

V.K.2 Fuel Cell Research at the University of South Carolina*

John W. Van Zee
University of South Carolina
301 Main Street
Columbia, SC 29208
Phone: (803) 777-2285; Fax: (803) 777-8142
E-mail: vanzee@cec.sc.edu

DOE Technology Development Manager:
Donna Ho
Phone: (202) 586-8000; Fax: (202) 586-9811
E-mail: Donna.Ho@ee.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753
E-mail: Reginald.Tyler@go.doe.gov

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Technical Targets

The first sub-project is developing Nb-doped TiO₂ supports for catalyst with the goal:

- Durability of electrocatalysts with cycling: 2015 target <30 mV loss after 100 h @1.2 V

The other sub-projects all relate to improving durability to achieve the durability targets of 5,000 h for transportation applications and 40,000 h for stationary applications. The second sub-project is developing an understanding of the levels of contaminants that impact automotive H₂ fuel quality. The data, models, and rate constants allow the DOE H₂ Quality team to predict performance loss mechanism and effects.

The third sub-project is providing information for the technical task associated with selecting the seal technologies in the second quarter 2011 that will allow the system to meet the durability target.

The fourth sub-project is providing information for stationary systems that allows one to assess durability at 40,000 hours and predict the time when stack power is less than 10% of the rated power.

Objectives

This project consists of four sub-projects. The primary objective of each sub-project is:

- Develop high surface-area non-carbon supported catalysts with improved corrosion resistance.
- Obtain data and rate constants for performance losses caused by fuel contaminants in support of the H₂ Quality team.
- Develop a fundamental understanding of degradation mechanisms of existing gaskets and test the performance of improved materials.
- Obtain data and develop models of polybenzimidazole (PBI)-type high temperature membranes.

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) Cost
- (B) Durability
- (C) Performance

Accomplishments

- Developed a Nb-doped TiO₂ support that displays catalytic activity equivalent to Pt/C for high levels of doping.
 - The synthesized support has a mesoporous structure and a surface area of approximately 150 m² g⁻¹, which is much higher than that reported in the literature.
- Obtained anode overpotential data as required by the H₂ Quality team.
 - Data for concentrations below the fuel standard indicate 10 mV of additional polarization at 25 psig and 60°C for 0.4 mg/cm² Pt on the anode.
- Developed laboratory characterization methodologies for understanding stress relaxation, chemical stability, and leaching of contaminants for low-cost seals.
- Measured water content as a function of temperature and water partial pressure for commercial PBI membranes.



Introduction

Sub-project #1 focused on increasing the life of the electrodes in polymer electrolyte membrane (PEM) fuel cells by replacing the carbon support of the platinum catalysts with a non-corroding, inexpensive metal such as titanium oxide. This material typically has low conductivity and low surface area but if these can be overcome, it may be preferable to carbon because it does not undergo corrosion at high potentials. Sub-project #2 focused on providing data that can be used to set international specifications for hydrogen quality used by fuel cell vehicles. These specifications are important because ultra-pure H₂ will be expensive but contaminants will affect the life of the fuel cell.

The third sub-project measured the properties of low-cost seal materials to help with the selection and design of new materials. We focused on understanding the mechanisms of failure, designing accelerated measurement procedures, and quantifying the contaminants that leach from these materials and thereby decrease the life of the fuel cell. The fourth sub-project measured the properties of a high-temperature membrane that quantify its interactions with water vapor during operation of a stationary fuel cell. These properties can be used in a model to predict lifetime and failure mechanisms.

Approach

To achieve the objectives of sub-project #1, niobium-doped titania-based catalyst supports were synthesized and characterized. The characterizations included surface and spectroscopic methods, electrochemical and corrosion methods, and stability analysis and performance studies of the supports loaded with catalysts. To obtain the data for sub-project #2, we performed polarization experiments using GORE PRIMEA[®] Series 57 membrane electrode assemblies (MEAs) exposed to neat hydrogen and very low concentrations of CO contaminated hydrogen. Data for these commercially available electrodes complement the work of investigators at the National Renewable Energy Laboratory, Argonne National Laboratory (ANL), Savannah River National Laboratory, Los Alamos National Laboratory, and at other universities. The DOE H₂ Quality team chose CO as a “canary” indicative of the ability to clean hydrogen in pressure swing adsorption operations.

Researchers on sub-project #3 were guided by industrial members in the National Science Foundation Center for Fuel Cells [1]. In an effort to develop accelerated testing protocols, seal materials were aged at different temperatures, with and without stress and deformation, while being exposed to two different solutions. One solution simulates a beginning-of-life fuel cell environment (denoted below as a regular

solution) and the other solution contains trace chemicals that accelerate degradation and that may be present towards the end of life (denoted in the following as the accelerated testing solution). The materials were characterized for chemical stability using attenuated total reflectance Fourier transform infrared (ATR-FTIR), scanning electron microscopy, X-ray photoelectron spectroscopy, and leachant solution analysis at weekly intervals. We characterized the mechanical properties and structural integrity by measuring ductility, hardness, elastic modulus, and stress relaxation. In sub-project #4, measurement techniques were developed to rapidly measure the mass gain of PBI membranes exposed to different mixtures of water vapor and air. These techniques include in situ water balance and water accumulation experiments as well as ex situ isotherm and water accumulation experiments.

Results

In the past year for sub-project #1, the synthesis procedures (i.e., sol-gel and hydrothermal methods) have been studied in an effort to understand the interactions between the amount of dopant, the conductivity, the electrochemical surface area, and the catalytic activity. That is, as reported last year, the electrical conductivity showed a maximum for 25% Nb. Also, last year we reported that the electrochemical active surface area (ECSA) of a Pt catalyst deposited on the Nb-TiO₂ was comparable to that of Pt catalyst supported on carbon (Pt/C) and that the new supported catalyst is selective for the 4-electron reaction pathway since the maximum H₂O₂ production is 4% of the current. This year our X-ray diffraction studies indicate that the Nb acts to stabilize the anatase form of the support and that the conductivity is low for both the anatase and the rutile phases. However, these materials function well as catalysts despite the low conductivity as the weight of conductive metal (i.e., either “dopant,” coating metal, or catalyst) is increased.

This year in sub-project #2, we completed the studies of CO poisoning at concentrations that span the specification for fuel quality (i.e., 0.2 ppm). These measurements used the techniques, reported last year, appropriate to ensure steady-state reproducible data. An example of this data, reported to the H₂ Quality team, is shown in Figure 1 for the anode overpotential caused by CO contamination at 60°C at back pressures of 0/0 psig and 25/25 psig on the anode/cathode. We used the typical automotive inlet relative humidity condition of 75/25% (anode/cathode) and varied the partial pressure of CO from 10 to 0.1 ppm. This range of partial pressures is necessary to determine if the poisoning mechanism changes, to develop cell models [2], and to test models of stack recycle being developed at ANL [3-5]. We also obtained data for 80°C, which

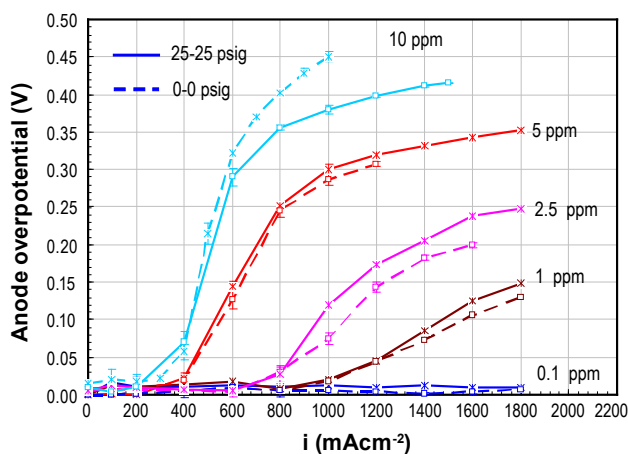


FIGURE 1. Steady-state effects of pressure and CO concentration on the anode overpotential at 60°C for a GORE 57 Series MEA with anode/cathode (A/C) stoichiometry = 1.2/2.0 and A/C relative humidity = 75%/25%.

shows, as expected, that the polarization is less than that at 60°C.

In Figure 1 the plateaus indicative of CO oxidation appear only for concentrations of 2.5 ppm and higher. At the lower concentrations of 1 ppm, the anode overpotential maybe insufficient to oxidize electrochemically the CO at cell current densities of 1.8 A/cm², indicating no electrochemical oxidation of CO and an ECSA controlled by the adsorption isotherm. Thus, any recycle loop for the fuel that results in an increase of CO to 1 ppm will result in 120 to 150 mV of polarization or voltage loss per cell at 1.8 A/cm². Figure 2 expands the scale for the 0.1-ppm data to reveal polarization of 10 mV at 25 psig and 60°C. Note the errors bars of ± 5 mV for these polarizations and that we claim that these error bars are consistent with the measurement limits for data obtained from 25 cm² and 50 cm² cells.

Figure 3 shows an example of the chemical stability data obtained in sub-project #3 this year. There, the changes in the concentration of silicate are shown for the low-cost liquid silicone elastomer (DLS), the silicone copolymeric resin (DC), and the florosilicone rubber (DFS) for exposure in the accelerated testing solution (A-) and the regular solution (R-). The increases in the silicate leachant concentration for the A-DLS and A-DC materials correlate to the rate of change in the weight loss of these materials (not shown). ATR-FTIR analysis of the DLS material showed chemical changes in the backbone and cross-linking domains after three weeks of exposure to the accelerated testing solution and no significant changes after 15 weeks of exposure to the regular solution. Measurements of the elastic modulus for the A-DC material showed a gradual decrease over time and a significant change between 20 and after 25

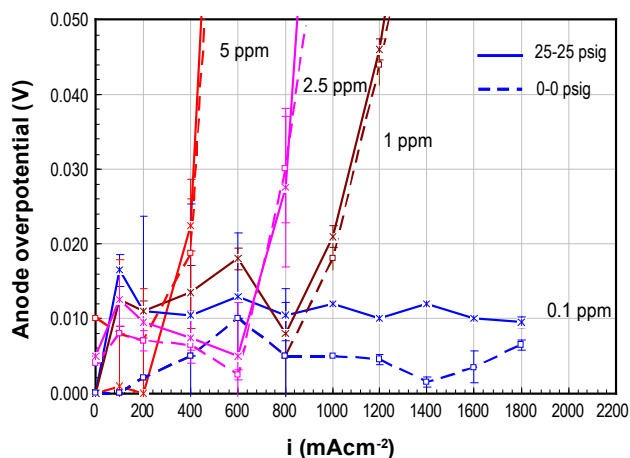


FIGURE 2. Expanded view of low overpotential region of Figure 1 showing error bars and an overpotential essentially independent of current density at 0.1 ppm CO in H₂.

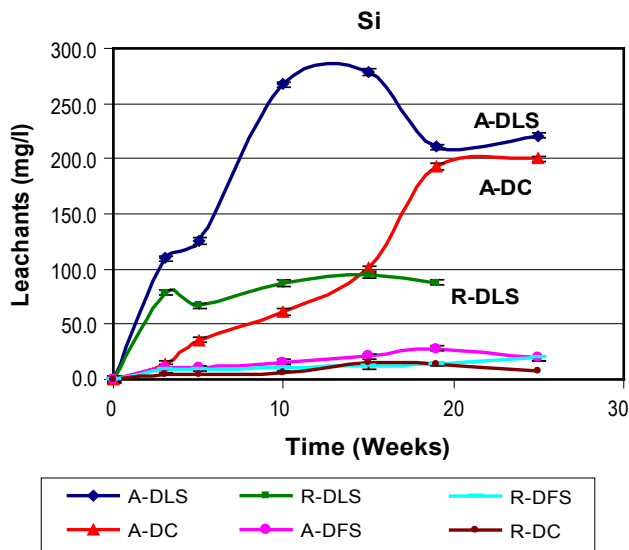


FIGURE 3. The change in silicate leachant concentration during 25 weeks of chemical stability testing at 80°C. The acronyms for the materials are defined in the text. A-DLS, A-DC and A-DFS correspond to samples in the accelerated testing solution and R-DLS, R-DC, and R-DFS correspond to samples exposed to the regular solution.

weeks which may correlate with the increase in silicate shown in Figure 3.

In sub-project #4 this year, we used our previously developed techniques to measure the equilibrium water content of a PBI-MEA as a function of temperature and water vapor pressure. Figure 4 shows these data and that the moles of water per mole of acid bound in the PBI structure increases sharply for temperatures of 120°C or less. This increase has implications when there are inadvertent shutdowns during operation or during laboratory testing. Heretofore, experimentalists

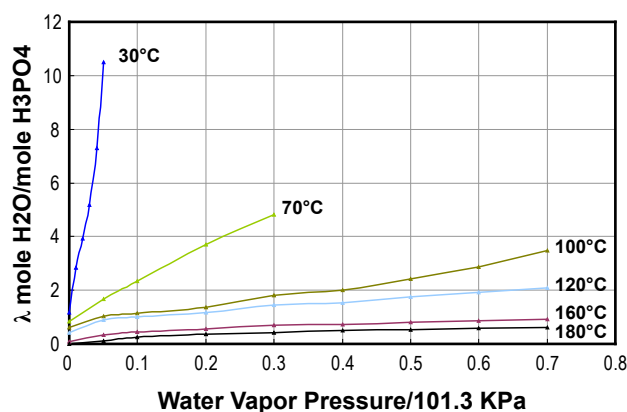


FIGURE 4. Effect of water vapor pressure (dimensionless by 101.3 kPa) and temperature on water content (λ = mol fraction of water/phosphoric acid) for Celtec® P Series 1000 PBI-MEAs.

were concerned about carbon corrosion of the electrode by the cathode air during shutdown or unexpected interruption of the current at high temperatures and these data indicate that low temperature excursion history also should be part of the information reported with long-term performance data for these MEAs. We also measured the rate of adsorption of water into the PBI MEA due to a step change in inlet humidity and those data show a time-constant of 500 and 2,500 seconds, respectively at 70 and 50°C. These time constants can be compared with one of less than 100 seconds for temperatures greater than 100°C. Desorption of water was slower at a given temperature.

Conclusions and Future Directions

Sub-project #1 prepared supported catalysts that have comparable activity to existing Pt/C catalysts, probably because the conductivity and the surface area was increased.

Sub-project #2 provided data not previously available and which was suitable for comparison with other MEAs over an operating range that allows parameter estimation. The data for concentrations lower than the proposed specifications allow the effect of recycle and contaminant accumulation to be assessed. We will complete this sub-project with measurements to assess the interaction of CO with NH₃ once the lower loading MEAs are provided by the H₂ Quality team.

In sub-project #3, large silicate concentrations were observed in the leachant from some low-cost seal materials with the accelerated testing solutions. ATR-FTIR successfully detected backbone and cross-linked changes prior to significant weight loss or leachant concentrations.

Sub-project #4 obtained new data characterizing the adsorption of water in a PBI membrane as a function of

temperature. These data also suggest the need to report the temperature history with durability data.

FY 2009 Publications/Presentations

1. R.E. Fuentes, B.L. García and J.W. Weidner, "A Nb-Doped TiO₂ Electrocatalyst for Use in Direct Methanol Fuel Cells," *Electrochem. Soc. Trans.* **12**, 1, 239 (2008).
2. Y. Jung, S. Park, P. Ganesan, and B. N. Popov, "Electrochemical Studies of Unsupported PtIr Electrocatalyst As Bifunctional Oxygen Electrode in a Unitized Regenerative Fuel Cell (URFC)," *Electrochem. Soc. Trans.* **16** (2008) 1117.
3. P. Ganesan, S. Huang, and Branko N. Popov, "Preparation and Characterization of Pt/NbTiO₂ Cathode Catalysts for Unitized Regenerative Fuel Cells (URFCs)," *Electrochem. Soc. Trans.* **16** (2008) 1143.
4. S. Shimpalee and J.W. Van Zee, "Non-uniform Current Distributions in PEM Fuel Cells," #1080 in *Meeting Abstracts*, Vol. 2009-1, The Electrochemical Society, Pennington, NJ.
5. J. St-Pierre, "PEMFC Contamination Model: Competitive Adsorption Followed by an Electrochemical Reaction," *J. Electrochem. Soc.*, **156** (2009) B291-B300.
6. J. St-Pierre, "Air Impurities," in *Polymer Electrolyte Fuel Cell Durability*, Edited by F. N. Büchi, M. Inaba, T.J. Schmidt, Springer, 2009, pp. 289-321.
7. J. St-Pierre, N. Jia, R. Rahmani, "PEMFC Contamination Model: Competitive Adsorption Demonstrated with NO₂," *J. Electrochem. Soc.*, 155 (2008) B315-B320.
8. J. St-Pierre, "PEMFC Contamination Model: Competitive Adsorption Followed by an Electrochemical Reaction," *Electrochem. Soc. Trans.*, **16** (2) (2008) 677-686.
9. J. Tan, Y.J. Chao, H. Wang, J. Gong, J.W. Van Zee, "Chemical and mechanical stability of EPDM in a PEM fuel cell environment," *Polymer Degradation and Stability*, doi:10.1016/j.polymdegradstab.2009.07.009.
10. J.Z. Tan; Y.J. Chao, X. Li, and J.W. Van Zee, "Microindentation Test For Assessing The Mechanical Properties of Silicone Rubber Exposed to a Simulated PEM Fuel Cell Environment," *J. of Fuel Cell Science and Technology*, 6 (4) 2009.
11. J.Z. Tan, Y.J. Chao, J.W. Van Zee, X. Li, X. Wang, M. Yang, "Assessment of Mechanical Properties of Fluoroelastomer and EPDM in a Simulated PEM Fuel Cell Environment by Micro Indentation Test," *Materials Science And Engineering A-Structural Materials Properties Microstructure And Processing*, **496** (1-2) 464-470 (2008).
12. J.Z. Tan; Y.J. Chao, Y. Min, C.T. Williams, and J.W. Van Zee, "Degradation Characteristics of Elastomeric Gasket Materials in a Simulated PEM Fuel Cell Environment," *J. of Materials Engineering and Performance*, **17**(6) 785-792 (2008).

References

1. www.fuelcells.sc.edu.
2. J. St-Pierre, D.P. Wilkinson, S. Knights, M.L. Bos, *J. New Mater. Electrochem. Syst.*, 3 (2000) 99-106.
3. R.K. Ahluwalia, X. Wang, *J. Power Sources*, 162 (2006) 502.
4. R.K. Ahluwalia, X. Wang, *J. Power Sources* 171 (2007) 63.
5. R.K. Ahluwalia, X. Wang, *J. Power Sources* 180 (2008) 122.