

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

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Objectives

This project consists of four subprojects. The primary objective of each subproject is:

- Develop high surface area, non-carbon supported catalysts with improved corrosion resistance.
- Obtain data and rate constants for contaminant poisoning 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) Durability
- (B) Cost
- (C) Performance

Technical Targets

The first subproject is developing Nb-doped TiO₂ catalyst supports with the goals:

- Durability of electrocatalysts with cycling >5,000 h
- Electrochemical area loss <40%

The second subproject is developing an understanding of the levels of contaminants that impact automotive hydrogen fuel quality. The data, models, and rate constants allow the DOE H₂ Quality team to predict performance loss mechanisms and effects.

The third subproject is providing information for the technical task associated with down-selecting the seal technologies in 2Q 2011.

The fourth subproject will provide information for stationary systems that allows one to assess when stack durability at <10% rated power degradation is less than 40,000 h.

Accomplishments

- Developed a Nb-doped TiO₂ support with high surface area and electrical conductivity:
 - The synthesized support has a mesoporous structure and a surface area of approximately 80-150 m² g⁻¹, which is much higher than that reported in the literature.
 - Initial tests indicate low corrosion and comparable polarization for the oxygen reduction reaction (ORR).
- Obtained anode overpotential data required by the H₂ Quality team.
- Determined isotherms and rate constants from these data for modeling efforts.
- Measured water content as a function of temperature and relative humidity for commercial PBI membranes.



Introduction

Subproject 1 is 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. This

subproject focuses on synthesizing this material to increase the surface area, increasing the conductivity by doping it with niobium, preparing platinum electrocatalysts on the new materials, and measuring the performance of this new electrode for oxygen reduction. Subproject 2 is 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 hydrogen will be expensive but improper specifications may affect the life of the fuel cell.

The third subproject is concerned with measuring the properties of low-cost gaskets and seal materials to help with the selection and design of new materials. These seals keep the gases and coolants separated and prevent leaks in the stack. This project is focused on understanding the mechanisms of failure, designing accelerated measurement procedures, and measuring the contaminants that leach out of these seals and may decrease the life of the fuel cell. The fourth subproject is focused on measuring properties of a high-temperature membrane and quantifying 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 subproject 1, Nb-doped titanium dioxide was synthesized using two sol-gel procedures and a hydrothermal procedure. The first sol-gel method developed a modification of the procedure of Yan et al. [1]. The second procedure was developed using an adaptation from the paper of Cassiers et al. [2]. The third procedure used a solution of niobium ethoxide and titanium isopropoxide and then activated the Nb dopant with heat treatment in a hydrogen atmosphere. Physical characterizations were performed using X-ray diffraction and X-ray photoelectron spectroscopy, and Brunauer-Emmett-Teller gas adsorption techniques. Electrochemical characterizations were performed using a rotating ring disk electrode (RRDE) to measure oxygen and peroxide formation. To obtain the data for subproject 2, we performed polarization experiments using GORE PRIMEA® Series 57 membrane electrode assemblies (MEAs) exposed to neat hydrogen and CO contaminated hydrogen. Data for these commercially available electrodes has not been reported. We varied the CO concentration with the goal of providing data on isotherm and rate constants that can be used in models to predict the effects of poisoning. CO has received much attention and it was chosen by the International Standards Organization and the DOE H₂ Quality team as a “canary” indicative of the ability to clean hydrogen. Temperature, relative humidity, and pressure were changed at a given CO concentration.

Researchers on subproject 3 were guided by industrial members in the National Science Foundation Center for Fuel Cells [3] and selected a broad range of commercially available seal materials for testing. The materials were aged in simulated and accelerated fuel cell environments both with and without stress and deformation. The chemical and thermal stability was characterized during constant stress and constant displacement tests. The mechanical stability was also characterized and related to accelerated life testing procedures. In subproject 4, measurement techniques were developed to rapidly measure the mass gain of PBI membranes exposed to different mixtures of water vapor and air.

Results

In subproject 1 the support prepared by the low-temperature sol-gel methods produced a surface area of 181 m²/g which is comparable with 240 m²/g for a commercial carbon black (Vulcan XC-72R) and much greater than the 1.4 m²/g for a similar composition Nb-doped TiO₂ support reported Chen et al. [4] that was synthesized by a high-temperature route. For the hydrothermally prepared materials, the electronic conductivity, surface area, and the chemical and electrochemical stabilities could be optimized by adjusting the metal salt composition, the dopant concentration in the support, and the heat-treatment temperature. The electrical conductivity showed a maximum for 25% Nb and 700°C and the increase in conductivity was due to the presence of Ti³⁺ and Nb²⁺. Cyclic voltammetry showed the electrochemical active surface area of a Pt catalyst deposited on the Nb-TiO₂ was comparable to that of Pt catalyst supported on carbon (Pt/C). Figure 1 shows the effect of increasing the Pt loading on the ORR. This activity is comparable to that of Pt/C catalysts. Figure 2 shows that the new supported catalyst is selective for the 4 electron reaction pathway since the maximum H₂O₂ production is 4% of the current. These data were obtained with a RRDE with saturated O₂ in 0.5 M H₂SO₄. Studies of durability and cycling are currently underway.

In subproject 2, triple path 25-cm² serpentine cells were used to obtain polarization curves as a function of CO poisoning. The anode over-potential data were obtained by subtracting polarization curves at the same current density. Figure 3 shows an example of the data obtained for the anode polarization caused by CO poisoning at 80°C for two pressures. We obtained data for 80°C and 60°C at back pressures of 0/0 psig and 25/25 psig on the anode/cathode, respectively. We used the typical automotive relative humidity of 75/25% (anode/cathode) and varied the partial pressure of CO from 100 to 10 ppm. Studies are continuing with 0.1, 1.0 and 2.5 ppm. This range of partial pressures (i.e., 100 ppm to 0.1 ppm) is necessary to determine if the

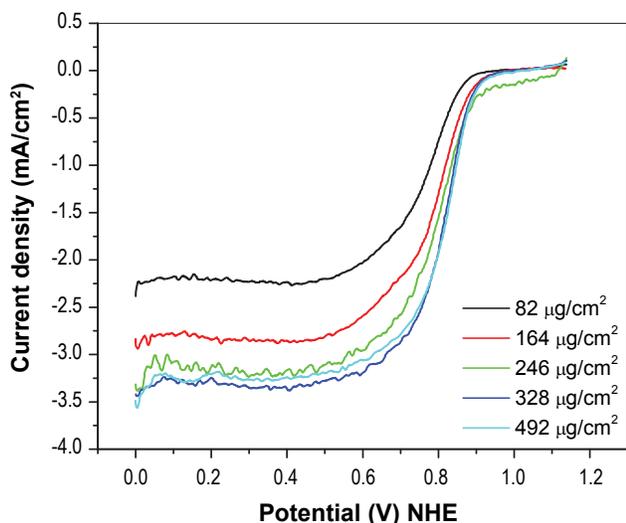


FIGURE 1. Effect of loading for Pt/Nb-TiO₂ catalysts on oxygen reduction reaction at 5 mV/s in 0.5 M H₂SO₄. The catalytic activity is comparable to Pt/C electrocatalysts.

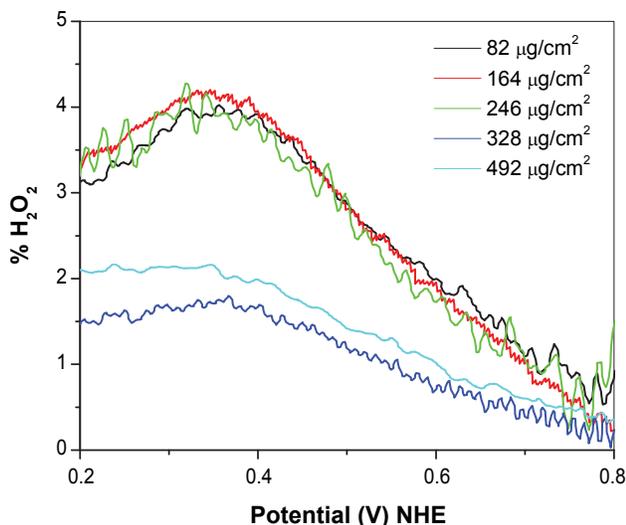


FIGURE 2. Effect of loading for Pt/Nb-TiO₂ catalysts on H₂O₂ production measured at a RRDE during oxygen reduction reaction at 5 mV/s in 0.5 M H₂SO₄. The catalytic activity produces less than 4% H₂O₂.

mechanism changes and for use in the cell models [5] and models of stack recycle being developed at Argonne National Laboratory [6-8]. In addition, progress has been made with researchers at Oak Ridge National Laboratory through the award of a sub-contract to develop their spatially resolved capillary inlet mass spectrometry technique as a method to explore intra-fuel cell measurements of contaminants. The measurements are in progress at the date of this report.

In the interest of space, we refer the reader to our publications and the figures therein for details of results of our work on gaskets and seals (i.e., subproject 3).

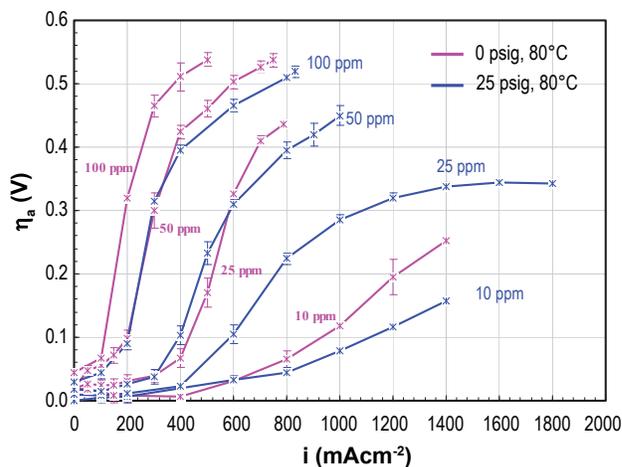


FIGURE 3. Pressure dependence of CO poisoning on anode overpotential at 80°C for GORE Series 57 MEA at 1.2/2.0 stoichiometry.

Subproject 3 is developing life prediction methodologies germane to low-cost gaskets and seal materials. Failure mechanisms will be identified and failure modes analyzed. In subproject 4, we measured the response of water absorption into the PBI MEA due to a step change in inlet humidity. An apparatus was designed and a technique was developed to obtain the isotherm data shown in Figure 4. To obtain the data at 90 and 100°C we need to slow the scan rate so that the data are representative of equilibrium and do not have a hysteresis corresponding to adsorption and desorption during increases and decreases in the partial pressure of water. We measured the acid loss and we will report and analyze weight change data relative to dry membrane mass in future refereed publications. The dashed line at 90°C above 0.5 water vapor pressure may correspond to some acid loss from the membrane since we are close to the saturation pressure of 0.69. The experimental conditions corresponded to temperatures between 90°C and 160°C and this range was used to provide data to understand failure modes as the cell heats and cools. The apparatus was shown schematically in slides prepared for the 2008 Annual Merit Review and are available from the author. The apparatus obtains the desired flowrates of water at temperatures above normal boiling by mixing a humid and a dry stream. The apparatus is able to achieve water partial pressure scanning rates between 0.01 to 0.002 (kPa/101 kPa/min).

Conclusions and Future Directions

Subproject 1 prepared supported catalysts that have comparable activity to existing Pt/C catalysts, probably because the conductivity and the surface area was increased over previously published materials. Future work will assess the durability and corrosion characteristics for these new materials.

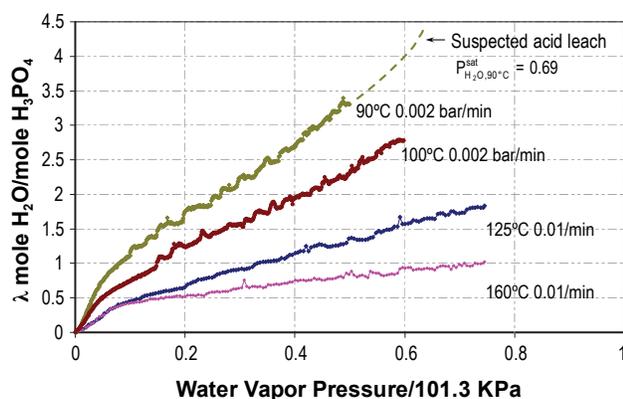


FIGURE 4. Effect of water vapor pressure (dimensionless by 101.3 kPa) and temperature on water content (mol fraction of water/phosphoric acid) for Celtec® P Series 1000 MEA.

Subproject 2 provided data not previously available and which was suitable for comparison with other MEAs and loadings over an operating range that allows parameter estimation. These data are complementary to other groups and an ongoing modeling effort within the DOE. Data for lower concentrations are in progress and a consistent set of parameters for this MEA is being obtained.

Subproject 3 examined the physical and chemical surface degradation of low-cost materials and compared them to higher-cost materials using optical microscopy, environmental scanning electron microscopy analysis, and attenuated total reflectance-Fourier transform infrared. Lechant products were identified and characterized for eight materials at simulated and accelerated fuel cell conditions. A micro-indentation test was developed for assessing the mechanical properties of the gasket materials. Future work will include using dynamical mechanical analysis and compression stress relaxation tests for assessing the dynamic mechanical properties of the gasket materials and to monitor the retained seal force under fuel cell conditions.

Subproject 4 obtained new data characterizing the adsorption of water in a PBI membrane as a function of temperature. These data should be useful for modeling how temperature affects the loss of acid and the durability of these stationary fuel cells.

FY 2008 Publications/Presentations

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5. Jinzhu Tan, Y.J. Chao, J.W. Van Zee, W-k. Lee, "Degradation of Elastomeric Gasket Materials in PEM fuel cells," *Materials Science and Engineering A*, 445–446, 669–675 (2007).
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