IV.B.2 Electrodes for Hydrogen-Air PEM Fuel Cells

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Objectives

- Evaluate the effects of fuel and air impurities on fuel cell (FC) performance
- Identify methods to mitigate negative effects of impurities
- Lower Pt-catalyst content in membrane electrode assemblies (MEAs) and improve catalyst utilization
- Develop low-cost, high-surface-area support materials that "replace" precious-metal supports or improve Pt activity for oxygen reduction
- Evaluate catalyst durability

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:

- O. Stack Materials and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Study the effects of air impurities on cathode performance (e.g., SO_2, NO_2)
- Determine the effects of low H_2S concentrations on anode performance
- Identify materials or devices able to mitigate negative effects of impurities
- Test performance and durability of new low-Pt-content catalysts
- Prepare low-cost Pt-catalyst supports and test them
- Study the durability of Pt-alloy catalysts in fuel cells (e.g., measure Ru cross-over)
- Correlate MEA component changes and performance after long-term operation
- Collaborate with the United States Fuel Cell Council (USFCC) to develop a "Single Cell Testing Protocol"

Accomplishments

- Demonstrated operation of the 2 wt% Pt-20 wt% Ru anode catalyst, with a loading of 18 μg Pt/cm^2, running on H_2/air and on H_2 + 50ppm CO + 3% air bleed/air with small voltage losses for 868 hrs
- Showed negative and irreversible effects of low SO_2 and H_2S levels on FC performance, and demonstrated that filtration is an effective alternative for mitigating this problem

- Achieved significant performance with low-Pt-content cathode catalyst
- Produced low-cost and small-particle (<10 nm) materials for supporting Pt monolayers
- Observed Ru migration from anode to cathode under operating conditions
- Contributed to develop the USFCC "Single Cell Testing Protocol"

Future Directions

- Determine threshold SO_2 tolerance without special air filter
- Study the effect of other air impurities on FC performance
- Explore strategies for SO_2 and H_2S cleaning (de-poisoning) during operation
- Evaluate stability of low-Pt-content cathode catalysts in long-term tests
- Continue formulation of new high-surface-area catalyst supports to improve Pt utilization
- Test Ru migration during long-term operation
- Continue participation in USFCC activities such as Single Cell Testing Protocol and formulation of durability tests for MEA components

Introduction

The realization of the so-called Hydrogen Economy rests mainly on proton exchange membrane (PEM) fuel cell development. The state-of-the-art of these devices provides reasonable performance for automotive applications. However, the cost of fuel cell materials, such as catalysts, membranes and bipolar plates, is a major hurdle to that goal. Pt-based catalysts are the only materials able to deliver the required performance, and the target of 0.6 grams precious metal per kilowatt for the year 2005 appears difficult to achieve on time. The issue becomes more complex when purity of both hydrogen fuel and air comes in to place. The presence of even trace levels of some impurities, such as CO and H_2S (from fuel) and SO_2 (from air), has negative effects on cell performance. In addition, the durability and material endurance can be affected by the presence of impurities.

Our project strives to solve these problems. Our specific work on catalysts is directed to lower the intrinsic Pt-catalyst loadings and also to increase Pt utilization by means of new catalyst supports and more efficient catalyst layer structures. We are also studying the effects of some major impurities on performance and, at the same time, finding materials and devices for mitigating the negative effects.

Approach

In the short term, reformed fuels (e.g., natural gas, gasoline) will be the major sources of H_2. However, the reforming process generates considerable amounts of CO that poisons Pt-catalyst surfaces and degrades cell performance to unacceptably low levels. The two most effective strategies for achieving CO tolerance are (a) the use of supported Pt-Ru alloy catalysts, which are considerably more tolerant than Pt alone (Ru reacts with water, forming Ru-OH, which is able to oxidize adjacent $Pt\text{-}CO_{ads}$ species to CO_2), and (b) bleeding a small amount of air (1 to 3 v%) into the fuel feed stream. O_2 reacts chemically with $Pt\text{-}CO_{ads}$ to produce CO_2 and restore active Pt sites. Depending on anode catalyst loadings, the combination of these two methods is able to tolerate levels of CO as high as 250 ppm. Here we present CO-tolerance results employing this combined approach.

Hydrogen sulfide is a potential fuel impurity generated in the reforming process from sulfur compounds found in fossil hydrocarbons. H_2S poisons Pt catalysts due to strong chemisorption on catalyst surfaces. Poisoning with this impurity is irreversible, which means that further operation with clean air does not reactivate the catalyst surface.

We have studied the effect of trace levels of sulfur dioxide on cathode operation. SO_2 also chemisorbs on Pt-catalysts, degrading fuel cell operation considerably. Likewise, poisoning with SO_2 is irreversible. The best strategy for dealing with these sulfur compounds is to keep them outside of the fuel cell system.

Most of the commercial catalysts used in PEM fuel cells are carbon-supported Pt or Pt alloys. Although the metal is highly dispersed in the form of particles ranging from 2 to 5 nm, only a fraction of the atoms (about 25%) are on the surface. Therefore, the majority of the Pt is not accessible to the reactants. The catalyst utilization becomes even lower in the MEA catalyst layer due to insufficient ionic or reactant access, which isolates many of the Pt electrochemically active sites. An effective approach for improving Pt utilization is to use suitable supports able to disperse Pt atoms as monolayers. Thus, most of the Pt content would be at the surface, available for the electrochemical reactions that generate power in fuel cells.

Long-term fuel cell operation can result in catalyst migration, particle coarsening and redistribution. These changes can lead to performance degradation due to losses in active catalyst surface area.

Results

Anode catalysts consisting of Pt-Ru alloys have been shown to be more tolerant to CO in the fuel stream than platinum alone. However, the commercially available materials are still expensive due to their high Pt contents. R. Adzic and co-workers from Brookhaven National Laboratory (BNL) have prepared new catalysts with much lower platinum loading. One material contained only 2% platinum and 20% ruthenium on a carbon support. An 868-hour performance test was carried out at Los Alamos National Laboratory (LANL) using this catalyst in a fuel cell anode with a loading of 18 µg Pt/cm^2, approximately 1/10 of a normal loading. The results are shown in Figure 1. No voltage losses after 868 hours of operation at fixed current were observed when the cell was operated on clean H_2. The losses were only 16 mV when operated with H_2 containing
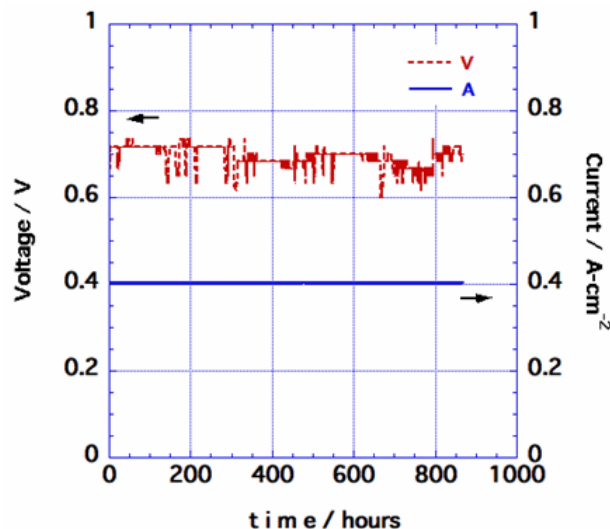
Voltage losses after 868 hr of testing:

	initial V	final V
* with neat H_2:	0.717	0.717 ($\pm$ 0.009)
* H_2+CO+3% air:	0.697	0.701 ($\pm$ 0.013)
* total loss due to CO: 16 mV		

Figure 1. Performance of low-Pt-content anode catalysts. The anode contained **18 µg Pt/cm^2** (2% Pt-20% Ru, BNL). The cathode loading was 0.2 mg Pt/cm^2 (20% Pt ETEK). The 50-cm^2 cell ran at 20 A constant current for a total time of 868 hr in mixed mode (630 hr on neat H_2 and 238 hr on H_2+50 ppm CO+3% air). T_{cell} = 80 °C. BNL catalyst prepared by R. Adzic et al.

50 ppm CO and 3% air. This is an exceptionally promising result that could have a major impact on lowering fuel cell costs and bringing the technology closer to commercialization.

The effects of 50 ppb of H_2S are shown in Figure 2. After 400 hours of operation at constant voltage, the cell current dropped to 60% of its original value. As shown in the same figure, full tolerance to this level of contamination was achieved using a homemade H_2S scrubber for 1000 hours.

One of the most common ambient air impurities is sulfur dioxide, generated during fossil fuel combustion. Figure 3 shows the performances of a fuel cell whose air intake contained 500 ppb of SO_2. Even this low level of impurity degraded the cell performance when the cathode became exposed to
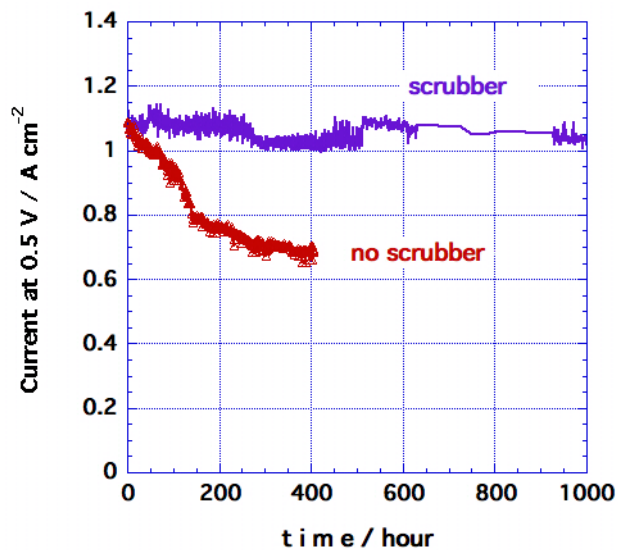
Figure 2. Effect of 50 ppb H_2S on anode performance with and without scrubber. The homemade scrubber was prepared from a ZnO-based composite (G-72, United Catalysts). 5 cm^2 cell; T = 80 ^oC; Loadings: 0.2 mg Pt/cm^2 at each electrode.
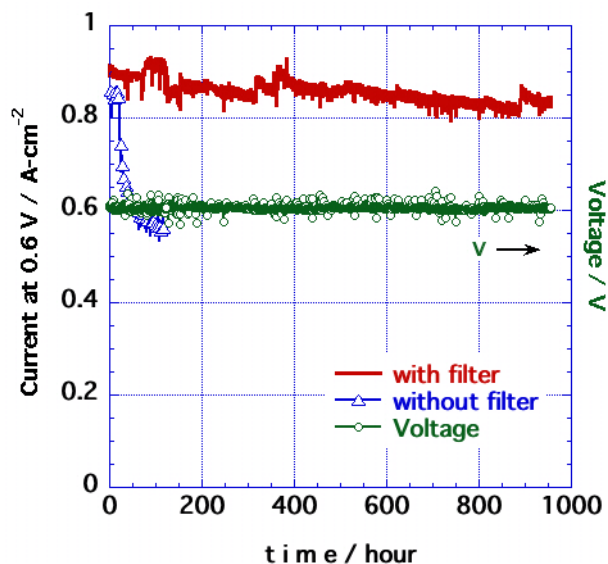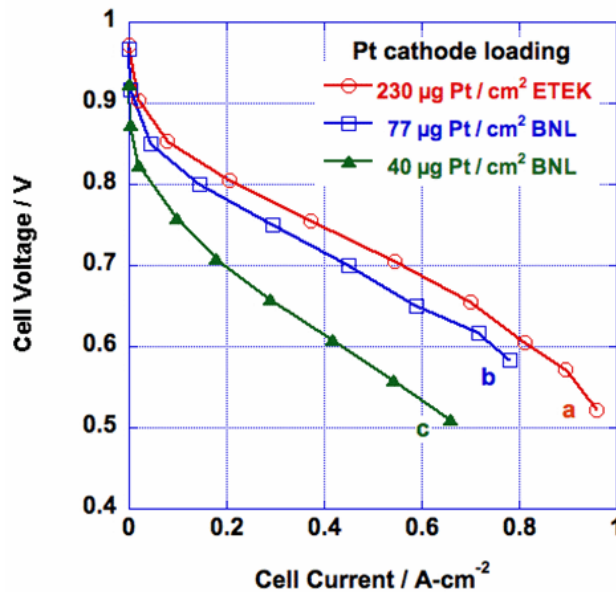

Figure 3. Effect of 500 ppb SO_2 on cathode performance with and without filter in constant voltage mode tests. 50 cm^2 cell; T= 80 ^oC; Loadings: 0.2 mg Pt/cm^2 at each electrode; Filter: Donaldson FC Test Filter FCX400027.

Metal Loading / kW
Calculated using currents at 0.6 V.

cell	g (Pt+Pd)*/kW	g Pt */kW
a	0.92	0.92
b	1.4	0.59
c	1.6	0.80

(*) anode+cathode

Figure 4. Performance of two FCs with low Pt loading at the cathode. The FC cathodes contained **40 µg Pt/cm^2 and 77 µg Pt/cm^2** (4% Pt-20% Pd, BNL), respectively. BNL catalyst prepared by R. Adzic et al. Performance of a reference cell loaded with 0.23 mg Pt/cm^2 (20% Pt/C ETEK) at the cathode is also shown. The anode loading was 0.2 mg Pt/cm^2 (20% Pt/C ETEK). Cell sizes: 50 cm^2. T = 80 ^oC.

it (test without filter). The same plot shows the performance when the contaminated air was injected into the cathode after passing across a commercial chemical filter. This result demonstrates that upstream air cleaning, using a suitable filter, is an effective alternative in achieving full tolerance to this pollutant.

We have also tested low-Pt-content cathodes. The catalyst composition was 4 wt% Pt-20 wt% Pd/C, prepared by R. Adzic and co-workers at BNL. Figure 4 shows FC performance obtained with cathodes containing 40 and 77 µg Pt/cm^2 of this catalyst. A reference polarization curve using a commercial catalyst with a higher loading is also

shown for comparison. Values in inset table indicate that performance of cell **b** (0.59 g Pt/kW) represents a significant improvement in lowering the overall Pt loading.

A somewhat different approach for lowering the precious metal content is to develop low-cost, high-surface-area support materials. Working toward this goal, we have produced <10 nm carbide particles able to support 5 wt% Pt. X-ray diffraction analysis of this composite indicates that the majority of platinum is noncrystalline (in monolayers). FC performance tests will be carried out with these supports.

Catalyst stability and its effect on performance durability have been receiving more attention recently. We have observed that Ru from a Pt-Ru/C anode catalyst migrates to the Pt cathode after operation. The extent of Ru migration depends on operating time or can be accelerated by keeping the anode at high potential. The peak at 0.7 V in the test cell curve (Figure 5a) indicates the presence of Ru in the cathode. Figure 5b shows a polarization curve obtained after Ru migration to the cathode. A reference curve from an equivalent Ru-free cell is included for comparison. The closeness of both curves suggests that Ru migration does not have a significant impact on performance.

Conclusions

We have shown that a level of 50 ppm CO in the fuel stream could be tolerated with a Pt/Ru catalyst at a very low Pt loading (18 µg Pt/cm^2) when combined with air bleed. This catalyst was also shown to be quite stable under normal operating conditions, exhibiting no performance losses over 860 hours.

We have found that even trace levels of SO_2 (air impurity) and H_2S (fuel impurity) have negative and irreversible effects on FC performance. Long-term tests indicate that these compounds will have to be removed from the fuel or the air (e.g., by filtration) prior to use in the FC system to ensure continued performance and durability.

With new catalysts for cathodes (Pt-Pd/C, BNL), we have demonstrated performances that represent significant improvement in lowering the overall Pt loading.
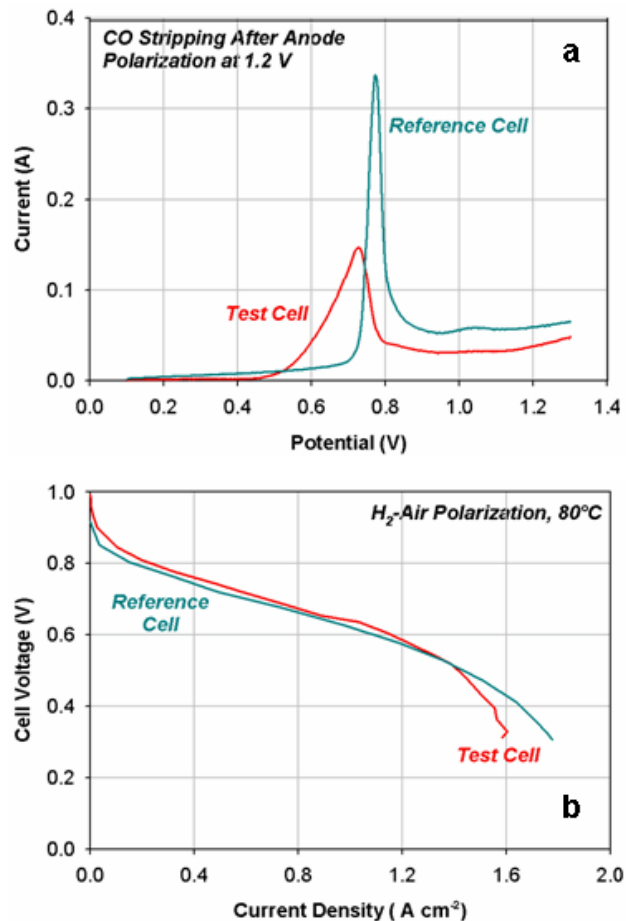

Figure 5. Ru migration (crossover) (a) FC cathode voltammogram showing CO-stripping waves after anode polarization at 1.2 V (b) FC polarization curve after Ru crossover from anode to cathode. Results with a Ru-free reference cell are also shown for comparison.

FY 2004 Presentations and Publications

1. F. Uribe, J. Valerio, F. Garzon, and T. Zawodzinski, "PEM Fuel Cell Reconfigured Anodes for Enhancing CO Tolerance with Air Bleed", *Electrochem. Solid-State Lett.* (2004), in press.

2. K. Sasaki, J. X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R. R. Adzic, *Electrochim. Acta* (2004), in press.

3. P. Adcock, S. Pacheco, K. Norman, and F. Uribe, Investigation of Reconfigured Anodes with

Carbon-Supported Oxide Catalyst in PEM Fuel Cells; submitted to *J. Electrochem. Soc.* (2004).

4. J. Xie, D. Wood, D. Wayne, T. Zawodzinski, P. Atanassova, and R. Borup, Durability of Polymer Electrolyte Fuel Cells at High Humidity Conditions, *J. Electrochem. Soc. (2004)*, submitted.

5. K. Sasaki, Y. Mo, J. X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R. R. Adzic, Pt Submonolayers on Metal Nanoparticles – Novel Electrocatalysts for H_2 Oxidation and O_2 Reduction, *Electrochim. Acta*, **48**, 3841 (2003).

6. P. Adcock, K. Norman, E. Brosha, F. Garzon and F. Uribe, Advanced Studies of Reconfigured Anodes for High CO-Tolerance PEM Fuel Cells, 204th ECS Meeting, Orlando, FL, October 2003. Abstract 1037.

7. M. Mikkola, T. Rockward and F. Uribe, The Effect of NaCl in Cathode Air Stream on PEMFC Performance, 205th Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 331.

8. F. Uribe, J. Valerio and T. Rockward, Effects of Some Air Impurities on PEM Fuel Cell Performance, 205th Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 332.

9. F. Uribe, "Effect of Impurities in Proton Exchange Membrane Fuel Cells", Invited talk at the GM Fuel Cell Center, Rochester, NY (2003).

10. F. Uribe, "Electrodes for H_2 and Air PEM Fuel Cells, Invited talk for the FreedomCAR Fuel Cell Tech Team, Detroit, MI (October 2003).

Special Recognitions & Award/Patents Issued

1. F. Uribe and T. Zawodzinski, "Method for Improving Fuel Cell Performance", Patent No. US 6,635,369 B2 (October 21, 2003).

2. This project was selected by the FreedomCAR Fuel Cell Tech Team as one of the "Top Ten 2003 Accomplishments" of the DOE Fuel Cell Program (December 16, 2003).