
IV.E.7 Feasibility of a SOFC Stack Integrated Optical Chemical Sensor

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Objectives

- Design of thermally stable nano-cermet using radio frequency magnetron sputtering techniques.
- Synthesis of nano-cermet with a narrow particle diameter distribution.
- Probe Au nanoparticle surface plasmon resonance (SPR) properties and Pd-YSZ (yttria-stabilized zirconia) optical properties as a function of temperature and chemical exposure.

Approach

- Synthesis of Au-YSZ nano-cermet using physical vapor deposition techniques.
- Characterize Au nanoparticles using optical and microstructural analytical techniques.
- Testing of thermal stability (500-1,000°C) of nano-cermet and their corresponding optical properties.
- Determine the thermal and chemical stability (CO, NO₂, hydrogen) of nano-cermet and the corresponding optical properties.

Accomplishments

- The detection of H₂ with a detection limit of 100 ppm using all-optical techniques was demonstrated at an operating temperature of 500°C in the presence of an air carrier gas.
- The detection of NO₂ with a detection limit of 5 ppm using all-optical techniques was demonstrated at an operating temperature of 500°C in the presence of an air carrier gas.
- Performed initial sensor testing studies for the detection of ethanol (as a representative hydrocarbon target gas) at an operating temperature of 500°C in the presence of an air carrier gas. Easily detect 150 ppm of ethanol with no obvious carbon contamination.

Future Directions

- Evaluate the long term stability of the Au-YSZ films towards both temperature and CO, H₂ and NO₂ exposures. Increase detection selectivity between the target gases
- Evaluate the sensing properties of the Au-YSZ tailored nanocomposite films for the detection of sulfur compounds

Introduction

The Department of Energy is investigating the feasibility of harsh environment compatible chemical sensors based on monitoring the surface plasmon resonance (SPR) bands of metal nanoparticle doped YSZ nano-cermet, as a function of changes in its chemical environment (e.g. exposures to CO, H₂, NO₂ and hydrocarbons) and changes in temperature (500-900°C). In particular, Au nanoparticles exhibit a strong SPR band whose shape and spectral position is not only highly dependent on the refractive index of the host medium but also on chemical reactions at the interface between the metal and the surrounding environment [1].

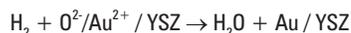
Approach

The Au-YSZ nanocomposite films are deposited using dual target confocal physical vapor deposition, with the metal and metal oxide sputtering gun deposition rates tuned to achieve the desired metal to metal oxide composition. Thermal annealing in argon at temperatures above their respective operating temperatures is used both to thermally stabilize the films and also to grow nanoparticles of a given size. Materials characterization of the films using scanning electron microscopy (SEM), Auger spectroscopy, Rutherford backscattering spectroscopy (RBS) and X-ray diffraction (XRD) analyses is used to determine the microstructural and composition properties. Ex-situ optical characterization using ultraviolet-to-visible (UV-Vis) absorption spectroscopy and spectro-ellipsometric analysis is used to correlate the material properties with the resulting optical properties. *In situ* UV-Vis spectroscopy utilizing a charge coupled device (CCD) based detection system as a function of both temperature and chemical exposure is used to determine the gas sensing properties with a time resolution on the seconds scale. Test gases include, CO, NO₂, hydrogen and hydrocarbons which will provide a range of reducing and oxidizing environments whose absorption

spectra effects combined with theoretical calculations will help deconvolute changes in both the dielectric and the chemical environment surrounding the bimetallic and metallic nanoparticles.

Results

From our previous work we have determined that O_2 at high temperatures reacts to form O_2^- which then occupy the oxygen vacancies in the YSZ matrix. In doing so, electrons are removed from the gold nanoparticle causing a redshift in the SPR band. Highlights of the last year has included further studies of the CO reaction but much of the effort this current year has included H_2 , NO_2 and ethanol sensing studies. As the reaction of CO with the bound O_2^- is a prerequisite for the oxidation of CO, it is likely that H_2 will interact in a similar manner with O_2^- and form water as the reaction product, while donating electrons back to the gold nanoparticle, as per the following reaction scheme:



The hydrogen exposure experiments we have performed cause a blue shift and a narrowing of the SPR band in support of the above reaction mechanism. The data analysis of these reactions was performed in a similar manner as done for the CO studies. The H_2 sensing signal is shown in Figure 1 and has a response time of ~ 40 s, while the recovery time has only one stage and is comparable to the response time.

We have also studied the temperature dependence of the H_2 reaction and as shown in Figure 2 for 1% hydrogen in air exposures there is no change in the SPR band at room temperature upon exposure to the hydrogen gas mixture. The reaction onset appears at a lower temperature than observed for the CO reactions at $\sim 200^\circ C$, which is still consistent with the onset of

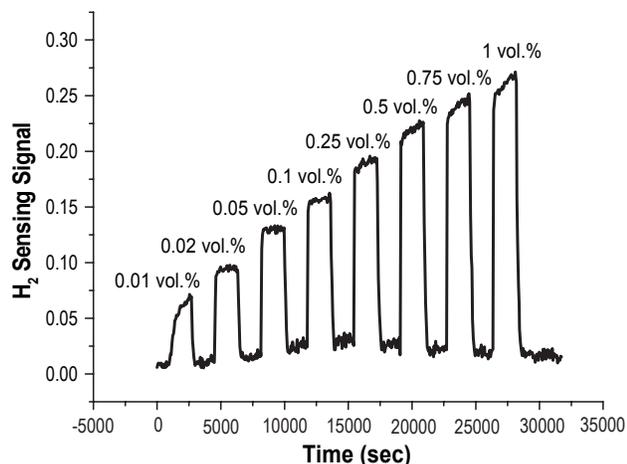


FIGURE 1. H_2 Sensing Signal as a Function of Time for Repeated 0.01, 0.02, 0.05, 0.1, 0.25, 0.5, 0.75 and 1% H_2 in Air Exposures at $500^\circ C$

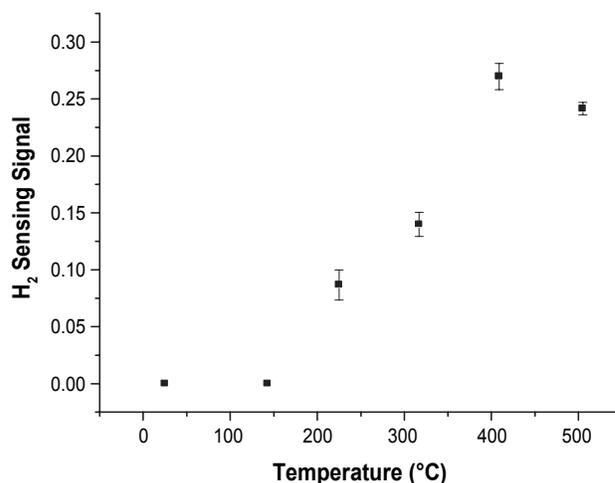
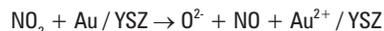


FIGURE 2. Sensing Signal Dependence on Temperature for 1% H_2 in Air Exposures

the O^{2-} formation on YSZ matrices. The H_2 sensing signal change appears to saturate at 400 and $500^\circ C$. Furthermore, the sensing signal was also dependent on the presence of oxygen as hydrogen was not detectable for H_2 mixtures in pure nitrogen at any of the operating temperatures, thus further supporting the proposed sensing mechanism.

NO_2 Sensing Studies

We have performed a series of exposure studies which demonstrate the reversible detection of NO_2 which show a detection limit of 5 ppm at $500^\circ C$ in the presence of air. The reaction of NO_2 on the Au-YSZ matrix is significantly different than the H_2 and CO studies. While H_2 and CO require a reaction with O^{2-} to induce a sensing signal, NO_2 catalytically reacts on hot gold particles forming NO and O atoms. The O atoms then subsequently react at the tri-phase boundary forming O^{2-} ions and remove electrons from the Au nanoparticles causing a red shift in the SPR band similar to that observed for O_2 reacting with the Au-YSZ matrix. A series of NO_2 exposure experiments were performed at



an operating temperature of $500^\circ C$ with NO_2 concentrations from 1 ppm to 100 ppm as shown in Figure 3 which displays signal change vs. time. The NO_2 detection limit as seen in this figure is 5 ppm with reversible signal changes observed over the entire three day experiment. As indicated in the above reaction scheme NO_2 would not require any oxygen to be present in order to induce a signal change in the SPR band. In fact, the extra oxygen present in the Au-YSZ matrix would likely cause the detection limit for NO_2 to be lower as the matrix is nearly saturated with O^{2-} ions. Initial oxygen titration experiments with oxygen at 5 and

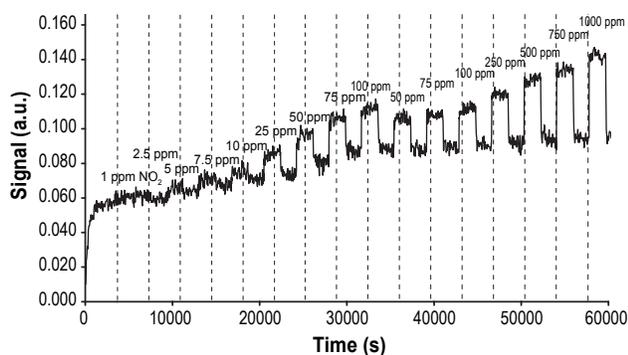


FIGURE 3. Signal Change vs. Time for NO₂ Exposures in Air at 500°C

10 vol% levels has determined that at all NO₂ levels the signal change is greater with less oxygen present in the gas mixture.

Hydrocarbon Detection – Ethanol at 500°C

The last portion of the work we have performed this year has been focused on the detection of hydrocarbons at elevated temperatures, which served as a prelude to the detection of sulfur containing hydrocarbons. Ethanol was our test hydrocarbon and its vapors were picked up and mixed into the gas stream through the use of a bubbler pick-up source. By varying the volumetric split of flow through the bubbler we are able to deliver ethanol exposures of 150, 1,500 and 5,000 ppm for these experiments. Figure 4 displays the change in sensing signal vs. time for these ethanol exposures and it is clear that we are able to reversibly detect ethanol under these conditions. Analysis of the change in the SPR band's peak position and full width at half maximum indicate that the characteristic blue shift and narrowing of the SPR band upon reaction with O²⁻, leading to electron donation back to the gold nanoparticles is the reaction mechanism for the detection of ethanol. We have performed a total of 20 hours of ethanol exposure experiments to date and at this point the detection of 150 ppm of ethanol as seen in the figures has quite a bit of contrast which should allow for future studies and development of more sensitive Au-YSZ films for the detection of hydrocarbons. However, of particular interest to the studies is that the Au-YSZ films have no obvious problems with carbon buildup due to the catalytic reaction of ethanol which should produce CO₂ and water as the by-products of this reaction. As ethanol produces a strong change in the SPR band, it is likely that we will not be able to distinguish sulfur containing hydrocarbons from non-sulfur containing

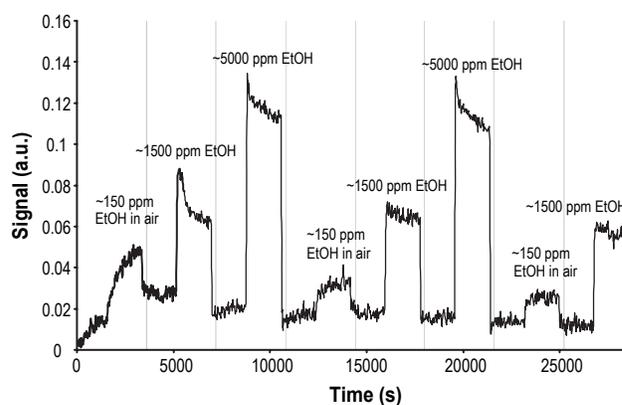


FIGURE 4. Signal Change vs. Time for Ethanol Exposures in Air at 500°C

hydrocarbons without extra treatments to our sensing materials. These are efforts that are currently being investigated so as to increase the selectivity of our materials set.

Conclusions

- Was able to demonstrate the detection of hydrogen with a detection limit of 100 ppm at an operating temperature of 500°C in the presence of air.
- The detection of NO₂ was achieved with a detection limit of 5 ppm and the sensing mechanism does not require the presence of O²⁻ ions.
- Tested the Au-YSZ nanocomposite for the detection of ethanol. The sensing mechanism is the same as that for CO and H₂. No obvious problems with carbon contamination were evident after a 20 hr exposure experiment.
- Future work would entail further development of Au-YSZ materials which provide a selective response to the target gas.

FY 2007 Publications/Presentations

1. "Development and Characterization of Au-YSZ Surface Plasmon Resonance Based Sensing Materials: High Temperature Detection of CO", George Sirinakis, Rezina Siddique, Ian Manning, Philip H. Rogers, Michael A. Carpenter, *J. Phys. Chem. B*, 110, 13508 (2006).

References

1. Kreibig, U.; Vollmer, M.; *Optical Properties of Metal Clusters*; Springer, New York, 1995.