V.E.2 Fundamental Effects of Impurities on Fuel Cell Performance and Durability

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Objectives

- Investigate the effect of impurities in the hydrogen fuel streams on the operation and durability of fuel cells. These impurities include water, hydrocarbons (including formaldehyde, formic acid), oxygen, inert gases (He, N_2, Ar), CO_2, CO, sulfur-containing gases, ammonia, halogenated compounds and particulates.
- Propose mechanisms for how impurities in the hydrogen fuel stream affect the components of the fuel cell catalyst and polymer membrane.
- Determine strategies to reduce the poisoning effect of these impurities.
- Disseminate findings so that they are available to other members of the DOE Hydrogen Quality team and to FreedomCAR technical teams.

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) Performance

Technical Targets

This project is addressing fundamental research into effects and mechanisms of impurities on the performance and durability of polymer electrolyte membrane (PEM) fuel cell systems. The activity broadly supports the following technical targets established by DOE:

- By 2010, develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/kW; by 2015, a cost of $30/kW.
- By 2011, develop a distributed generation PEM fuel cell system operating on natural gas or liquefied petroleum gas that achieves 40% electrical efficiency and 40,000 hours durability at $750/kW.

Accomplishments

- Extensively characterized MEA components (C, 20 wt% Pt/C, 30 wt% Nafion®/C, 30 wt% Nafion®-Pt/C) using Brunauer-Emmett-Teller total surface area measurement, chemisorption of H_2 and NH_3, X-ray diffraction, and Fourier transform infrared (FT-IR).
- Developed methodologies for studying H_2 activation on Pt and proton site availability on Nafion®/C and Nafion®-Pt/C in the absence and presence of impurity poisons in the gas stream.
- Began an extensive investigation of the fundamentals of CO effects on H_2 activation on Pt and NH_3 poisoning of Nafion®.
- Bench-marked/validated fuel cell test station (FCTS) to DOE "round robin" MEA (prepared by Los Alamos National Laboratory [LANL]); measurements were repeatable (multiple runs) and reproducible (same results observed at other laboratories).
- Executed a long-term (400-hour) fuel cell test on a 50 cm^2 commercially-available MEA.
- Evaluated the effect of ammonia, as a hydrogen-feed stream contaminant (20 ppm) on the electrode ionomer. EIS was used to separate the resistances in the electrode and membrane.

- Demonstrated the effect of a chloro-hydrocarbon, tetrachloroethylene (150 ppm), a common dry cleaning agent contaminant, on fuel cell durability.

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Introduction

PEM fuel cells show significant potential to enable efficient, clean power for stationary and transportation applications, however, the present-day technology falls short of meeting the necessary product performance and durability requirement standards. An important limitation in the operational life of PEM fuel cells is caused by the presence of hydrogen-feed stream contaminants (e.g., ammonia, carbon monoxide, etc.). These contaminants degrade the functionality of ion exchange groups within the electrolyte, degrade catalyst activity, and result in a degradation of the overall fuel cell efficiency and operational performance.

Approach

This project is a unique combination of fundamental studies (at Clemson University) and fuel cell MEA durability testing at the Savannah River National Laboratory (SRNL), with MEAs tested at SRNL composed of the same materials as being investigated at Clemson. By determining the effect of impurities on the component parts of an MEA as well as overall fuel cell performance, a comprehensive mechanism of poisoning can be proposed which may aid in determining strategies for mitigating that effect. Development of an integrative model is also being undertaken. The fuel cell team at SRNL is integrated into the U.S. Fuel Cell Council Joint Hydrogen Quality Task Force (JHQTF), presently engaged to address the ISO (International Organization for Standardization) TC 197: Hydrogen Fuel – Product Specification: PEM fuel cell application for road vehicles.

Results

Fundamental investigations at Clemson University have expanded our knowledge of the MEA materials and the interactions between them and CO and NH_3. The addition of Pt and, especially, Nafion® significantly decreases the surface area of the carbon support from 226 m^2/g to 62 m^2/g for Nafion®-Pt/C. Pt particle sizes average 2.9 nm in diameter. Extensive FT-IR studies of Pt/C, Nafion®/C, and Nafion®-Pt/C have been carried out. It was found that CO does not adsorb to any significant degree on Nafion®/C, which explains the slight effect of CO on the proton sites of Nafion®/C. The shift in frequency of the Nafion® CF_2 ligand to a lower frequency for Nafion®-Pt/C indicates there is interaction between Pt and Nafion®. CO adsorbs less and more weakly on Nafion®-Pt/C, perhaps due to this interaction.

COH_X species appear to be formed on Pt/C in the presence of CO and H_2. These CO and COH_X species block Pt sites required for H_2 adsorption, resulting in lower performance of a PEM fuel cell.

Using the H_2-D_2 reaction to study hydrogen activation, it was found that Nafion®-Pt interactions cause H_2 dissociation to be somewhat inhibited on Nafion®-Pt/C. This effect may be due to interactions with sulfonic acid groups/CF_2. Pt/C is rapidly poisoned in 10 ppm of CO, suggesting that CO adsorbs strongly with a sticking probablility close to 1.

Using reaction characterization, the availability of proton sites on 30% Nafion®/C was found to be greater than on 30% Nafion®-Pt/C. Pt appears to catalyze removal of some of the S when Nafion® is added to Pt/C (S content decreases while F content remains constant). As expected, CO was found to have only a small effect on the acidity while NH_3 causes complete loss of proton sites. The poisoning effect of NH_3 is cumulative and even at 15 ppm appears to be practically irreversible.

A system for EIS was set up and used to study Nafion® 211 membranes under NH_3 poisoning conditions. The conductivity results were consistent with the literature and proved the applicability of EIS for studying the effects of impurities on membrane conductivity (Figure 1).

In terms of fuel cell investigations, an ARBIN FCTS was installed at SRNL and validated in conjunction with the U.S. Fuel Cell Council JHQTF "round-robin" MEA. The MEA was prepared by LANL [Nafion® 112, anode and cathode loadings: 0.2 mg Pt/cm^2 (20% Pt/C, E-TEK), active area = 50 cm^2]. Test conditions were 1.2/2.0 stoichiometry (anode/cathode), and 100% relative humidity (RH). For all tests required by the JHQTF (hydrogen cross-over, cyclic-voltammetry
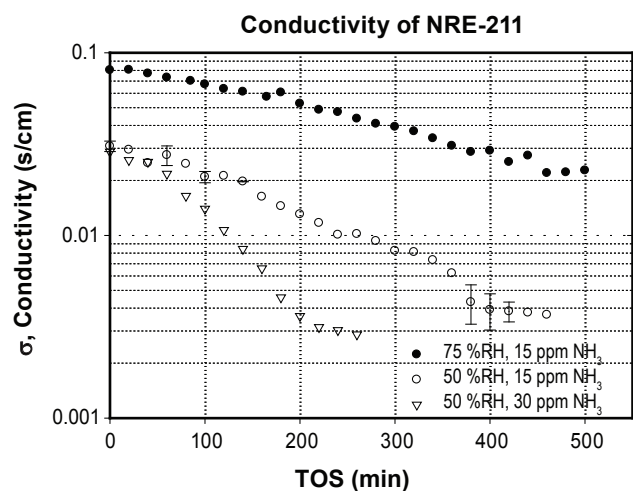

FIGURE 1. EIS Determined Conductivity of a NRE-211 Membrane at 80°C at different RHs and Ammonia Concentrations (He Atmosphere)
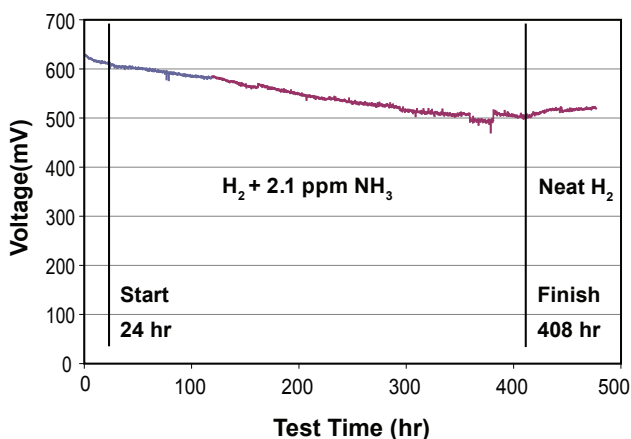
FIGURE 2. Fuel Cell Performance Decay of an Ion Power MEA at 60°C with 2 ppm NH$_3$

scans, polarization curves at two sets of conditions, and reproducibility), the SRNL FCTS performance matched those obtained at the other testing laboratories (LANL, University of Connecticut, University of South Carolina).

A long-term FCTS test (400 hours) with a commercially-available MEA (Ion Power) was performed at a NH$_3$ concentration of 2 ppm (60°C, atm pressure), as shown in Figure 2. Cell performance decreased linearly from 600 mV to 500 mV over the 400 hours, without achieving steady-state performance. Cell recovery was assessed over a 50-hour period, via neat hydrogen.

EIS was applied in the fuel cell to separate the resistances in the electrode and membrane, affected by a trace amount (20 ppm) of ammonia. The inductance corrected EIS spectra are shown in Figure 3. The membrane conductivity is the high frequency intercept of the impedance on the x-axis and the ionomer resistance is proportional to the length of the linear segment in the spectra between 1,090 Hz and 4 Hz. The resistance calculated from these spectra show that the ionomer resistance decreases much more than the resistance of the membrane and becomes the dominant loss in the cell.

The poisoning effect of 150 ppm of a chlorinated hydrocarbon, tetrachloroethylene (a typical dry cleaning agent), in H$_2$ was investigated at 60°C with a constant current density of 0.6 A/cm^2, 1.2/2.0 stoichiometric (anode/cathode), and 100% RH. The cell polarization during poisoning and recovery is shown in Figure 4.

Conclusions and Future Directions

Extensive characterization of the MEA materials and fundamental studies of the benchmark impurities of CO and NH$_3$ have been conducted, including:
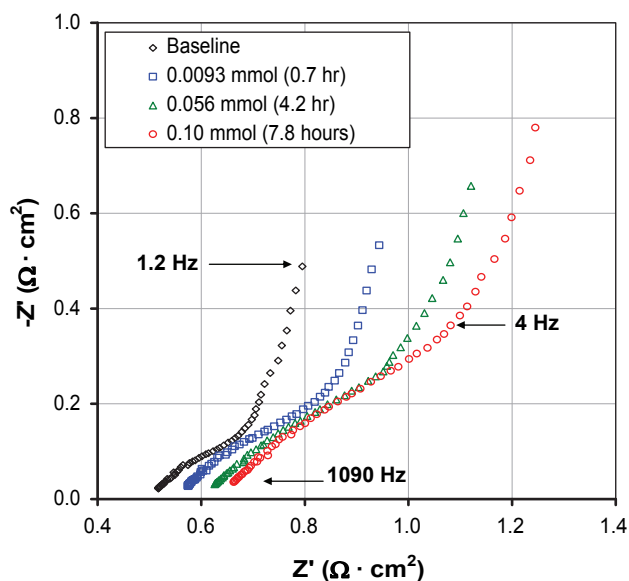

FIGURE 3. EIS Spectra during a 20 ppm NH$_3$ Poisoning Experiment in the PEM Fuel Cell at 60°C
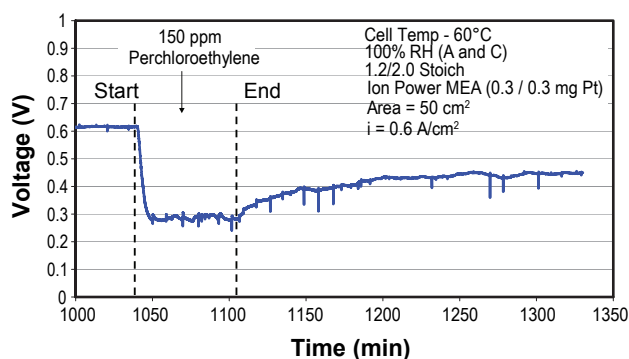

FIGURE 4. Poisoning of an Ion Power MEA with 150 ppm of Tetrachloroethylene at 60°C

- The nature of interactions between Pt and Nafion® in the catalyst layer.
- The impact of CO on H$_2$ activation.
- The effect of NH$_3$ on Nafion® conductivity and the availability of proton sites.

Modeling efforts are underway to link the results from fundamental studies to actual fuel cell performance so that the mechanisms of poisoning can be better understood.

The fuel cell testing laboratory at SRNL is now installed and calibrated. It is poised to provide significant contributions addressing the effect of trace quantities of impurities on PEM fuel cell performance and durability and assisting the U.S. Fuel Cell Council's JHQTF. Major studies to date have included:

- The long-term effect of trace NH_3 impurity, in the hydrogen feed stream, on fuel cell performance. EIS provided additional insight into the effect of the poison on the anode and membrane ionomer.
- The effect of low concentrations of a chlorinated hydrocarbon, tetrachloroethylene, on fuel cell performance.

Activities in the coming year will include:

- Completion and integration of the experimental investigations of the effects of CO and ammonia on the fuel cell components, the fundamental reactions and conductive properties, and fuel cell performance.

- Development of comprehensive mathematical models of the individual steps in the fuel cell as well as of the overall performance.
- Comparison of the mathematical models to the experimental results in the first bulleted item.
- Investigation of chlorinated hydrocarbons on the fuel cell components, the fundamental reactions and conductive properties, and fuel cell performance.

FY 2008 Publications/Presentations

1. "Characteristics of Pt-Nafion/C in PEM Fuel Cells (PEMFC)," North American Catalysis Society, Southeastern Section Meeting, September, 2007, Asheville, NC.