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

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• Savannah River National Laboratory, Aiken, SC
• John Deere, Charlotte, NC

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Objectives

- For various impurities of interest, measure the effect impurity concentration has on hydrogen and oxygen chemisorption on the Pt or PtRu catalysts used as proton exchange membrane fuel cell (PEMFC) electrodes.
- For various impurities of interest, measure the effect impurity concentration has on activation and reaction of hydrogen and oxygen on the Pt or PtRu catalyst electrodes.
- Determine the nature of the impurity species adsorbed on Pt and PtRu.
- Measure the effect of concentration (of the various impurities) on the proton sites on Nafion®, a polymeric material typically used as the proton exchange membrane (in particular, irreversible adsorption on these acid sites).
- Determine the nature of the impurity species adsorbed on the Nafion®.
- Determine the impact of the various impurities on fuel cell performance, such as mv loss/hr at a given current density.

- Propose a mechanism of action for each impurity in affecting the components of the fuel cell electrodes and polymeric membrane.
- Develop strategies/means to reduce the impact of these impurities on fuel cell performance.
- 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
(B) Cost
(C) Performance

Technical Targets

This project is investigating the effect of impurities on fuel cell performance and durability. Insights gained from these studies will be applied toward the design of membrane electrode assemblies (MEAs) that meet the following DOE 2010 MEA targets:

- Durability with cycling
    - At operating temp of ≤80°C: 5,000 hours
    - At operating temp of >80°C: 2,000 hours

- Performance @ rated power: 1,000 mW/cm^2
- Extent of performance (power density) degradation over lifetime: 10%
- Cost: $10/kW

✧   ✧   ✧   ✧   ✧

Approach

A Pt/C catalyst will be characterized by H_2-chemisorption, H_2-D_2 reaction, Fourier transform-infrared (FTIR), scanning electron microscopy/transmission electron microscopy (SEM/TEM), and energy dispersive X-ray (EDX) before and after operation in the presence of impurities. Nafion® will also be characterized by acid site titration, NH_3-chemisorpion, impedance analysis and FT-IR before and after operation with the hydrogen fuel containing impurities. At the same time, fuel cell studies will be carried out using a fuel cell test station system. Results from the fundamental studies will be combined with the

fuel cell studies and mechanisms for poisoning by gas impurities in the hydrogen fuel streams will be proposed. Based on the poisoning mechanisms, strategies to reduce the poisoning effect of these impurities will be suggested.

Accomplishments

In the few months since this project was started, commercial Pt/C and Nafion® have been acquired for use in preparing MEAs and for the fundamental studies. Extensive characterization of the Pt/C and Nafion®/C has been done using numerous techniques (SEM/TEM, energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) H_2 chemisorption, etc.). Figure 1 shows the TEM of fresh Pt/C and reduced Pt/C, illustrating Pt particles aggregated after reducing in H_2. On the fresh Pt/C, Pt particle sizes are about 1-2 nm; while on the reduced Pt/C, Pt particle sizes up to 10 nm can be observed. The aggregation of Pt on the reduced Pt/C can also be indicated by XRD patterns (Figure 2). EDS results showed that Pt, O, C and S are present on both fresh Pt/C and reduced Pt/C. Figure 3 shows the H_2

chemisorption on fresh, reduced Pt/C catalyst. The Pt dispersion is ca. 25.7%. In subsequent studies, we will feed CO in different concentrations in hydrogen and characterize its effect on the Pt/C catalyst. Using the H_2-D_2 exchange reaction, we will measure how the presence of CO affects the activation of H_2. FT-IR studies will also elucidate the nature of the adsorbed impurities. The comparison of the characterization results between the fresh catalyst and poisoned catalyst will provide some information on the poisoning mechanism of CO.

Impregnation of Nafion® ink on carbon powder (XC-72R) leads to a significant decrease of BET surface area. When the loading of Nafion® is 23 wt%, the surface area decreases to 81 m^2/g from 226 m^2/g. Figure 4 shows the EDS of 23 wt% Nafion®/C. From the EDS mapping, it can be seen that the Nafion® ionomer was uniformly dispersed on the carbon support. Elemental analysis results indicated that C, O, F and S are present on Nafion®/C and there are no other significant impurities. By the acid site titration method, it has been
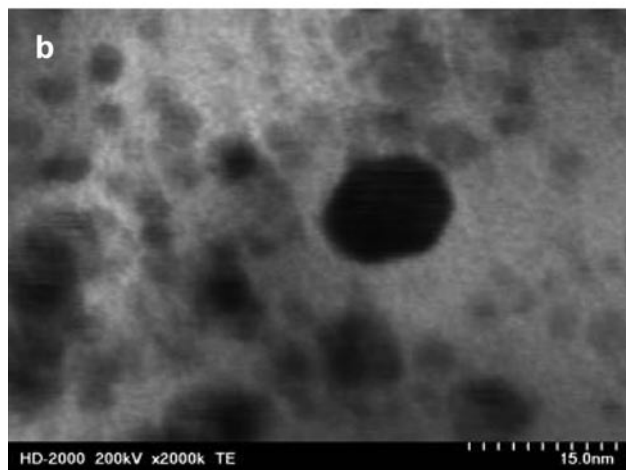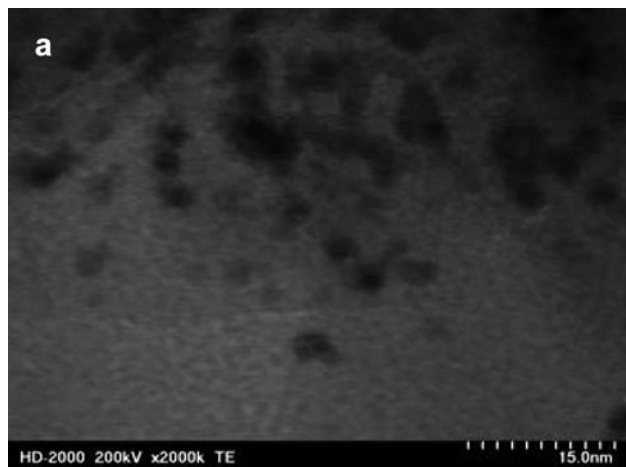

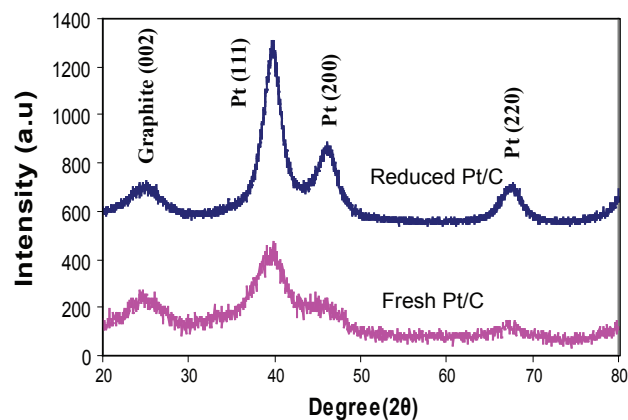**FIGURE 2.** XRD Patterns of Fresh Pt/C and Reduced Pt/C
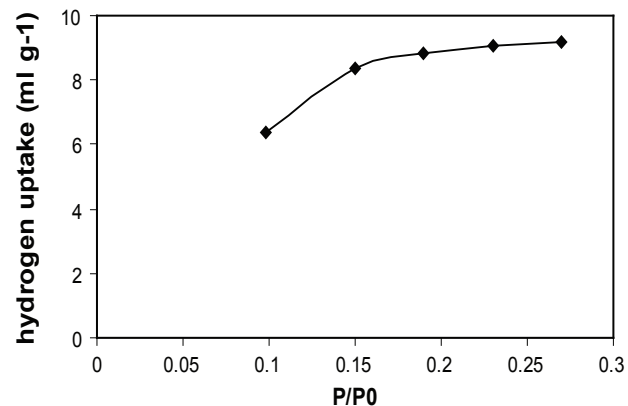
FIGURE 3. H_2 Taken Up by Fresh Pt/C Catalyst as a Funciton of H_2 Pressure at 35°C

FIGURE 1. TEM of Fresh Pt/C (a) and Reduced Pt/C (b)

found that the acid site densities of 25 wt% Nafion®/C and 30 wt% Nafion®/C are 70 ± 3 and 75 ± 1 µmol/g, respectively. In subsequent studies, we will feed NH_3 with different concentrations to the Nafion®/C and investigate the acid density changes due to the presence of NH_3. The ionic conductivities of Nafion® in the presence and absence of NH_3 will be measured using a two-electrode configuration by model 600 from Gamry potentiostat.

Based on a literature review and in conjunction with other DOE-supported researchers, the test protocols for the fuel cell studies have been developed. The experiments are divided into two main protocols: short duration contaminant survey (<100 hrs) and a long duration test (400 hrs). During the contaminant survey, the effect of a selected contaminant at different concentrations will be studied. First, a baseline performance will be acquired at galvanostatic conditions (1 A/cm^2). Before starting the impurity flow, a series of beginning of life (BOL) tests will be performed on the system. These tests will include polarization curves, cyclic voltammograms, and impedance spectroscopy. The performance at galvanostatic conditions will then be resumed with addition of an impurity in the fuel stream; the selected concentration will be based on the literature review. The voltage drop will be monitored for a period

of 10 hrs. After such a period, a second set of BOL tests will be taken and the impurity concentration shall be changed. These cycles will be repeated several times for a total of 100 hours. The idea is to calculate a dosage that will give a performance decay of 10% by the end of the long term test (400 hrs). Once a concentration is selected for the long duration test, a new MEA will be prepared. The long-term test will be performed in a similar manner to that of the contaminant survey. Before the test, baseline performance will be recorded as well as BOL tests. Then, the dosage that was calculated in the contaminant survey will be injected into the system and the voltage decay will be measured. At the end of 400 hours, the contaminated fuel will be purged from the system with clean fuel and a series of end-of-life (EOL) tests will be performed.

According to the test matrix, initial experiments will focus on establishing a baseline performance with clean fuel. Once all baseline measurements are completed, the effect of ammonia impurities in the fuel will be studied at galvanostatic conditions (1 A/cm^2).

Savannah River National Laboratory (SRNL) has completed its selection of the fuel cell test station (FCTS) system. Major components of the FCTS system are represented in Figure 5. At SRNL, a Kin-Tec mixture generator will be used in order to prepare H_2 standards
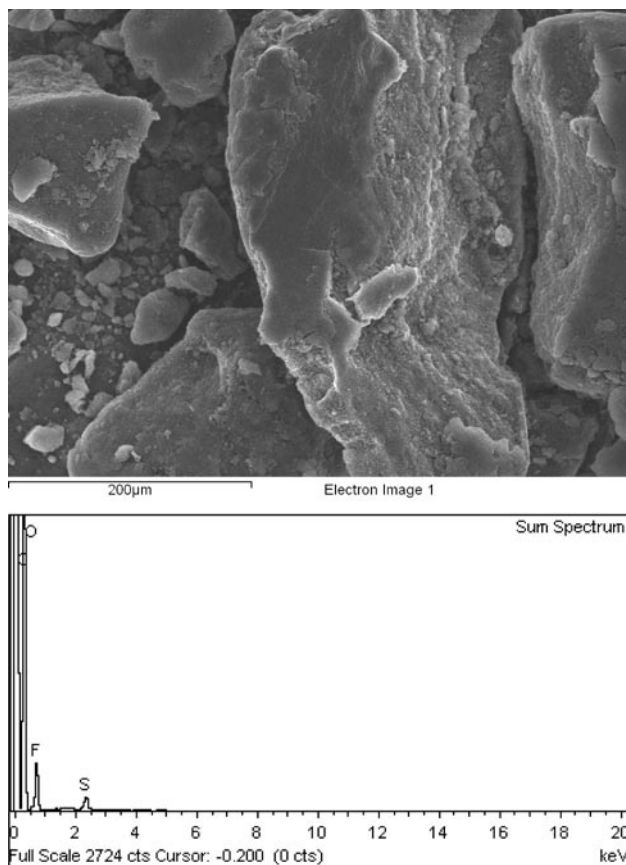

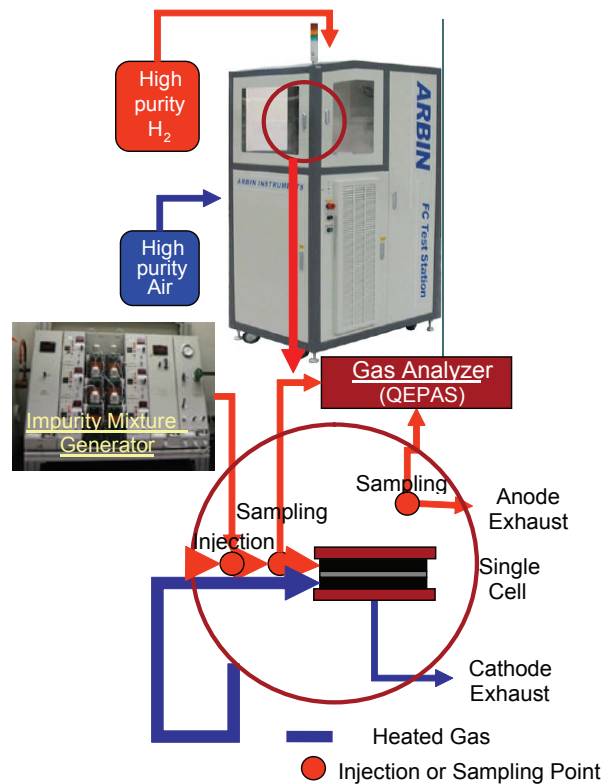**FIGURE 4.** EDS of 23 wt% Nafion®/C

FIGURE 5. Simplified Schematic of the FCTS System for Testing the Impurity Effect in a Single Cell

with a wide range of impurity concentrations. The impurities will then be injected into a humidified H_2 stream that will flow into the fuel cell. A FCTS 200H from Arbin has been selected (and ordered) due to its ability to test MEAs up to 50 cm^2 or larger in a safe manner. For this project, a 50 cm^2 cell will be used, in a long term test with the cell operating at 1 A/cm^2 and at a stoichiometry of 1.1/2.5 for H_2/air. This will consume approximately 390 cm^3/min of H_2 and 2101 cm^3/min of dry air at standard temperature and pressure.

FY 2007 Publications/Presentations

1. "Effect of Impurities on Fuel Cell Performance and Durability," oral presentation, Dept. of Energy Office of Hydrogen, Fuel Cell, and Infrastructure Technologies New Fuel Cell Projects Kickoff Meeting, Washington, D.C., Feb. 13–14, 2007.

2. 1st Quarterly Project Report, April, 2007.

3. "Effects of Impurities on Fuel Cell Performance and Durability," poster, 2007 Annual Dept. of Energy Hydrogen Program Review Meeting, Washington, D.C., May 15–18, 2007 (James G. Goodwin, Jr., Jack Zhang, Kitiya Hongsirikarn, Zhiming Liu, William Rhodes, Hector Colon-Mercado, and Peter Finamoore).