Carbon Monoxide Sensors For Reformate Powered Fuel Cells

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Objectives

Hydrogen reformate gas powered fuel cell systems require sensors for carbon monoxide level monitoring and feedback control.

- Develop a low temperature sensor for measuring 10-100 ppm range concentrations for stack poisoning control.
- Develop a high temperature sensor for the measurement of 0.1 to 2% carbon monoxide in the reformate gas for fuel processor control.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

Two electrochemical sensor types are being investigated for high and low temperature carbon monoxide sensing:

- An oxide solid electrolyte device based on the kinetics of the electrode reactions is being developed for both the high and low temperature applications.
  - Yttria-doped zirconia and gadolinia-doped ceria oxygen ion conductors and strontium yttrium zirconium oxide proton conductor are being investigated as the solid electrolyte.
  - Several metals, including Pt, Pd, Au, Ru and Ni, are being evaluated as the sensing and reference electrodes.
- A low temperature amperometric device based on the carbon monoxide inhibition of hydrogen oxidation kinetics at the electrodes of a polymer electrolyte membrane (PEM) fuel cell is being developed for the low temperature application.
  - Sensors based on perfluorosulfonic acid polymer electrolytes are being evaluated.
  - Different catalyst loadings of carbon supported and un-supported Pt, Ru and Pt/Ru alloys are being evaluated as electrodes.

Accomplishments

- Ceramic electrolyte based sensors that operate at 150-300^{o}C have been developed. These sensors respond well to 10-100 ppm carbon monoxide in a simulated reformate stream.

- Amperometric low temperature carbon monoxide sensors based on a polymer electrolyte have been developed and tested under a variety of conditions. These devices respond well at ambient temperature to 10-100 ppm carbon monoxide in hydrogen streams.
- Polymer electrolyte based sensors have been optimized to operate at 70^{o}C and respond to 100-1000 ppm of CO in a simulated reformate stream.

Future Directions

- Analyze the response time of the oxide and polymer electrolyte based sensors.
- Evaluate the performance of the polymer and oxide electrolyte based systems under practical fuel reformate conditions.
- Evaluate the stability of the response of the oxide electrolyte based sensors.
- Modify the electrodes of the oxide electrolyte based sensor to enable it to detect higher concentrations of CO (0.1-2%) at T > 250^{o}C.
- Demonstrate a prototype oxide based sensor with a patterned heater incorporated on the sensor electrolyte body.

Introduction

The detection and measurement of carbon monoxide in high temperature reformate streams is of vital importance to the successful implementation of fuel cells for transportation. Much research is being performed to optimize low cost fuel reformer systems that convert liquid hydrocarbon fuels to hydrogen gas containing fuel streams. This hydrogen gas typically feeds a polymer electrolyte membrane (PEM) fuel cell utilizing a platinum based anode. It is well known that low concentrations (10-100 ppm) of carbon monoxide impurities in hydrogen can severely degrade the performance of PEM fuel cell anodes.[1] This performance degradation is due to strong adsorption of carbon monoxide on the electro-active platinum surface sites where hydrogen is normally oxidized to protons.[1]

Therefore, the proper design of combined fuel cell stack and reformer systems must pay careful attention to the minimization of carbon monoxide before the processed fuel stream enters the stack. Many reformer systems use a secondary preferential oxidation (PrOx) reactor that selectively oxidizes the carbon monoxide present in the reformate stream. The efficiency of this PrOx reactor will depend on the accurate and rapid measurement of the inlet (or outlet) CO concentration at the reactor. Moreover, current fuel cells use air-bleeding methods to reduce the carbon monoxide poisoning of the Pt anode. Since this method involves the mixing of 2-6% air with the fuel stream, it results in a decrease in the energy efficiency of the fuel cell system and can greatly benefit from the accurate determination of the CO content of the fuel stream entering the stack. Hence, CO sensors that measure the CO content of the fuel stream before and after the PrOx reactor can be used for feedback control, thus allowing these integrated fuel cell systems to operate at maximum energy efficiency. We are designing and developing solid-state electrochemical sensors meeting these criteria, leading to the demonstration of prototype sensors.

Approach

High temperature carbon monoxide sensors. Los Alamos National Laboratory (LANL) is developing high temperature zirconia- and ceria-based electrochemical sensors to measure CO in hydrogen streams. These sensors would operate at 150-400^{o}C and can be used for feedback control either before or after the PrOx reactor. We have successfully developed novel mixed-potential sensors that are capable of measuring ppm levels of CO in air. The unique design of these sensors makes them robust, stable and reproducible.[2,3] In this project, we are working on modifying the electrodes of these devices to enable them to work in a hydrogen atmosphere.

We are also exploring the possibility of using proton-conducting electrolytes and using these sensors in an amperometric mode.

Low temperature carbon monoxide sensors. Low temperature carbon monoxide sensors based on the reversible carbon monoxide adsorptive poisoning of precious metal electrodes are also being developed at LANL. The addition of metals such as ruthenium to the platinum anode catalyst is known to greatly improve the hydrogen-oxidation kinetics in the presence of CO. An amperometric sensor that senses the differential CO inhibition of the hydrogen oxidation reaction at 2 electrodes can be fabricated from a platinum electrode, a proton conductor and a platinum ruthenium alloy electrode. While the current density of the platinum electrode will be influenced by the surface coverage of carbon monoxide, the current density at the Pt/Ru alloy electrode should be relatively unaffected. This difference in the electrode current density in the presence of CO can be used to fabricate a low temperature CO sensor. In this project, we are optimizing the electrode composition, precious metal loading and operating temperature of these ampereometric sensors in order to develop a CO sensor that will sense 1-100 ppm CO in the inlet fuel stream of a fuel cell stack.

Results

Oxide electrolyte based sensors were prepared by sputtering or brush-painting various metal electrodes on to oxygen-ion conducting electrolytes. The sensor configuration is shown in Figure 1, where the electrolyte used was either $Zr_{0.85}Y_{0.15}O_{1.95}$ (YSZ) or $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), and the electrodes used were selected from Pt, Ru, Pd, Au or Ni. The substrate was 0.5 mm thick, and the electrodes were 0.5-100 μm thick. When a CGO electrolyte with 1 μm thick Pt and Ni sputtered electrodes was exposed to CO, an electromagnetic field (EMF) that was proportional to the CO concentration developed across the Pt and Ni electrodes. The response of this sensor to 100-500 ppm CO in a base gas of 68%H_2/29%CO_2/ 3%H_2O at an operating temperature of 250°C is shown in Figure 2 (circles). The Pt electrode was positive with respect to the Ni electrode, indicating that CO poisoning lowers the EMF (less negative) of the Pt electrode. However, the response to CO decayed over time, probably due to some irreversible poisoning of the Ni electrode. When the sensor was operated at a negative bias of 1 μamp, the stability of the sensor was found to improve. This improvement in the stability of the sensor, shown in Figure 2 (squares), can be

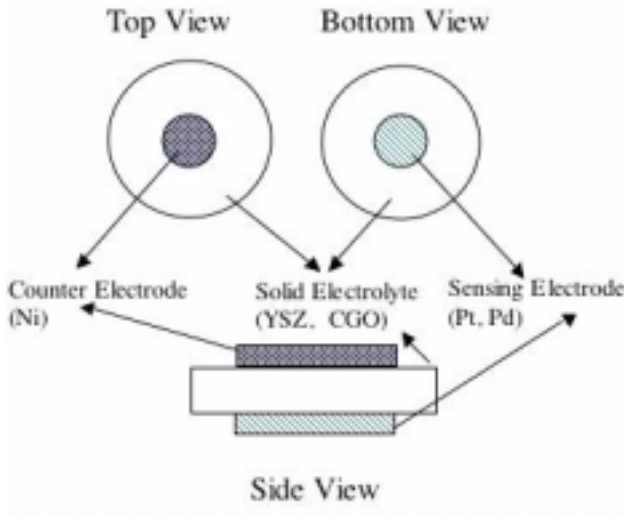

Figure 1. Schematic of Sensor Configuration

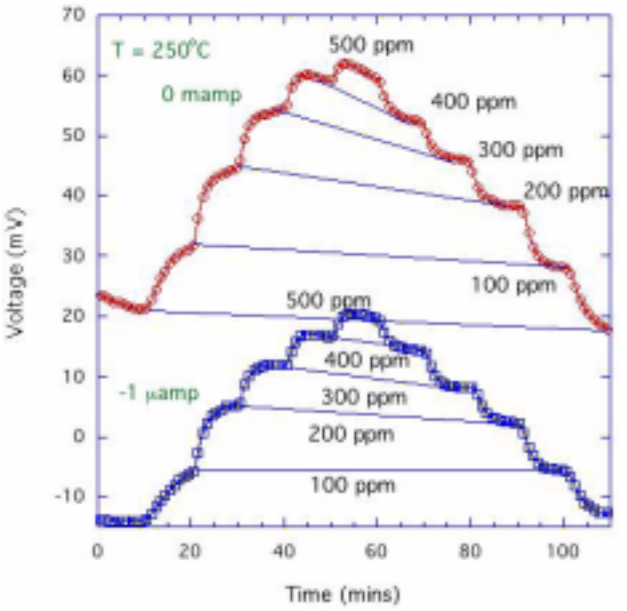

Figure 2. Response of a Pt/CGO/Ni sensor to 100-500 ppm CO in a Base Gas of 68%H_2/29%CO_2/ 3%H_2O at an Operating Temperature of 250°C [Bias = 0 μamp (circles); Bias = –1 μamp (squares).]

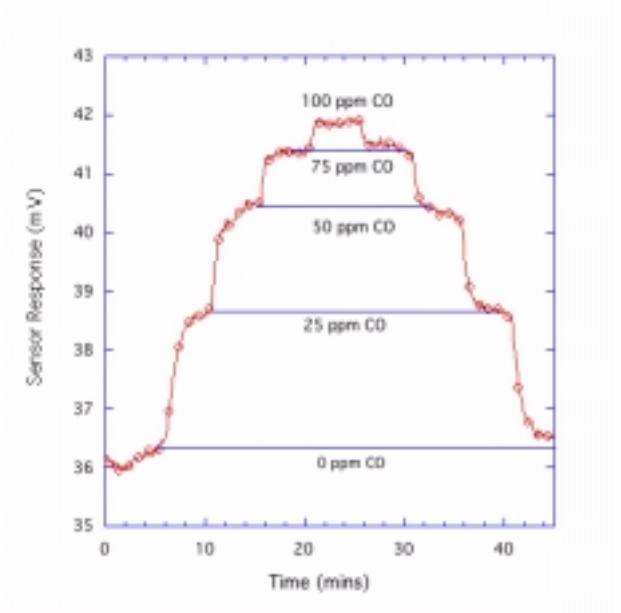

Figure 3. Response of a Pt/CGO/Ni Sensor to 25-100 ppm CO in a Base Gas of 68%H_2/29%CO_2/ 3%H_2O at an Operating Temperature of 240°C

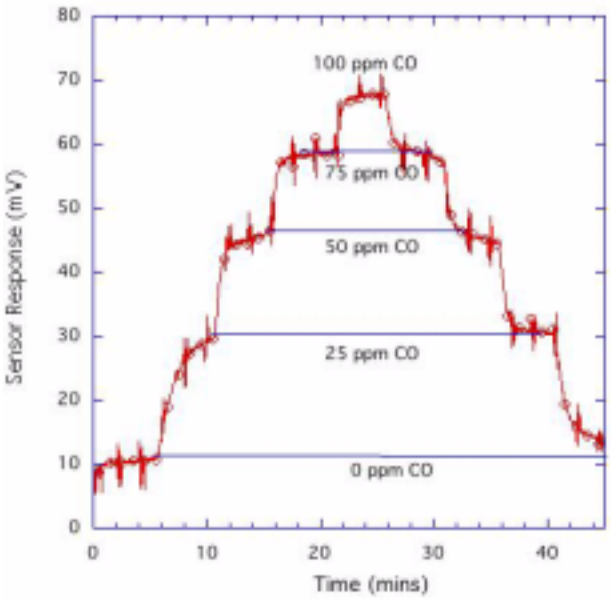

Figure 4. Response of a Pd/YSZ/Ni Sensor to 25-100 ppm CO in a Base Gas of 68%H_2/29%CO_2/ 3%H_2O at an Operating Temperature of 185°C

attributed to the cleaning of the CO from the surface of the Ni electrode.

The stability of the CGO-electrolyte based sensors was found to improve with a decrease in the operating temperature and the total exposure to CO of the sensor electrodes. This is demonstrated by the sensor response to 25-100 ppm CO at 240°C (Figure 3). A stable sensor response of 6 mV was obtained for 100 ppm of CO in a 68%H_2/29%CO_2/3%H_2O fuel stream. Moreover, this response was found to be largely independent of the H_2 and H_2O content of the fuel stream. However, this sensor did show some decay in the response when exposed to 100 ppm CO for greater than 1 hour.

The sensor response to CO was optimized by studying various electrode and electrolyte combinations, and maximum response was obtained for a sensor using a YSZ electrolyte with a sputtered Ni electrode and a brush-painted Pd electrode. This sensor had a response of 60 mV to 100 ppm CO in a base gas of 68%H_2/29%CO_2/3%H_2O at an operating temperature of 185°C, as shown in Figure 4. Although this is a 10 fold improvement in the sensor sensitivity as compared to the CGO based sensors, these sensors showed a similar decay in the sensor response when exposed to low concentrations of CO for long periods of time or high concentrations of CO for short periods. The response time of this sensor was less than 1 minute and was limited by the flow rates of the gases used in our experiment. This sensor also possessed the required sensitivity to detect 1-100 ppm of CO in the fuel inlet stream of the fuel cell stack and has the potential to be used to as a CO sensor for stack control.

Conclusions

- Developed polymer electrolyte based sensors for the monitoring of 10-100 ppm carbon monoxide at room temperature and 100-1000 ppm carbon monoxide at 70°C.
- Successfully developed oxide electrolyte based sensors for the detection of 10-100 ppm CO in the fuel inlet of a fuel cell stack. These sensors operate and T ≥ 150°C and have a response time less than 1 minute.
- Future work includes the optimization of the sensor response time and stability. The electrodes of this oxide sensor will be modified

to try and develop a CO sensor for reformer control that can measure 0.1 to 2% CO. A patterned heater will be incorporated in these sensors, and prototypes that work in a reformate stream will be demonstrated.

References

1. S. Gottesfeld and T. Zawodzinski in "*Advances in Electrochemical Science and Engineering*", **5**, pp. 219-225 (1998).

2. R. Mukundan, E. Brosha, and F. Garzon, Mixed Potential Sensors for CO Monitoring in Chemical and Biological Sensors and Analytical Methods II, PV 2001-18, pp. 464-469, The Electrochemical Society Inc. (2001).

3. Rangachary Mukundan, Eric. L. Brosha and Fernando H. Garzon, Electrodes for Solid State Gas Sensors, Patent Application Filed, S.N. 10/ 175,252, June 18, (2002).

FY 2003 Publications/Presentations

1. R. Mukundan, E. L. Brosha, and F. H. Garzon, "An electrochemical sensor for the detection of carbon monoxide in hydrogen containing streams". To be presented at the 204th Meeting of the Electrochemical Society, Florida, October 12-17 (2003).

2. R. Mukundan, E. L. Brosha, and F. H. Garzon, "A low temperature sensor for the detection of carbon monoxide in hydrogen". Presented at the SSI-14 Conference, California, June 24 (2003).

3. R. Mukundan, E. L. Brosha, and F. H. Garzon, "A low temperature sensor for the detection of carbon monoxide in hydrogen". Submitted to the special issue of the Journal of Solid State Ionics, May (2003).