VI.2 Electrochemical Sensors for PEMFC Vehicles

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Objectives

- Develop a hydrogen safety sensor operating below 500°C with a 1 second or less response time and low sensitivity to humidity and hydrocarbons.
- Develop a hydrogen fuel loop sensor for monitoring fuel supply to the fuel cell (supplied either from on-board tank storage or reforming system). Sensor will need to measure hydrogen in the concentration range of 10 to 100%.
- Develop a CO sensor for reformate 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 Research, Development and Demonstration Plan:

- B. Sensors

Approach

Safety Sensor

- Utilize proven solid state electrochemical sensor technology and oxygen ion conducting materials similar to automotive exhaust gas oxygen sensors
- Use 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 Loop Sensor

- Develop and characterize an amperometric sensor using a known proton conducting oxide electrolyte
- Correlate 'pumping' current with hydrogen concentration in simulated fuel gas environments
- Reduce operating temperature by applying novel sol-gel fabrication techniques to deposit a thin electrolyte layer
- Insure electrolyte stability in various fuel gas environments by performing appropriate thermal characterization and electrochemical testing

Accomplishments

Safety Sensor

- Extended range of H_2 concentration measurement up to 10%
- Performed more detailed analysis of operating mechanism

- Evaluated the effects of electrode thickness
- Carefully documented sensor response times

Fuel Loop Sensor

- Demonstrated a laboratory prototype based on a doped-strontium zirconate
- Demonstrated zirconate electrolyte to provide sufficient sensitivity and to be stable in CO_2
- Showed sensor response to be linear with logarithm of H_2 concentration
- Showed the response time to be approximately 5 seconds from 2% to 100% H_2

Future Directions

Safety Sensor

- Finalize sensor design
- Locate industrial partner interested in testing/commercialization (Ford and Ballard have agreed to test sensor)

Fuel Loop Sensor

- Evaluate various materials, processing techniques, and designs
- Fabricate first prototype
- Develop detailed understanding of ageing mechanisms
- Develop integrated 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, fuel cell manufacturers have indicated that they have a strong need for a hydrogen fuel loop sensor. This sensor is needed regardless of whether hydrogen is supplied from on-board storage systems or generated in a reformer. The need for a hydrogen fuel loop sensor is obvious in the case of on-board reforming where a variable mixture of H_2, H_2O, N_2, CO, CO_2, and residual hydrocarbons is generated and supplied to the PEMFC. For on-board storage systems, the sensor is needed because fuel cell vehicles (FCVs) use exhaust gas recirculation and therefore there could be build-up of water, nitrogen, and other diluents in the fuel stream. In either case, a fuel loop sensor is 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 H_2 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 nearing completion, 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 to the PEMFC. Both of these sensors are being developed by applying novel materials to solid state electrochemical sensors.

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 ion-conducting electrolyte. One electrode serves as a “reference” and the other as a “sensing” electrode. Note that strict electrochemical nomenclature is not being

followed here as the Pt "reference" electrode does not obtain a poised stable potential to which the "sensing" electrode can be referenced. The electrode materials are selected so that they have different catalytic activities toward the oxidation of hydrogen gas. This causes the electrodes to individually reach a potential that is dictated by electrochemical kinetics. The sensor operates by measuring the potential difference between these electrodes 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 principal whereby the hydrogen is electrochemically dissociated and pumped through a proton-conducting ceramic membrane. 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 reformate environment. However, since these materials tend to be comparatively poor proton conductors, the operating temperature will be required to be fairly high (~600°C). The second part of the developmental effort will be to explore techniques for reducing the operating temperature including reducing the electrolyte thickness, and attempting to identify alternative proton conductors 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.

Results

Safety Sensor

During FY 2003, an integrated safety sensor was demonstrated which had good sensitivity and response time while operating at 440°C. In the integrated design, the yttria-stabilized zirconia (YSZ) electrolyte is deposited onto the surface of an alumina substrate containing an integrated Pt resistive heater [2]. At 440°C, the sensor exhibited a baseline near 0 mV in the absence of H_2, and a reproducible response of ~225 or 250 mV to 3300 ppm (0.33%) H_2 in air containing 10% and 100% relative humidity, respectively. The sensor had a response time of approximately one second. Finally, the sensor was shown to have a selectivity coefficient of about 5 for detection of hydrogen over CH_4, a potentially significant interfering gas.

During FY 2004, more extensive testing of non-integrated (non self-heated) sensors was performed in order to evaluate the performance over a wider range of H_2 concentrations (up to 10%). Non-integrated sensors were used in order to facilitate extensive testing of a large number of sensors without consuming the heated substrates, which embody high resource costs. In addition, testing was performed which provided for more extensive analysis of the operating mechanism, for evaluation of the effects of the thickness of the tin-doped indium oxide sensing electrodes, and for careful documentation of sensor response times. These results are discussed in more detail below.

Figure 1 shows the sensor response versus H_2 concentration at 450, 500 and 550°C. The sensor response is greater at 500°C than at 550°C at all H_2 concentrations. When the temperature is further reduced to 450°C, the sensitivity enhancement is smaller and decays with increasing H_2 concentration until the data converge with the 500°C data. This convergence was also exhibited by other sensors with different tin-doped indium oxide (ITO) thicknesses. This temperature dependence is probably related to either: a) smaller differences in the reaction kinetics between the ITO "sensing" electrode and the platinum "reference" electrode, resulting in a lower potential difference, or b) the inability of the entire

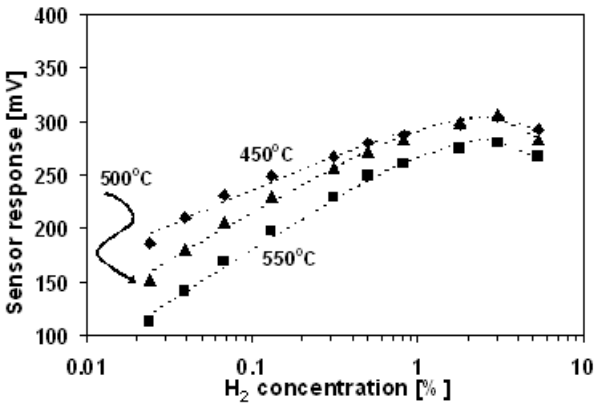

Figure 1. Safety Sensor Response versus H_2 Concentration at 450, 500 and 550°C [The dotted lines show the best fit of Eq. (1) to the data.]

system to reach the same quasi-equilibrium steady state as at higher temperature due in general to the reduced reaction kinetics, and in particular to the reduced oxide ion conductivity in the YSZ. For all temperatures, the sensor response in Figure 1 can be described by

$$E_m = C_1 + C_2 \ln[C(O_2)] - C_3 \ln[C(H_2)] \qquad (1)$$

where E_m is the measured response, C_1, C_2, and C_3 are constants, and $C(O_2)$ and $C(H_2)$ are the oxygen and hydrogen concentrations, respectively. The dotted lines in the Figure represent the best fit of Eq. (1) to the data at the three temperatures.

Sensor response times were measured at different H_2 concentrations. These data are shown in Figure 2, during operation at 500°C, where the response times were calculated from the baseline to 90% of full response (t_{90}) and from 10% to 90% of the full response ($t_{10\text{-}90}$). The latter value is probably somewhat more accurate in that there is a noise-limited error involved in identifying the point at which the sensor response deviates from the baseline. Based on these data, response times decrease with increasing H_2 concentration and are less than 1 second for concentrations greater than 0.03%. This is completely acceptable for a hydrogen sensor to be used in safety applications for hydrogen leaks on vehicles.

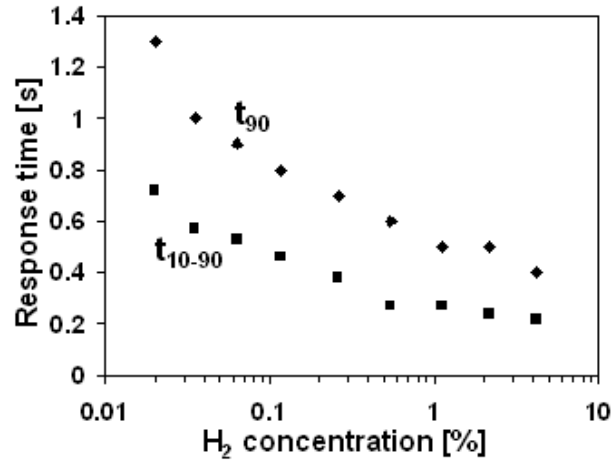

Figure 2. Safety Sensor Response Time as a Function of H_2 Concentration [Response times are measured from the baseline to 90% of the full response (t_{90}) and from 10% to 90% of the full response ($t_{10\text{-}90}$).]

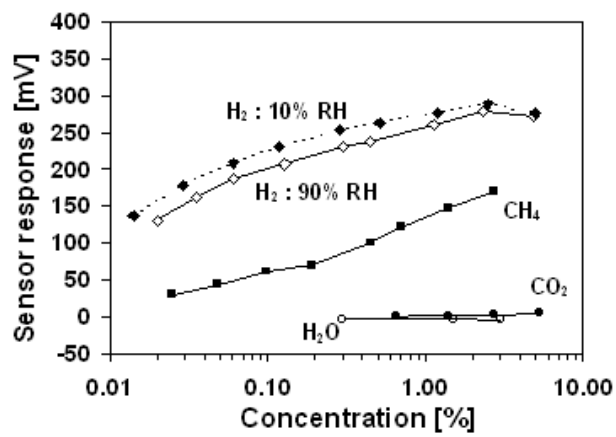

Figure 3. Safety Sensor Response at 500°C to H_2 in 10% and 90% Relative Humidity (RH) [Also shown are the response to CH_4, CO_2, and H_2O.]

Figure 3 shows the sensor response to H_2, H_2O, CO_2 and CH_4, when operated at 500°C in 10% and 90% relative humidity. The indicated CO_2 concentrations represent the excess above the ambient air level (~1%). These data indicate that the sensor is fairly insensitive to relative humidity in the 10-90% range, with a change in response of not more than 10% (in the positive direction) in going from 10% to 90%. In addition, the sensor response is stable and reproducible over this same humidity

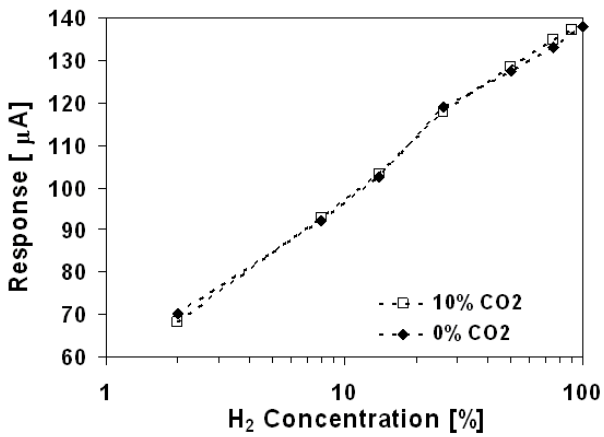

Figure 4. Fuel Loop Sensor Response versus H_2 Concentration at 600°C [Two tests are shown: 0 and 10% CO_2. In both cases the test gas includes 20 % H_2O in a balance of N_2. The applied bias is 250 mV.]

range for the duration of the test. It can be seen that the sensor is not responsive to H_2O or CO_2 over the ranges tested. In contrast, the sensor responds to CH_4, although with a significantly lower response than to H_2 (the sensor is approximately five and three times more sensitive to H_2 than to CH_4 at 0.1% and 5% concentration, respectively).

Fuel Loop Sensor

Development of the hydrogen fuel loop 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 show a linear response to the logarithm of the H_2 concentration in the test gas. As shown in the figure, the cross-sensitivity to CO_2 is negligible for concentrations up to 10% or more. 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 with H_2 concentration.

Conclusions

An H_2 safety sensor has been demonstrated with high sensitivity, fast response time, and good selectivity to H_2 in ambient air. We have elicited interest from industrial collaborators who are interested in testing the sensor in fuel cell systems. A candidate electrolyte has been identified for the hydrogen fuel loop sensor. Preliminary laboratory prototypes have been fabricated and are being tested. The sensor has been shown to be insensitive to CO_2. Ongoing developmental efforts for the fuel loop 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 loop sensor.

References

1. G. Lu, N. Miura and N. Yamazoe, "High temperature hydrogen sensor based on stabilized zirconia and a metal oxide electrode," *Sensors and Act.*, **B35-36**, (1996) 130-135.

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

FY 2004 Publications/Presentations

1. L. P. Martin, Q. Pham, and R. S. Glass, Electrochemical Hydrogen Sensor for Safety Monitoring, accepted for publication in *Solid State Ionics* (April 2004). See also *Proceedings of The 14th International Meeting on Solid State Ionics*, Asilomar, CA (June 22-27, 2003).

2. L. P. Martin and R. S. Glass, "Hydrogen Sensor Based on Yttria-Stabilized Zirconia Electrolyte and Tin-Doped Indium Oxide Sensing Electrode," submitted for publication in *The Journal of The Electrochemical Society* (April, 2004).

3. L. Peter Martin and Robert S. Glass, "Electrochemical Sensors for PEMFC Vehicles," presented at The 2004 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review, Philadelphia, PA (May 27, 2004).

4. L. P. Martin, A.-Q. Pham, and R. S. Glass, "Hydrogen Sensor Based on Yttria-Stabilized Zirconia Electrolyte and Rh-Promoted ITO Sensing Electrode," presented at The 204th Meeting of The Electrochemical Society, Orlando, FL (October 12-17, 2003).