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Mixed potential sensors utilizing a machined, dense indium-tin oxide working electrode (In_2O_3:SnO_2; 90%:10%), a Pt wire counter electrode, and porous YSZ electrolyte were prepared using ceramic tape casting methods. The response of these devices to hydrogen concentrations up to 2% in air were studied from 600 to 740°C. The sensor response exhibited a reversible behavior and a fast response time with sensitivity increasing with decreasing temperature. GC analysis confirmed significant heterogeneous oxidation of the H_2 on heated furnace tube wall surfaces thus driving sensor response at H_2 concentrations greater than a few hundred ppm. The transition to a cold wall, miniature platform heater significantly reduced hydrogen oxidation although some flow rate dependence remains.

Introduction

The DOE Hydrogen Codes and Standards program is part of an international effort to develop and establish a global technical regulation for Hydrogen/Fuel Cell Vehicles (HFCV) that attains equivalent levels of safety as those for conventional gasoline powered vehicles but does not restrict future technologies. Based on a comparison of existing regulations and standards of HFCV with conventional vehicles, the goal of the program is to investigate and consider the main differences in safety and environmental aspects and what items need to be regulated based on justification. Parallel work is being conducted by other Federal Agencies such as the DOT and NHTSA with the initiation of a four-year research program on hydrogen fuel cell vehicles that includes studies on electrical isolation, FMEA for compressed gas HFCVs, evaluation and comparative analysis of existing and draft regulations and standards, and compressed hydrogen fuel container integrity testing.

One important requirement for implementation of HFCVs is an inexpensive, reliable, and long-lived sensor (usual requirements for present day vehicles) for the detection of H_2. There are several sensor technologies that have been developed to detect hydrogen, including deployed systems to detect leaks in manned space systems and hydrogen safety sensors for laboratory and industrial usage. The most common technologies are based on catalytic bead combustible gas sensors, infrared absorption, electrochemical oxidation of hydrogen, or the resistance/capacitance change of Pd-based materials. While the Pd-based sensors have excellent selectivity, they need frequent calibration like other similar resistance measurement-based technologies. On the other hand, electrochemical sensors that operate close to room temperature (similar to commercially-available CO sensors) exhibit better stability, but possess short life times and are susceptible to poisoning or humidity cross interference. In contrast, electrochemical devices that utilize high temperature-based ceramic electrolytes are largely unaffected by changes in humidity and are more resilient to electrode or electrolyte poisoning.

As part of the Hydrogen Codes and Standards program, LANL and LLNL are working together to develop and test inexpensive, zirconia-based, mixed potential sensors for H_2 detection in air. Previous work conducted at LLNL showed that indium tin oxide (ITO) electrodes produced a stable mixed potential response in the presence of up to 5% of H_2 in air with no response to CO_2 or water vapor *(1,2)*. The sensor also showed desirable characteristics with respect to response time and resistance to aging, and degradation due to thermal cycling. In this work, we will present recent results obtained after preparing new ITO-based devices using techniques pioneered at LANL for the preparation of stable electrochemical interfaces for mixed potential type sensor applications *(3-6)*.

Experimental

Indium-tin oxide working electrodes were first prepared from a commercially available, 2” diameter RF magnetron sputtering target (Alfa, In_2O_3:SnO_2; 90%:10%). Small rectangular electrodes were cut from this source roughly 1mm x 2mm x 10mm using a diamond saw. The counter electrode consisted of annealed Pt wire, 0.01” (0.25mm) in diameter.

The electrolyte powder was first cast into a tape using a conventional tape casting process. For example, the YSZ electrolyte powder (Tosoh) was dried at 100-150°C for approximately one hour. This dried powder was mixed with solvents (xylene, ethyl alcohol and fish oil) and ball milled for 24 hours. Plasticizers and binders (S-160, UCON and B-98) were then added to this mixture and further ball milled for 24 hours. The mill was then discharged and de-aired for approximately 10 minutes at approximately 20-25 inches of Hg. This slurry was cast onto a Si-coated Mylar (G10JRM) carrier film using a standard doctor blade apparatus with a gap of approximately 0.05” to 0.2”.

Once the tape was cast, it was allowed to partially dry (approximately 10-20 minutes). This resulted in a tape that was dry on the outside (facing air) and still very wet on the inside (in contact with the carrier film). This tape was then turned upside down manually so as to expose the wet side to air while the dry side was in contact with the carrier film. The pre-fabricated electrodes were then placed on the wet surfaces of the tape as shown and the tape was folded onto itself in order to enclose the electrodes within the electrolyte (Figure 1). An alternative to folding the tape back onto itself is that another partially dry tape of approximately the same dimensions can be placed over the tape containing the electrodes with the wet sides contacting each other. This electrolyte tape, with the partially enclosed electrodes, was allowed to air dry fully to form the green sensor body. Using this procedure, individual sensors could be cut out of the green tape either by using a razor blade or scissors as shown in Figure 1. In general, as many electrode combinations as needed, can be placed in between the tapes to form multiple sensors. The electrodes can be metal wires, metal foils, ceramic pellets or ceramic tapes. Sensor arrays with more than 2 electrodes can easily be made using this method. Figure 1 shows an illustration of forming two sensors and how one of the tape cast sensor appeared after cutting the green body and removing excess YSZ electrolyte material.

After green body sensor preparation, the sensor precursors were placed onto an alumina block and placed into a box furnace for removal of organics, and sintering and densification steps. As described in greater detail elsewhere *(6)*, a sintering and densifications schedule was selected in order to insure a porous, but mechanically stable, electrolyte. This insured gas access to the dense electrodes through portions of the minimally catalytic active YSZ electrolyte.

The completed sensor was transferred either to a tube furnace (if heated by *ex-situ* means) or onto a MHI micro-platform heater (if operated in a cold-wall environment) for testing. A Keithley 2400 Sourcemeter was used to measure sensor voltages. A HP 5890 Series II gas chromatograph using a Molesieve™ 5A column, TCD detector, and UHP Ar carrier provided inlet and outlet H_2 concentrations.

Results and Discussion

Figure 2 is the response of a YSZ-based mixed potential sensor utilizing an ITO working electrode operating at 640°C to 1000, 2000, 5000, 10,000, 15,000, and 20,000ppm of H_2 in air. The heat was provided by 1” O.D. quartz tube furnace with a hot zone of approximately 6 inches long. As can be seen from Figure 2, there is a significant decrease in sensor voltage above a H_2 concentration of 15,000ppm. A sampling pump was used to extract a gas sample and pump the sample to a sampling valve on the GC inlet. The sampling loop was 0.25cc in volume. The gas chromatography experiments performed on the inlet and outlet gases to and from the tube furnace revealed that there was significant H_2 oxidation under the testing conditions. For example when 1% H_2 was used at the inlet only 0.3% was observed at the outlet indicating that 70% of the H_2 was being oxidized along our heater tube. Based on these GC experiments, the sensor response in Figure 2 is not an artifact of the sensor but rather of the effect of heterogeneous catalysis on the surfaces of the heated ceramic and glass components. The H_2 concentration actually being measured by the device is less than 2000ppm or a loss of H_2 due to catalysis of almost 90%. In previous work, we showed the influence of heterogeneous CO and HC catalysis on mixed-potential sensor selectivity *(7)* although the amount of catalysis reported in this work was not to the extent seen here.

The elimination of hot surfaces such as the long lengths of inner furnace tube surfaces and the alumina surfaces that serve as sensor support and guides for Pt lead wires would be minimized if the sensor were placed on top of a small platform heater. This would reduce the amount of H_2 heterogeneously oxidized on these heated surfaces. We obtained a small electric heater (0.75” dia.) coil from Micropyretics Heaters International. The small coil was placed on top of a porous alumina platform. We bedded the coil in alumina-based ceramic adhesive and placed a dense alumina disk on top of the coil. In this configuration, none of the surface of the electrically heated coil was exposed to the test atmosphere. The ITO/YSZ/Pt sensor that produced the results shown in Figure 2 was placed on top of the dense alumina platform and secured in place with small dabs of Aremco™ silver epoxy. The use of silver epoxy adhesive served to secure the sensor onto the platform as well as enhanced thermal conductivity from the platform to the sensor. A single type K thermocouple served to measure the surface temperature of the platform as well as serve as control input to a digital, self-tuning furnace controller. A custom quartz cap was made so that air and hydrogen would flow across the surface of the sensor while minimizing contact with the remaining exposed surfaces that may be active for the catalytic oxidation of the hydrogen.

Figure 3 is a cross section illustration of the new experimental setup that eliminates a significant amount of heated surface area. This design safely accommodated the MHI heater while minimizing the internal volume of the quartz tube compared to the previous flow-through setup. An inspection of Figure 3 will show that this configuration did introduce some dead volume; therefore, while sensor response time upon initial exposure to a given concentration of H_2 decreased, the presence of dead volume increased the time to return to baseline once the H_2 is removed from the test gas stream. The new test assembly was wired to a self-tuning furnace controller. Compressed air was flowed at 200sccm; higher flow rates cooled the sensor and increased the demands on the platform heater. The baseline stability of the newly configured sensor was monitored while the controller self tuned.

Since this experimental configuration lacked a thermocouple directly monitoring the sensor temperature, we used an initial H_2 concentration of 5000ppm to adjust the sensor temperature such that the voltage produced by the sensor could be matched to the 5000ppm voltage level obtained using the large tube furnace. The platform temperature was set at 682 ±1°C. The response to a series of H_2 concentrations was then studied. The response to 2000, 5000, 10000, 15000, and 20000ppm of H_2 in air is show in Figure 4. The sensor behaves in a similar manner to the larger tube furnace with one substantial difference: the heterogeneous catalysis was substantially reduced as the 20,000ppm H_2 level is slightly higher than the 15,000ppm level. A close inspection of Figure 4 will show excursions from the steady state voltage levels at 2000 and 10000ppm H_2; this behavior may have been caused by the cooling effect of the increased gas flow across the device and evidence of the difficulty that this particular furnace controller had to maintain a stable temperature. The stability of the sensor's temperature was optimized by self-tuning the furnace controller while fine-tuning the current supplied to the heater by making alterations to the step down transformer at the new flow rate. The flow rate was dropped to 100sccm and the device exhibited lass saturation seen in Figure 4 despite the fact that one would expect that the amount of heterogeneous catalysts would actually increase at the lower flow rate since contact time would increase.

The platform temperature was varied from 600 to 740°C and the sensor response was measured during the same applied [H_2] profile. Figure 5 shows that the sensor response voltage was lower as the sensor/platform temperature increased. Figure 5 show a large change in the voltage difference between baseline (0% H_2) and the first level (2000ppm H_2) with temperature however the voltage differences between subsequent [H_2] increases were very similar. Thus, if low-level sensitivity were preferred, a lower operating temperature would be desired; however, if discerning [H_2] levels that approach the hydrogen LEL are desired, the set-point temperature is not as important as temperature stability once the sensor is calibrated.

Figure 6 shows the flow rate dependence of the heterogeneous catalysis of the H_2 on the surfaces of the heater platform, Pt lead wires, and on the surfaces of the sensor itself. As one would expect, the faster flow rate leads to less H_2 oxidation because of reduced contact times. Figure 6 combines the sensor response from Figure 4 against the GC data measured at the Outlet from Figure 5. The sensor was periodically tested over a 300 hours and the markers in Figure 6 are the average measured voltages for each [H_2] level. The error bars represent the spread in measured sensor voltage levels. These data were fitted to logarithmic functions with excellent fit.

These last two figures illustrate how important reducing extraneous heated surface areas. Ideally, only the electro-active, triple phase interface would be at elevated temperature. These results affirm previous work *(1,2)* that the ITO working electrode is a desirable material for H_2 sensors and clearly shows compatibility with the LANL approach of utilizing dense electrodes and porous solid electrolytes. To significantly reduce the size of the device – which will reduce power requirements and greatly reduced surface area exposed to promote heterogeneous catalysis – recent advances made by LANL in thin-film mixed potential sensor development will be applied *(8,9)*. Figure 8 shows a 2mm x 2mm tape cast alumina substrate with a Pt heater applied using screen-printing methods. Co-planar, dense Pt and ITO electrodes will be applied to the top surface and a porous YSZ electrolyte will be grown on top of, and partially covering the electrodes. We have shown in previous work *(8)* that thin film–based mixed potential sensors made in this manner, preserve the well-defined electro-active interfaces demonstrated by the tape-cast sensors presented in this work. These methods and experiments will be the focus of future studies.

References

1. L.P. Martin, A-Q. Pham, R.S. Glass, *Solid State Ionics* **175** (2004) 527.
2. L.P. Martin, A.-Q. Pham, R.S. Glass, *J. Electrochem. Soc.* **152** (4) (2005) H43.
3. R. Mukundan, E. L. Brosha, and F. H. Garzon, *US Patent # 6,605,202* (2003).
4. R. Mukundan, E. L. Brosha, and F. H. Garzon, *US Patent # 6,656,336* (2003).
5. R. Mukundan, E.L. Brosha, F. Garzon, "Mixed Potential Sensors: From Understanding to Applications," ECS Transactions, 208th Meeting of the Electrochemical Society, Los Angeles, CA, (2005).
6. R. Mukundan, E.L. Brosha, and F.H. Garzon, "Tape Cast Sensors and Method for Making," Patent applied for Docket #104,887.
7. E. L. Brosha, R. Mukundan, and F. H. Garzon, "The Role of Heterogeneous Catalysis in the Gas-Sensing Selectivity of High-Temperature Mixed Potential Sensors," proceedings of the 202nd meeting of the Electrochemical Society, Salt Lake City, Utah, October 21-25, 2002.
8. F. Garzon, R. Mukundan, and E. L. Brosha, *US Patent* # 7,264,700 (2007).
9. E. L. Brosha, R. Mukundan, R. Lujan, F. H. Garzon, *Sensors and Actuators B* 119 (2006) 398.

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Figures

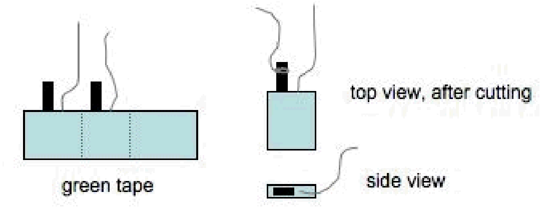

Figure 1. Illustration of tape cast method for forming mixed potential sensors utilizing dense electrodes and porous YSZ electrolyte.

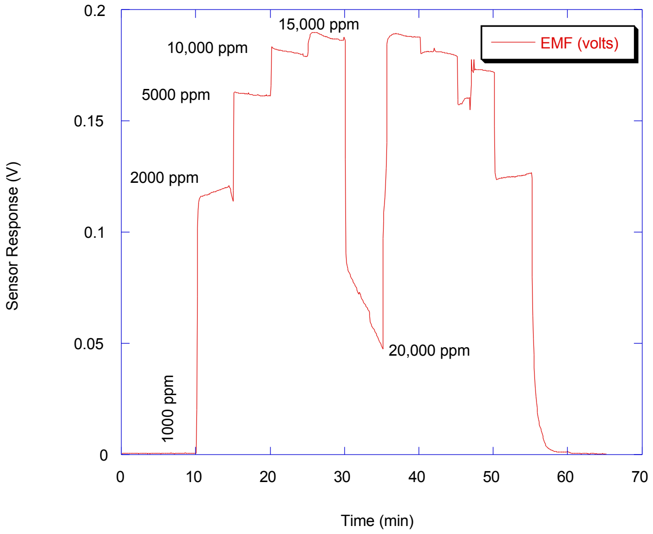

Figure 2. Response of a LANL/LLNL tape cast ITO/YSZ/Pt sensor to step-wise increases in H_2 concentration in air. Sensor temperature was 640°C maintained using a 1” O.D.

quartz tube furnace.

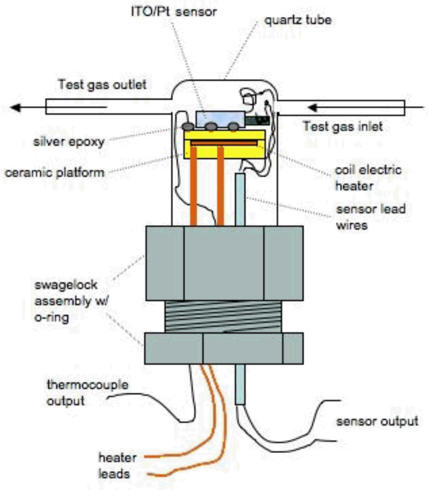

Figure 3. Low volume, cold-wall test cell incorporating a LANL/LLNL ITO mixed potential H_2 sensor mounted on top of a miniature platform electric heater.

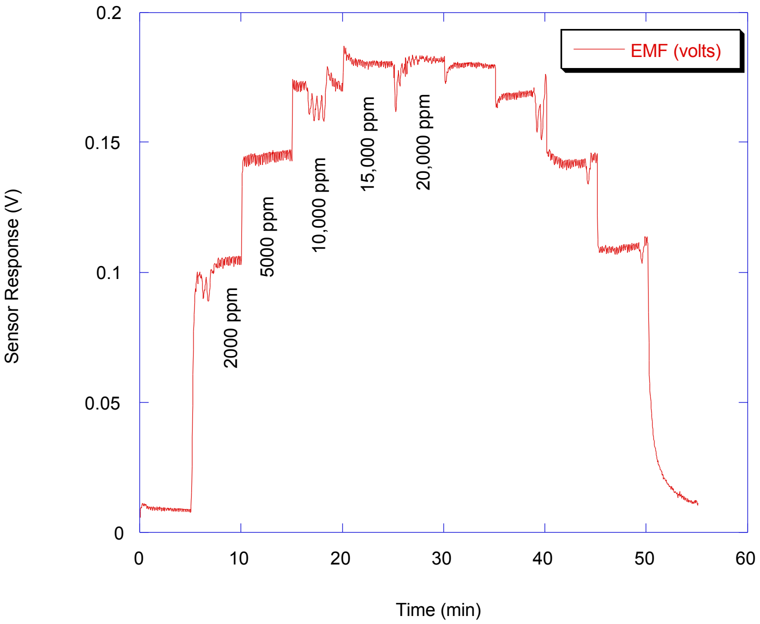

Figure 4. The response of the self-heated, ITO sensor utilizing a cold-wall set-up at a set point of 682°C to 0.2, 0.5, 1.0, 1.5, and 2.0% H_2 in air flowing at 100sccm.

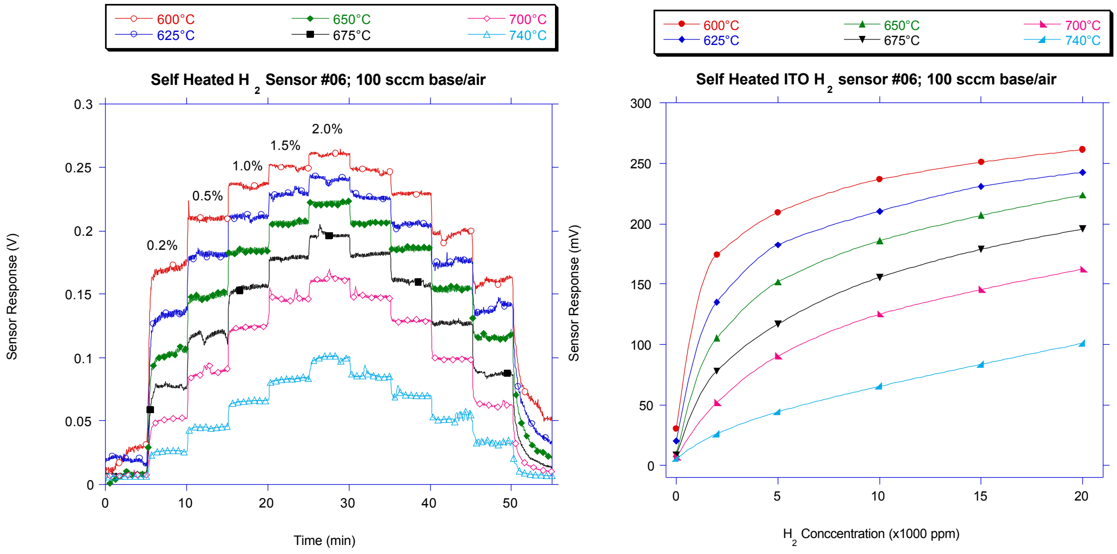

Figure 5. Temperature optimization experiments of the platform-heated ITO H_2 sensor and cold-wall set up with platform temperature maintained from 600 to 740°C.

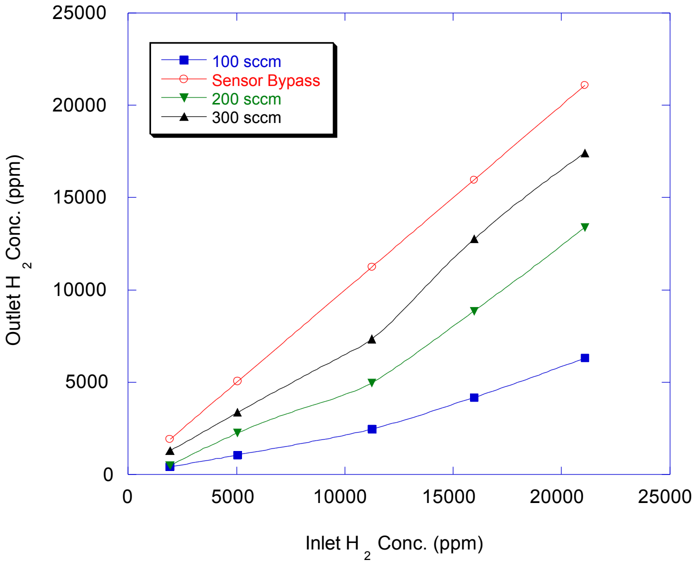

Figure 6. Inlet and outlet H_2 concentrations measured using GC analysis via and extractive sampling pump as a function of flow rate through the cold-wall cell. The sensor/platform temperature is 650°C.

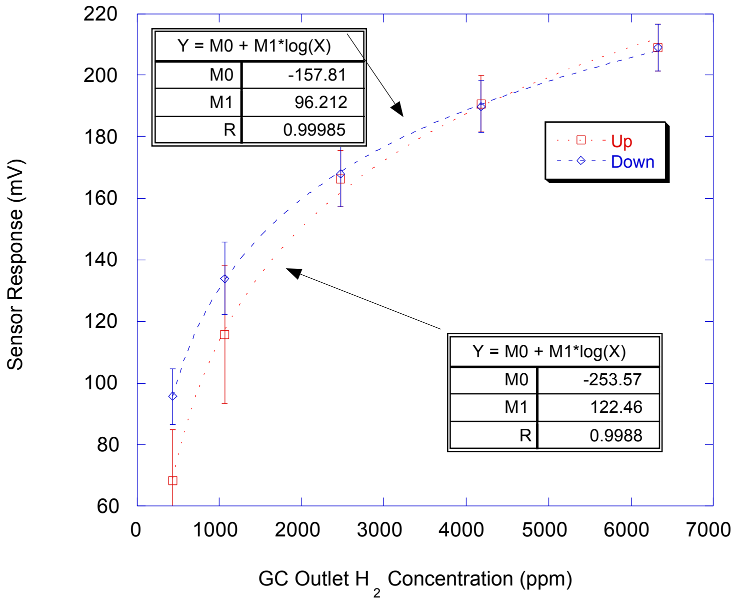

Figure 7. Plot of sensor response versus outlet H_2 concentration as determined using GC analysis at a platform temperature of 650°C. The error bars mark the range in sensor voltages recorded at fixed $[H_2]$ levels as testing was carried out over a 300-hour period.

Figure 8. To minimize power requirements, and to maximize the reduction in

heterogeneous catalysis, alumina substrates have been prepared incorporating a screen-printed Pt heater. The miniature (2mm x 2mm) substrate will support vapor deposited ITO and Pt electrodes with a porous YSZ electrolyte.