

VII.I.10 Electrochemical Sensors for PEMFC Vehicles

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Objectives

- Develop a prototype hydrogen safety sensor with a 1 second (1 s) or less response time and low sensitivity to humidity, carbon dioxide, and hydrocarbons.
- Develop a prototype hydrogen fuel loop sensor for monitoring fuel supply to the fuel cell. The sensor will need to measure hydrogen in the concentration range between 25 to 100% with a 0.1-1 s response time.

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

Technical Targets

Table 1. LLNL Progress Toward Meeting DOE Sensor Targets

Parameter	Units	2010 Target	Current Status
Response Time-Safety	Seconds	<1 s	<1 s for H ₂ concentration > 0.02%
Response Time - Fuel	Seconds	0.1-1	Approx. 5
Measurement Range - Safety	Percent	1-5%	0.03 - 5.5%
Interference Resistance - Safety	–	Low response to hydrocarbons, CO ₂ , O ₂ , etc	To-date, Good selectivity against H ₂ O, CO ₂ , and CH ₄ demonstrated
Interference Resistance - Fuel	–	Low response to H ₂ O, CO ₂ , N ₂	Negligible response to H ₂ O, CH ₄ , N ₂ , and up to 10% CO ₂
Gas environment - Safety	–	Ambient air, 10-98% RH	Stable in ambient air and 10-100% RH (only 10% effect over 10-100% RH range)

RH = relative humidity

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 using a thin film sensor architecture achieved through the use of physical vapor deposition and tape casting or novel sol-gel techniques for fabrication/deposition of the electrodes and electrolyte.
- Ensure sensor stability in various fuel gas environments by performing appropriate thermal, aging, chemical and microstructural, and electrochemical characterization.

Accomplishments

Safety Sensor

- Demonstrated response time under 1 s for concentrations greater than 0.02%.
- Further clarified response mechanism.
- Prepared first integrated prototypes for test by industrial partners.

Fuel Loop Sensor

- Sensor response time was measured to be approximately 5 s. It was determined that this relatively long response time was due to the thickness of the electrolyte. A thinner electrolyte should allow us to reach the goal of 0.1-1 s response time.
- Identified and developed new technology for making thin film architecture for decreasing response time.

Future Directions

Safety Sensor

- Develop a refined fabrication procedure for the sensor and perform real-world, long-term sensor testing in conjunction with industrial partners (Ford and Ballard).
- Transfer technology to industry for commercialization.

Fuel Loop Sensor

- Develop thin film design to reduce operating temperature.
- Evaluate alternative electrolyte materials to reduce operating temperature.
- Fabricate first prototype.
- 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. For on-board storage systems, the sensor is needed because fuel cell vehicles 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 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. For that portion of the project, we have completed much of the materials development work. Further attention to fabrication, with an end-goal of developing mass fabrication procedures, is needed. This includes developing thin film miniaturized sensors and integrated packaging with heating elements. Real-world testing must be done with industrial partners. The fuel loop sensor is intended to monitor the fuel quality (i.e., percent hydrogen) in the gas stream supplied to the PEMFC. As a result of funding limitations, the development of the fuel loop sensor has been delayed in FY 2005. 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 attain 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. Our efforts have been directed towards a safety sensor that uses a metal oxide (indium oxide) doped to promote electronic conductivity.

The hydrogen fuel loop 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. Sensors using this mode of measurement are known as amperometric sensors. It is necessary to pursue this type of sensor as the safety sensor discussed above, which operates in the potentiometric mode, does not have adequate sensitivity at the higher hydrogen concentrations in the fuel loop (the optimum response range for the safety sensor is 0.03-5.5% hydrogen). 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 fuel loop environment. For adequate proton conductivity the operating temperature for the sensor must be fairly high (~600°C). On-chip resistance heaters can be used to achieve surface temperatures in this range for thin film devices. 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 is discussed below.

Results

In prior efforts, a laboratory prototype hydrogen safety sensor was demonstrated that had good sensitivity and response time. This sensor is based on a tin-doped indium oxide electrode and yttria-stabilized zirconia electrolyte. During FY 2003, the principal accomplishment was to modify the sensor to reduce the operating temperature to below 500°C. In FY 2004, extensive characterization of sensor performance was performed over an expanded range of hydrogen and interfering gas concentrations. The sensor shows high sensitivity and a response time of one second or less for hydrogen concentrations in the range of 0.03 to 5.5% in air. Cross-sensitivity to H₂O, CO, and CO₂ were shown to be low. The

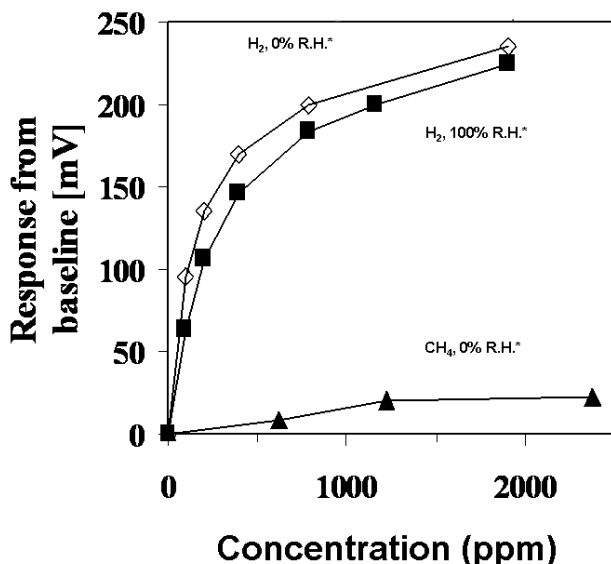


Figure 1. Safety Sensor Response to Hydrogen in Presence of 0 and 100% RH, and to Methane at 0% RH

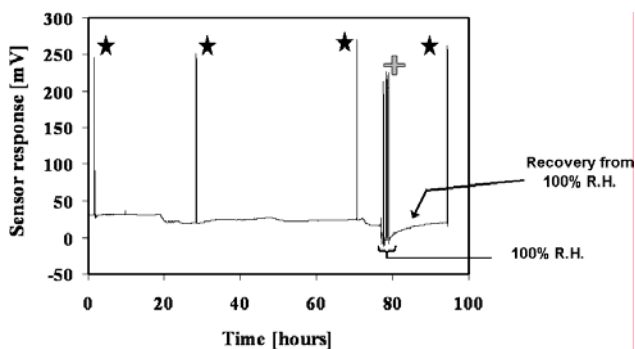


Figure 2. Long-Term Baseline Testing Showing Response to Spikes of Hydrogen at 0% and 100% RH (2000 ppm H₂, 0% RH; 2000 ppm H₂, 100% RH)

response to methane, a potentially significant source of interference for such a sensor, is lower than that for hydrogen by a factor of 2-5 times at 1% concentrations. This selectivity to H₂ improves at lower concentrations. The selectivity to water (up to 100% relative humidity, RH) and methane is shown in Figure 1. Longer-term testing has demonstrated excellent baseline stability and reproducible response. Data have been obtained up to 280 hours testing. As an example, baseline stability data are shown in Figure 2, along with the response to a “spike” of 100% RH. A slight (~10%) reduction in

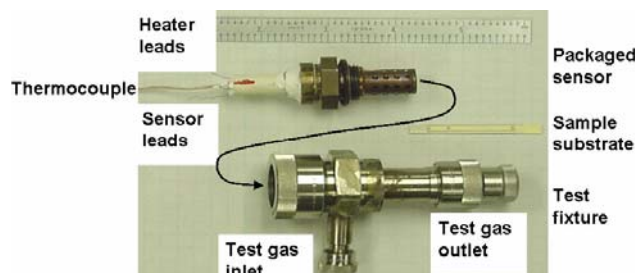


Figure 3. Prototype, Integrated Hydrogen Safety Sensors

sensitivity in the presence of high relative humidity is considered to be acceptable based on discussions with commercial end-users. These discussions indicated that for existing, commercially-available sensors, generally severe degradation in performance occurs with high humidity. Considerable characterization of electrode thickness effects and operating mechanism were also performed in FY 2004 and FY 2005. Quantitative sensor operating algorithms have been developed and were reported in a peer-reviewed journal published during this reporting period [J. Electrochem. Soc., 152(4), H43-H47 (2005)].

During FY 2005, prototype integrated sensors were developed for testing using commercial oxygen sensor housings. These prototypes are shown in Figure 3. The sensors are currently being evaluated at an industrial partner laboratory (Ford).

The additional work that remains for the hydrogen safety sensor is to develop a fabrication process for the sensor that has potential for mass fabrication. Common semiconductor manufacturing methods employing thin film deposition will be explored. Dense thin films of electrode and electrolyte materials will be deposited by radio frequency magnetron sputtering vapor deposition or an electron beam evaporation process onto a thin yttrium-zirconium oxide solid electrolyte. The technology has been proven for the development of nitric oxide sensors. Using such methods, we can produce a device with a very well defined triple phase (that is, where the electrode, electrolyte, and gas phase meet). We anticipate that the end result will be a higher signal response and better device-to-device response reproducibility. Once this is developed, the sensor must be re-examined to ensure that the fabrication process produces sensors that

maintain the desirable characteristics we have noted in the laboratory prototypes. Real-world, longer-term testing must also be done.

Development of the hydrogen fuel loop sensor has just begun. Initial results previously reported were obtained from a sensor fabricated from an electrolyte consisting of a pressed and sintered strontium zirconate powder. In initial testing, the sensor response, operated at 600°C, appears proportional to the logarithm of the H₂ concentration in the range from 5-95% by volume, in a balance of 1-20% H₂O in N₂. Further testing indicated negligible cross-sensitivity to CO₂. Sol-gel techniques are being developed to allow spin-coating of very thin (tens of nanometers) electrolyte layers. An even more promising technology for sensor fabrication, for both the fuel loop as well as the safety sensor, involves tape casting and physical vapor deposition of thin film structures. The development of these thin film sensors will enable faster sensor response, as well as affording mass production potential. The thin film approach is currently being evaluated.

Conclusions

A hydrogen safety sensor has been demonstrated with high sensitivity, fast response time, and good selectivity to hydrogen in ambient air. During FY 2005, prototype integrated sensors were developed

for testing using commercial oxygen sensor housings. The additional work that remains for the hydrogen safety sensor is to develop a fabrication process for the sensor that has potential for mass fabrication, and perform real-world, long-term testing on these sensors. For the hydrogen fuel loop sensor, candidate materials have been identified. Preliminary results have been obtained indicating suitable response to hydrogen; however, the sensor has unacceptably long response times. We have identified fabrication processes for creating thin film architectures for the fuel loop sensor that should decrease resistance effects and thereby improve response time and other performance characteristics.

FY 2005 Publications/Presentations

1. L. P. Martin and R. S. Glass, "Hydrogen Sensor Based on Ytria-Stabilized Zirconia Electrolyte and Tin-Doped Indium Oxide Electrode," *Journal of the Electrochemical Society*, 152(4), H43-H47 (2005).
2. L. P. Martin and R. S. Glass, "Electrochemical Sensors for PEMFC Vehicles," presented at Hydrogen Safety, Codes and Standards Tech Team Meeting, Detroit, MI, October 27, 2004.

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.