IV.H.11 CO Sensors for Fuel Cell Applications

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Objectives

- Develop an intermediate temperature reformate pre-stack CO sensor to detect 1-100 ppm CO at < 150^{o}C with a response time of 0.1-1 sec and an uncertainty of 1%-10%.
- Develop a high temperature CO sensor to detect 100-1000 ppm CO at ~ 250^{o}C with a response time of 0.1-1 sec and an uncertainty of 1%-10%.

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 Research, Development and Demonstration Plan:

- B. Sensors

Approach

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

- An amperometric device based on the carbon monoxide inhibition of hydrogen oxidation kinetics at the electrodes of a 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.
- An solid oxide electrolyte device based on the kinetics of the electrode reactions is being developed for both the high and low temperature application.
  - Yttria-doped zirconia and gadolinia-doped ceria oxygen ion conductors 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.

Accomplishments

- Low temperature electrochemical sensors have been developed to sense CO concentrations between 10-1000 ppm in a reformate stream.
- The detection range and response time of the CO sensors can be tuned by adjusting the precious metal loading of the sensing electrode.

High temperature carbon monoxide sensors

High temperature zirconia and ceria-based electrochemical sensors to measure CO in hydrogen streams are also being developed at LANL. 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] In this project we are working on modifying the electrodes of these devices to enable them to work in a hydrogen atmosphere.

Results

Low temperature carbon monoxide sensors

The PEM based sensors are amperometric sensors that use adsorption of CO on the working electrode to reduce the current flow at a given potential. In previous years we demonstrated a CO sensor working at room temperature that was sensitive to 0-100 ppm CO. However when the operating temperature was raised to 70-80^{o}C, the sensitivity greatly decreased (100-1000 ppm). In this fiscal year we were able to optimize these sensors in order to successfully meet the DOE requirements (except response time at low CO concentrations) for a pre-stack CO sensor.

The sensors were made of Nafion 117 electrolyte and Pt/Ru (50/50 alloy)/Nafion pseudo reference electrodes with a precious metal loading of 10 mg/cm^2. The working electrode was either Pt/C/Nafion at a Pt loading of 0.2 mg/cm^2 or Pt/Nafion at a Pt loading of 10 mg/cm^2. The sensors (Figure 1) were approximately 0.25 cm^2 in area and were sandwiched between double-sided carbon/teflon gas diffusion layers (E-Tek). The sensors were inserted in the exhaust stream of a PrOx reactor where the total flow rate was approximately 125 L/min and the gas consisted of 0-2000 ppm CO in a 40% H_2, 25% N_2, 17.5% CO_2, 17.5% H_2O stream. A non-dispersive infrared (NDIR) CO analyzer (California Analytical Instruments) was used to measure the actual CO content of the gas downstream of the sensor.

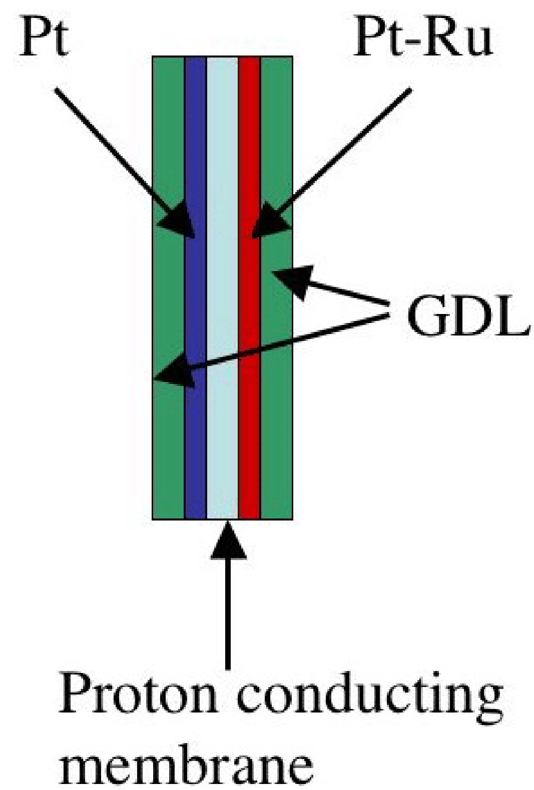

Figure 1. Schematic of a low temperature Nafion based sensor. GDL = Gas diffusion layer (E-TEK), Pt-Ru = 10 mg/cm^2 of Pt/Ru (50/50 alloy)/Nafion. Pt = either 0.2 mg/cm^2 of Pt/C/Nafion or 10 mg/cm^2 of Pt/Nafion. Proton conducting membrane = Nafion 117.

The response to 0 - 100 ppm CO of a PEM sensor with a catalyst loading of 0.2 mg/cm^2 is shown in Figure 2 along with the response of the NDIR CO analyzer. This sensor is very sensitive to low concentrations of CO where the sensor current at 0.3V decreased by 64% when the CO content increased from 0 to 100 ppm. Moreover, the response time of the sensor decreased with increasing concentrations of CO and was greater than a few minutes when the CO concentration was < 25 ppm and was 1 sec when the CO concentration was 75-100 ppm. The response of this sensor and that of the CO analyzer to cycling CO concentration between 50-150 ppm is shown in Figure 3. It is seen that the performance of this sensor is comparable to the response of the CO analyzer under these test conditions. This sensor meets all the DOE requirements except for the response time, which is

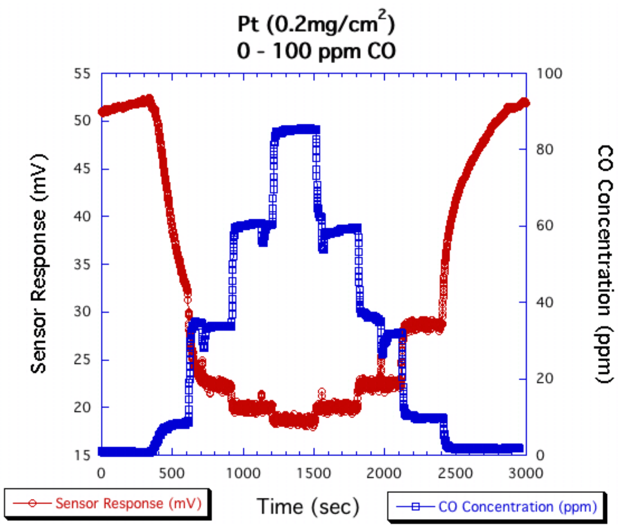

Figure 2. Response of PEM sensor with a 0.2 mg/cm^2 Pt/C/Nafion working electrode to 25, 50, 75, and 100 ppm CO at T = 85^{o}C and V = 0.3 V. The response of a NDIR CO analyzer is also shown for comparison.

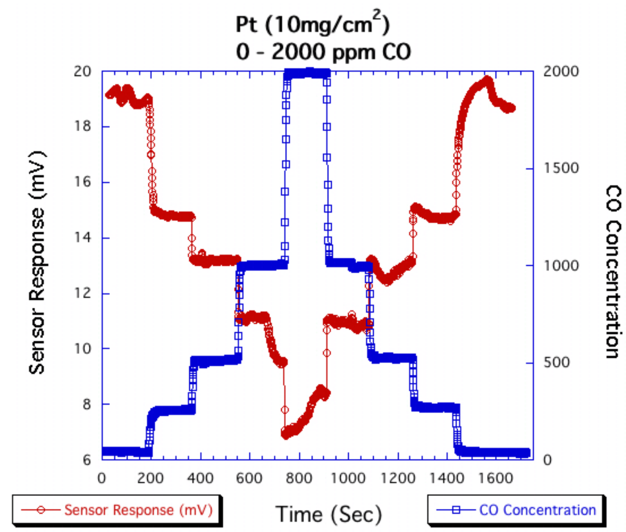

Figure 4. Response of PEM sensor with a 10 mg/cm^2 Pt/Nafion working electrode to 250, 500, 1000, and 2000 ppm CO at T = 80^{o}C and V = 0.1 V. The response of a NDIR CO analyzer is also shown for comparison.

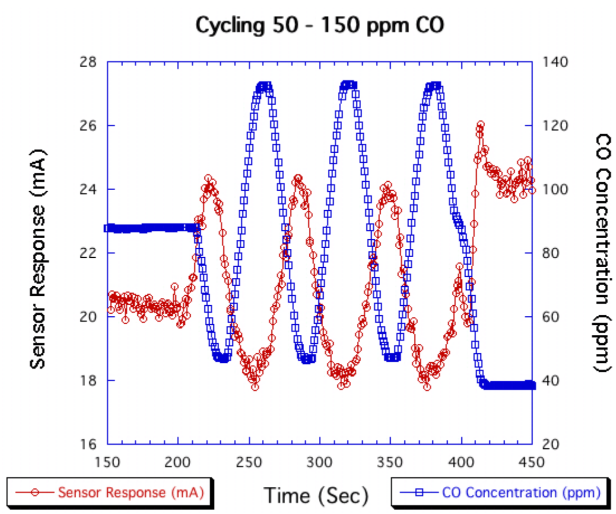

Figure 3. Response of PEM sensor with a 0.2 mg/cm^2 Pt/C/Nafion working electrode to cycling CO between 50 ppm and 150 ppm at T = 85^{o}C and V = 0.3 V. The response of a NDIR CO analyzer is also shown for comparison.

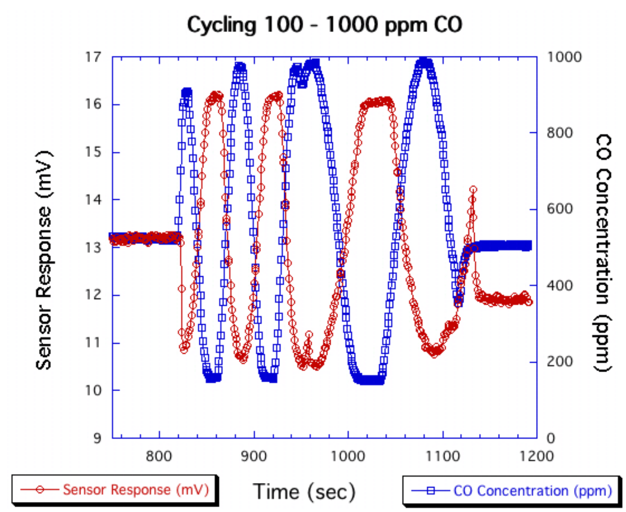

Figure 5. Response of PEM sensor with 10 mg/cm^2 Pt/Nafion working electrode to cycling CO between 100 ppm and 1000 ppm at T = 80^{o}C and V = 0.1 V. The response of a NDIR CO analyzer is also shown for comparison.

greater than DOE's prescribed 1 sec when the CO concentration drops below 75 ppm. However, this may not be a critical factor since the next generation of fuel cells is expected to be tolerant to low (< 50 ppm) levels of CO and the sensor response time improves to < 1 sec when the CO concentration is >75 ppm.

The response from the sensor with high catalyst loading (10 mg/cm^2) is presented in Figures 4 and 5. The response current at 0.1 V decreased by 68% as the

CO content increased from 0 to 2000 ppm. For this sensor, increasing the precious metal loading of the working electrode resulted in an increase in the sensor saturation limit and a decrease in the sensor sensitivity and response time. The response time of this sensor was comparable to that of the infrared analyzer at low CO concentration, while at high CO concentrations the sensor response times were significantly better than that of the analyzer. The response times of this sensor is sufficient to follow CO cycles between 100-1000 ppm with periods > 30 seconds. Therefore this sensor has the potential to monitor the inlet CO concentration to the PrOx reactor.

High temperature carbon monoxide sensors

In the previous year we had developed high temperature CO sensors based on ceria and zirconia electrolytes. A sensor with a $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) electrolyte and Ni and Pt electrodes had a response of 40 mV to 500 ppm of CO at 250°C. This sensor has the potential to monitor the input CO concentration to a PrOx reactor if its response time and stability could be improved. However, this sensor was externally heated using a furnace and could not be tested under practical conditions. During this fiscal year we designed a Pt heater (mask shown in Figure 6) that could be incorporated on the sensor body. Using standard photolithography and electron beam evaporation techniques we were able to successfully deposit a Pt strip heater on the CGO substrate of the sensor. The power requirement for this sensor was <5 watts with this heater design.

Figure 6. Mask of Heater Assembly for the High Temperature Sensors

Conclusions

- Low temperature pre-stack CO sensors based on Nafion membranes have been developed.
- The response time and sensitivity of these sensors can be tuned by adjusting the precious metal loading of the working electrode.
- A sensor with a Pt working electrode (0.2 mg/cm^2) meets all the requirements (except response time) listed by the DOE for a pre-stack CO sensor.
- The response time of these sensors is slow (several minutes) at low (<25 ppm) concentrations of CO and improves to <1 sec at high (>75 ppm) concentrations of CO.
- A heater has been incorporated into the high temperature oxide-based CO sensors reducing their power requirements to less than 5 watts.

References

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FY 2004 Publications/Presentations

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