systems.

Two advanced Pt alloy cathode catalyst systems developed at UTC FC were down-selected for the final phase of the project in April 2004. These systems are Pt₇₅Co₂₅/C and Pt₅₀Ir₂₅Co₂₅/C. Both of these catalyst systems showed significant improvements in activity in out-of-cell tests. Rotating disc electrode (RDE) experiments showed that specific activity of Pt₇₅Co₂₅/C is about 2-3 times of that of pure Pt/C, and Pt₅₀Ir₂₅Co₂₅/C activity is 1.5-2 times that of Pt/C system [5]. With the assumption of Tafel slope 70 mV/decade, such activity increases should lead to performance improvements of 12-28 mV in the kinetic region. In-cell tests conducted at UTC FC have demonstrated up to 25 mV improvements in kinetics for Pt₇₅Co₂₅/C cathodes in optimized MEAs. It was also demonstrated that with this increase in performance, a two-fold reduction in Pt loading can be achieved without performance loss. Figure 1 shows performance of two MEAs fabricated at UTRC. Cell "PEM472" has a Pt/C cathode with 0.4 mg Pt/cm² loading, and cell "PEM460" has an optimized Pt₇₅Co₂₅/C electrode with 0.2 mg Pt/cm² loading. As seen in the figure, similar performance was measured at all current densities from the two cells.

It has been suggested that a fundamental Pt instability problem exists at 120°C and potentials greater than 0.9 V [2]. The instability comes from accelerated Pt dissolution at higher temperatures and

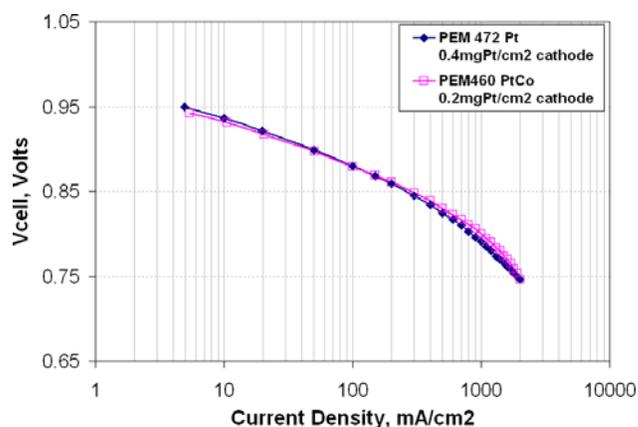


Figure 1. Performance Curves for Pt/C (0.4 mg Pt/cm²) and PtCo/C (0.2 mg Pt/cm²) Cathodes (Test conditions: 65°C, 1 atm, H₂/O₂)

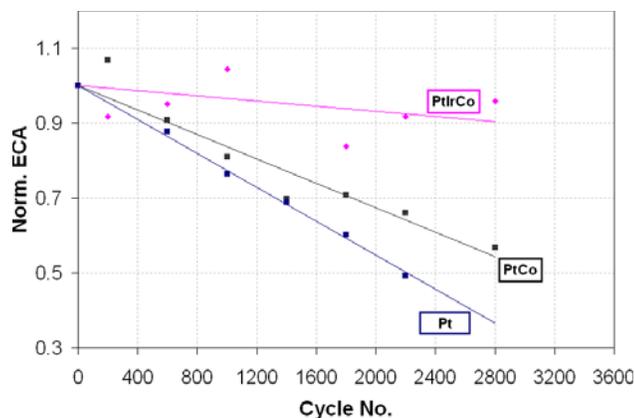


Figure 2. Electrochemical Area (ECA) Decrease During Cyclic Durability Tests (Cycling conditions: H_2/N_2 , $120^\circ C$, 50% RH, lower voltage 0.87 V, upper voltage – 1.05 V, 1.5 atm)

voltages. Using a semi-empirical model, it has been suggested that at $120^\circ C$ and 0.9 V, 50% Pt in a conventional electrode will dissolve in less than 150 hours. Using electrodes made of PtIrCo, we have shown less than 10% loss in Pt during highly accelerated potential cycle tests at $120^\circ C$. As seen in Figure 2, the electrochemical area loss for conventional Pt after 2800 cycles was 60%, while only 6% loss was observed for PtIrCo electrode. Resulting performance loss is shown in Figure 3.

Electron microprobe analysis of MEAs subjected to potential cycling tests showed no detectable Co or Ir in the membrane (see Figure 4).

Reduction of the peroxide formation on both cathode and anode electrodes would lead to a membrane life extension. Northeastern University conducted rotating ring disc electrode (RRDE) studies of peroxide formation on different cathode catalysts and has shown that peroxide formation is strongly accelerated in dry conditions. For the case of Pt catalyst, peroxide concentration increased almost 4 times for tests carried out in more concentrated acid (simulation of lower RH%). At the same time, peroxide detected on PtCo catalyst increased only twice between 1M and 4M acid solution. Table 3 summarizes results of these tests.

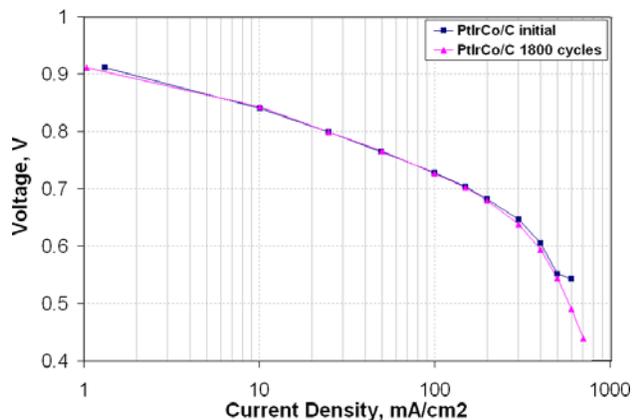
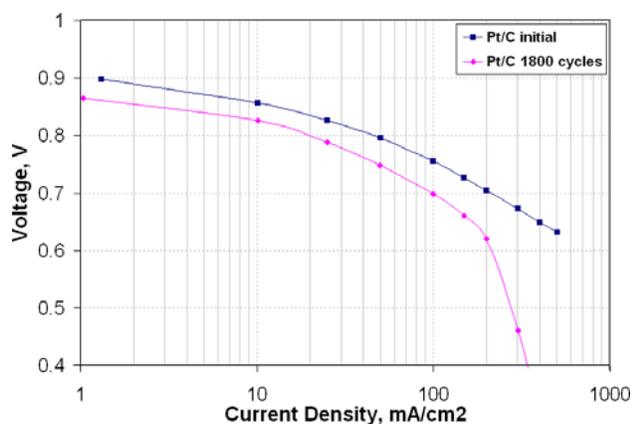


Figure 3. Performance Decay During Cyclic Durability Tests at High Temperature (Test conditions: $120^\circ C$, 50% RH, H_2/O_2)

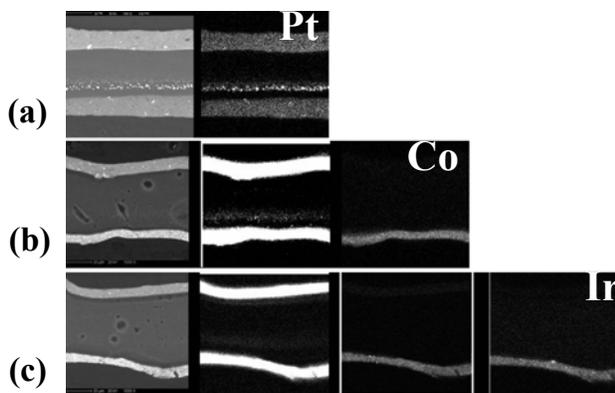


Figure 4. Electron Microprobe Analysis Images for (a) Pt/C, (b) $Pt_{75}Co_{25}/C$ and (c) $Pt_{50}Ir_{25}Co_{25}/C$ Catalysts after 2800 Cycles Between 0.87 mV and 1.05 mV vs. Reference Hydrogen Electrode at $120^\circ C$

Table 3. Peroxide Formation on Different Catalysts

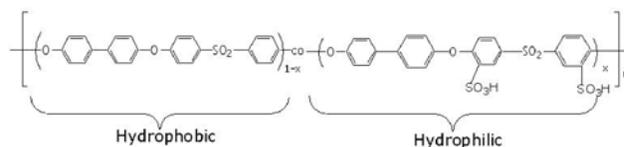
| Catalyst | %H ₂ O ₂ 1 M TFMSA [@0.7 V] | %H ₂ O ₂ 6 M TFMSA [@0.7 V] |
|----------|---|---|
| Pt/C | 0.114 | 0.416 |
| PtFe/C | 0.147 | 2.387 |
| PtCo/C | 0.151 | 0.301 |

High-Temperature Operation and Membrane Development

In Phase 1, two membranes based on different chemical systems (hydrocarbon membrane from VaTech and Nafion[®]-like membrane doped with solid acid conductors developed at UCONN) were selected and are currently being investigated as advanced membranes for HT application.

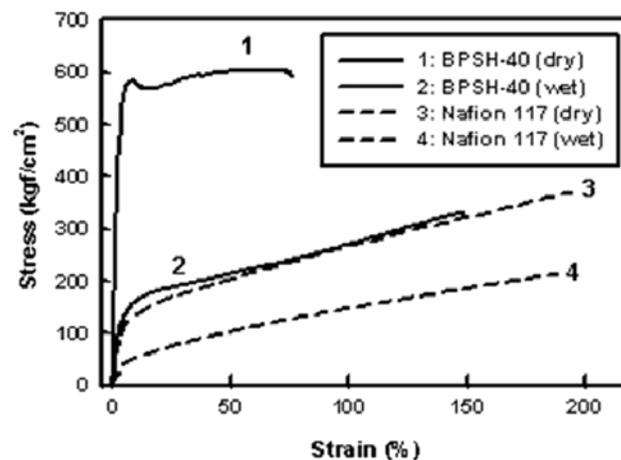
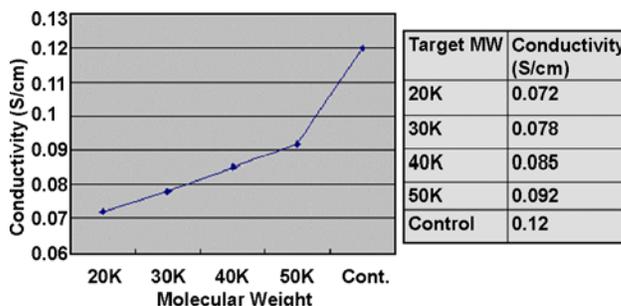
VaTech Membrane

The approach used by VaTech is based on direct copolymerization of wholly aromatic poly(arylene ether sulfone) sulfonic acid copolymers. The generalized structure of such polymer is shown in Figure 5. The 4,4'-biphenol-based poly(arylene ether sulfone) copolymers have been most extensively studied and have developed the acronym BPSH-XX, to represent bi-phenol in acidic form. The XX represents the molar fraction of sulfonic acid units in the copolymer repeat unit. These aromatic ionomers are copolymers that are comprised largely of repeating thermally stable aromatic rings, which are stiffer, stronger, and have higher glass transition temperatures than Nafion[®] and yet are designed to produce ductile films. VaTech has shown that the direct copolymerization has many advantages, such as enhanced stability; control of ion-containing sites; a wide variety of molecular structures; and the ability to make higher molecular weights, which translate into improved mechanical properties. These polymers showed much higher yield strength and modulus than the analogous perfluorinated copolymers (Figure 6).

**Figure 5.** General Structure of Wholly Aromatic Random Copolymer Developed by VaTech

MEAs with BPSH performance were fabricated by UTRC and have shown good performance at 80°C in fully humidified conditions. Some drop in performance was observed at lower RHs. VaTech's approach to improvement of membrane conductivity at low humidities is through the increase of molecular weight of the polymer used for the membrane. Dependence on molecular weight of polymer and membrane conductivity is shown in Figure 7. Higher molecular weight polymers are currently being fabricated, and their performance in fuel cells will be tested during Q3 2005.

Chemical stability of the BPSH-35 membrane was measured in-cell by the accelerated membrane degradation open circuit voltage (OCV) test. The cell was held at open circuit potential at 100°C and 25% RH. Hydrogen was passed through the anode and O₂ was passed through the cathode side of the cell. Nafion 112 was used as a baseline for this test. Hydrogen crossover was measured as an indicator of

**Figure 6.** Comparison of Stress-Strain Behavior of BPSH-40 and Nafion[®] 117**Figure 7.** Influence of Molecular Weight on the Conductivity of BPSH-35 Copolymers in Liquid Water at Room Temperature

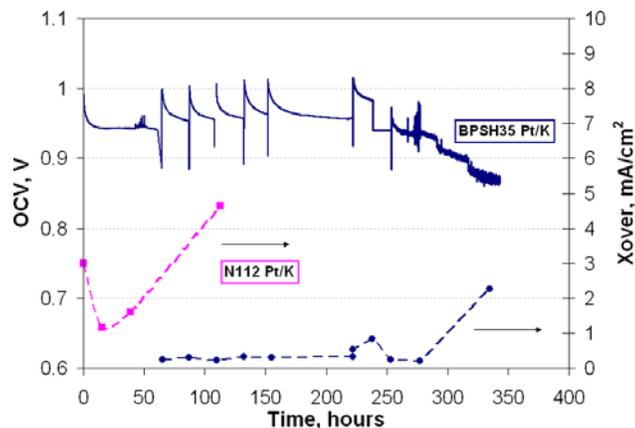


Figure 8. Durability of VaTech BPSH-35 Membrane

membrane thickness. OCV drop below 0.8 V was used as the failing criteria. As seen in Figure 8, BPSH insignificantly outlived the baseline in this test. The superior durability of the hydrocarbon membrane in this test comes from its inherently low oxygen permeability (about an order of magnitude lower than that of Nafion[®]). This accelerated test targets peroxide formation on the anode only. Peroxide is formed from the oxygen that crosses over from cathode to anode. Since cross-over of oxygen to the anode in the BPSH cell is much lower than in the Nafion[®] cell, the amount of peroxide formed on this electrode is also lower and membrane life is extended.

UCONN Membrane

The UCONN technical approach for high-temperature PEM catalyzed membranes integrates, on a molecular level, the proton-conducting Nafion[®] polymer with hygroscopic solid proton conductors such as phosphotungstic acid. This innovative nanocomposite material maintains low water vapor pressure and provides more water-independent proton conduction.

A new membrane formulation has been developed at UCONN during the last quarter. This membrane, designated as Series 4, and the fabrication process of this formulation are significantly different from the previous Series 2 membrane. Phosphotungstic acid (PTA) particles are precipitated in situ, resulting in much smaller particle

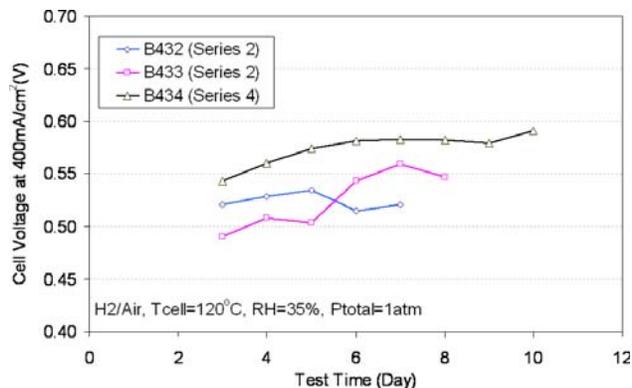


Figure 9. Performance and Stability of UCONN Series 2 and Series 4 Membranes

size. The PTA is added in Cs form, and the resulting membrane is processed in the Cs form, allowing for higher processing temperatures ($>180^{\circ}\text{C}$) and resulting in greater crystallinity (+durability) of the membrane as well as providing insoluble form of PTA. Figure 9 demonstrates performance of these cells at 120°C .

Fundamental studies carried out at UCONN and UTC FC have shown that additional performance benefit can be obtained at high-temperature operation through the use of advanced catalyst (PtCo) and low EW ionomer in cathodes. Observation agreed with the predictions by the model developed at UTC FC.

Conclusions

- PtCo MEAs were optimized, and a benefit of 20-25 mV was shown in-cell. Two-fold reduction of Pt loading is achieved with PtCo cathode catalyst without loss in performance.
- Up to 5x extension of cyclic durability of electrodes was achieved with the PtIrCo/C catalyst system.
- UCONN's new Series 4 membrane formulation shows improvement in performance and stability.
- VaTech's non-fluorinated hydrocarbon membrane lasted 5x longer compared to a PFSA-like membrane in an OCV accelerated test.

References

1. <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>
2. M. Mathias et al., Fuel Chemistry Division Preprints 2004, 46 (1)
3. US Patent 5,013,618
4. US Patent 4,447,506

FY 2005 Publications/Presentations

Over 25 publications in refereed journals and over 35 presentations have been published under this funding during current reporting period.

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2. Hossein Ghassemi, William Harrison, Tom A. Zawodzinski, Jr., and James E. McGrath; New Multiblock Copolymers Containing Hydrophilic-Hydrophobic Segments For Proton Exchange Membrane, *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1),68-69.
3. J. McGrath, Higher Temperature PEM Composite Systems for Fuel Cells, General Electric Global R&D Center, December 14, 2004.
4. Ramani, V., H. R. Kunz, J. M. Fenton. 2005. "Stabilized Heteropolyacid/Nafion® Composite Membranes for Elevated Temperature / Low Relative Humidity PEFC Operation." *Electrochimica Acta*, 50:5, 1181 (2005).
5. J. Fenton, "High Temperature Membrane Electrode Assembly Development for Proton Exchange Membrane Fuel Cells.", Small Fuel Cell Conference, "SMALL FUEL CELLS 2005," April 27-29, 2005, Loews L'Enfant Plaza, Washington, DC, USA.
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