

Electrochemical Sensors for Proton Exchange Membrane Fuel Cell Vehicles

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Objectives

- Develop a hydrogen safety sensor operating below 500°C with 1 second response time and low sensitivity to humidity and hydrocarbons
- Develop a hydrogen fuel sensor for reformat fuel monitoring for hydrogen concentrations ranging between 10 to 100%
- Develop a CO sensor for reformat fuel monitoring (future)

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 R,D&D Plan:

- B. Sensors

Approach

Safety sensor

- Utilize proven solid state electrochemical technology comparable to automotive exhaust gas oxygen sensors based on oxygen conducting ceramic electrolytes
- Apply novel nanocrystalline electrode materials with high electronic conductivity to reduce response time and operating temperature
- Design and build micro-sensor configuration to minimize heater power requirements

Fuel sensor

- Develop and characterize an amperometric sensor using a known proton conducting oxide electrolyte
- Correlate 'pumping' current with hydrogen concentration in simulated reformat gas
- Reduce operating temperature by applying novel electrode/electrolyte materials to enhance conductivity and surface exchange
- Ensure electrolyte stability in reformat environment by performing appropriate thermal characterization and electrochemical testing

Accomplishments

Safety sensor

- Operating temperature has been reduced to 430 - 460°C
- An integrated, planar heater/sensor design has been established (heated substrates supplied by Ford)

- Preliminary testing indicates no baseline drifting over several hundred hours
- External collaborators interested in testing/commercialization are being explored (Ford is currently testing)

Fuel sensor

- A candidate electrolyte with high stability versus CO₂ has been selected
- Preliminary laboratory prototypes have been fabricated and are being tested

Future Directions

Safety sensor

- Finalize sensor design
- Locate external collaborator interested in testing/commercialization (Ford has agreed to test sensor)

Fuel Sensor

- Evaluate various materials, processing techniques, and designs
- Fabricate first prototype
- Seek industrial collaboration
- Develop integrated fuel sensor

Introduction

Proton exchange membrane fuel cells (PEMFCs) are among the most promising clean power system technologies being developed for transportation applications. However, the use of hydrogen and other combustible gases for automotive applications requires new on-board safety sensors and controls to prevent fire and explosion hazards. In addition, if hydrogen fuel is supplied by an on-board reformer, additional control and monitoring devices are needed in order to protect and to efficiently operate the PEMFCs.

The purpose of this project is to design, fabricate, and demonstrate solid state electrochemical sensors for various H₂ monitoring applications on PEMFC vehicles. The first phase of the project has focused on the development of a hydrogen safety sensor intended to be deployed at critical locations on the vehicle to detect potentially dangerous hydrogen leakage. Currently, that portion of the project is being completed, and development of a hydrogen fuel sensor is being initiated. The fuel sensor is intended to monitor the fuel quality (i.e. percent hydrogen) in the gas stream supplied from an on-

board hydrogen reformer (reformate gas). Reformate gas is typically a severe environment containing a variable mixture of H₂, H₂O, N₂, CO, CO₂, and residual hydrocarbons. Both of these sensors are being developed by applying novel materials to established electrochemical sensor technologies.

Approach

Our approach to the hydrogen safety sensor is based on established solid-state electrochemical sensor technology. The proposed sensor consists of two electrodes on an oxygen conducting electrolyte. One electrode serves as a reference and the other as a sensing electrode. The electrode materials are selected so that they have different catalytic activities toward the oxidation of hydrogen gas. This causes the electrodes to reach some kinetically limited potential determined by the concentration of hydrogen in a hydrogen/air mixture. The sensor operates by measuring the difference between these electrode potentials, and the hydrogen concentration can be correlated with the magnitude of this potential difference. Similar sensors have been proposed in the past [1]; however, sensitivity and response speed were insufficient for the proposed safety sensor

application. We have proposed that by using a higher conductivity electrode material, response time can be reduced to the point where the sensor becomes suitable for the safety application. For that reason, the current safety sensor uses a metal oxide (indium oxide) doped to promote electronic conductivity. The resultant fast response, along with the sensitivity of the sensor, will be shown below.

The hydrogen fuel sensor operates on a very different principle whereby the hydrogen is electrochemically dissociated and pumped through a proton conducting ceramic membrane at high temperature. The pumping current (at constant applied voltage) can be correlated to the hydrogen concentration in the test gas. The approach to realizing this sensor will proceed in two parts. The first will be to demonstrate the sensing technology using a known proton conductor with established stability in the reformat environment. However, since these materials tend to be comparatively poor proton conductors, the operating temperature will be required to be fairly high ($\sim 600^{\circ}\text{C}$). The second part of the developmental effort will be to explore novel proton conductors to identify the best candidate providing the optimum combination of conductivity and stability for the proposed application. Once identified, this 'optimum' electrolyte will be implemented in the sensor technique demonstrated in the first part of the project. Progress towards these goals will be discussed below.

Accomplishments

Safety sensor. During the prior efforts, a safety sensor was demonstrated which had good sensitivity and response time, but relatively high operating temperature (500°C). That sensor consisted of electrodes on an unheated substrate, and testing required that the sensor be heated using a laboratory tube furnace. During FY 2003, the principal goals were to modify the sensor to reduce the operating temperature below 500°C , and to demonstrate an integrated, self-heated design. Figure 1 shows that integrated design, where the yttria-stabilized zirconia (YSZ) electrolyte is attached to the surface of an alumina substrate containing an integrated Pt resistive heater [2]. The one-inch scale bar in the figure shows the sensor size. Also shown in the figure are the electrode size and location. It is worth

noting that the electrodes are misaligned from the heating element, causing the power consumption ($\sim 5.4\text{ W}$ at 440°C) of this sensor to be $\sim 20\%$ elevated for a given temperature. This misalignment is being corrected in the next generation design.

Figure 2 shows the sensor response, at 440°C , to 3300 ppm (0.33%) H_2 in air containing 10% and 100% relative humidity. The data show the sensor baseline near 0 mV in the absence of H_2 , and a reproducible response of ~ 225 or 250 mV (10 and

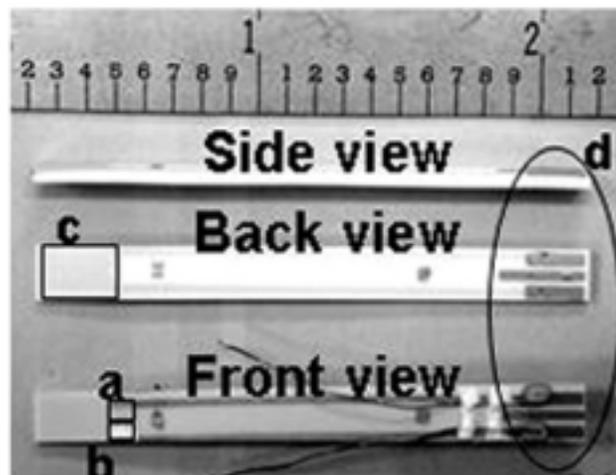


Figure 1. H_2 Safety Sensor Prototype Showing a) Sensing Electrode, b) Reference Electrodes, c) Resistive Heater, and d) Electrical Connections; the Scale Bar at the Top Is in Inches

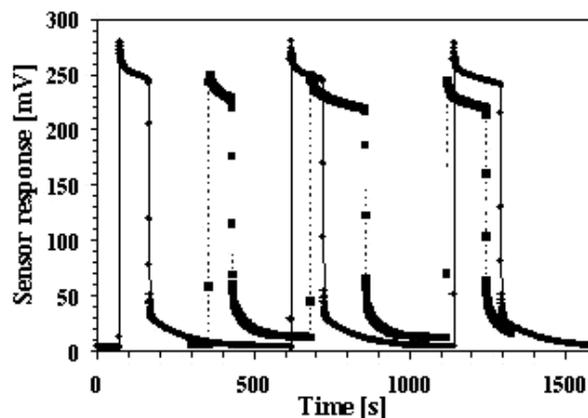


Figure 2. Response of the Hydrogen Safety Sensor, Operated at 440°C , to 3300 ppm H_2 in Air Containing 10% (squares) and 100% (crosses) Relative Humidity

100% relative humidity, respectively). It is clear that the sensor responds within approximately one second (which is the DOE technical target) to the addition of the H_2 . The slight overshoot is a consequence of the low operating temperature, and it may be possible to reduce this effect by modifying the reference electrode to reduce the interfering response there. Long term testing indicates that the sensor baseline is stable and that the sensor response is reproducible over a period of several hundred hours.

Figure 3 shows the response of the sensor, again at 440°C and in 10% and 100% relative humidity, to varying H_2 and CH_4 concentrations in air. The data show a slight ($\sim 10\%$) reduction in sensitivity in the presence of high relative humidity. This slight cross-sensitivity is considered to be acceptable since discussions with commercial end-users indicate generally severe degradation in performance with humidity for the commercially available sensors. The data also show that the sensor has a very high sensitivity at low H_2 concentration. This sensitivity is an attractive feature for early leak detection. Finally, the selectivity versus CH_4 is shown to be approximately five to one.

Fuel sensor. Development of the H_2 fuel sensor has been initiated, and a preliminary prototype sensor has been fabricated from a Sr-zirconate electrolyte with known stability in H_2O and CO_2 gas. Figure 4 shows the pumping current (i.e. the response) of that sensor operated at 600°C as a function of H_2

concentration. The test gas was composed of the indicated concentration of H_2 with 20% H_2O and a balance of N_2 . These data clearly demonstrate that the device is sensitive to the concentration of H_2 in the test gas. Further testing is underway to evaluate the cross-sensitivity to CO_2 and H_2O . By incorporation of a diffusion-limiting porous barrier over one of the electrodes, it should be feasible to force the response of the sensor to be linear versus the H_2 concentration.

Conclusions and Future Work

A H_2 safety sensor has been demonstrated with an integrated, self-heated design operating at $430 - 460^\circ\text{C}$. Preliminary testing indicates no baseline drifting over several hundred hours. External collaborators interested in testing/commercialization are being explored. A candidate electrolyte has been identified for the H_2 fuel sensor with high stability versus CO_2 . Preliminary laboratory prototypes have been fabricated and are being tested. Ongoing developmental efforts for the fuel sensor include evaluation of various materials, processing techniques, and designs. In addition, an industrial collaboration will be sought to facilitate the eventual commercialization of an integrated fuel sensor.

References

1. G. Lu, N. Miura and N. Yamazoe, "High-temperature hydrogen sensor based on stabilized

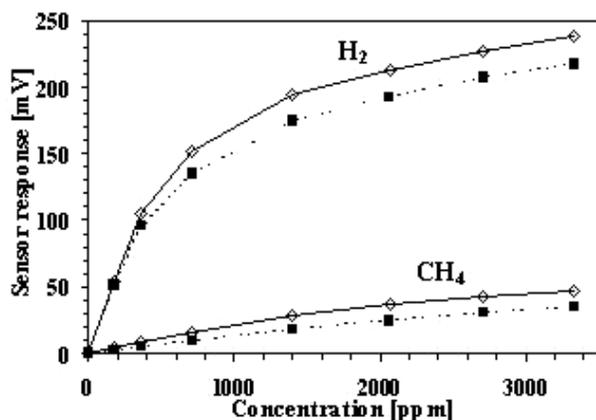


Figure 3. Response of the Sensor, Operated at 440°C , to H_2 and CH_4 in Air Containing 10% Relative Humidity (diamonds) and 100% Relative Humidity (squares)

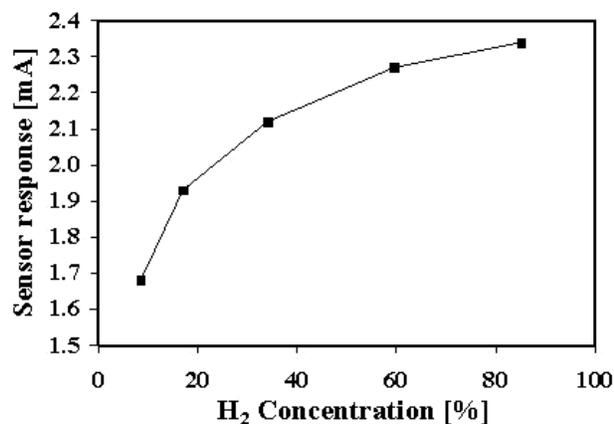


Figure 4. Fuel Sensor Response versus H_2 Concentration at 600°C , 20% H_2O , Balance N_2 ; Applied Bias Is 250 mV

zirconia and a metal oxide electrode," *Sensors and Act.*, B35-36, (1996) 130-135.

2. Supplied by Rick Soltis, Ford Research Center, Dearborn, MI.

Publications

1. L. P. Martin, Q. Pham, and R. S. Glass, "Electrochemical Hydrogen Sensor for Safety Monitoring," submitted for publication in *Solid State Ionics* (4/2003). Will be a peer-reviewed, special edition serving as Proceedings of The 14th International Meeting on Solid State Ionics.

Presentations

1. L. P. Martin and R. S. Glass, "Electrochemical Sensors for PEMFC Vehicles," presented at the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, (Berkeley, CA, May 19-22, 2003).
2. L. P. Martin, Q. Pham, and R. S. Glass, "Electrochemical Hydrogen Sensor for Safety Monitoring," poster presented at The 14th International Meeting on Solid State Ionics, (Monterey, CA, June 22-27, 2003).
3. L. P. Martin, A.-Q. Pham, and R. S. Glass, "Hydrogen Sensor Based on Yttria-Stabilized Zirconia Electrolyte and Rh-Promoted ITO Sensing Electrode," submitted for presentation at the 204th Meeting of the Electrochemical Society (Orlando, FL, October 12-17, 2003).