



## Praseodymium-Cerium Oxide as a Surface-Effect Gas Sensor

TODD S. STEFANIK & HARRY L. TULLER

*Massachusetts Institute of Technology, Department of Materials Science and Engineering, Crystal Physics and Electroceramics Laboratory, Cambridge, MA 02139, USA*

Submitted February 13, 2003; Revised February 13, 2004; Accepted February 17, 2004

**Abstract.** The gas sensing behavior of praseodymium doped cerium oxide ( $\text{Pr}_x\text{Ce}_{1-x}\text{O}_2$  or PCO) has been examined for 0–1000 ppm CO or  $\text{H}_2$  in a 10%  $\text{O}_2$  atmosphere at temperatures ranging from 250–350°C. Total conductivity as a function of temperature suggests that oxygen diffusion kinetics are slow below approximately 350°C. Devices with  $x = 0.05$  and 0.10 show stable,  $n$ -type gas sensing response, while those with  $x = 0.20$  exhibit significant drift in sensor output, presumably due to bulk oxygen migration. The response to CO is significantly stronger than that to  $\text{H}_2$  at 300°C, and at 350°C the response to  $\text{H}_2$  is nearly zero, resulting in a CO-selective gas sensing element. Suggestions for the source of selectivity in PCO are presented.

**Keywords:** selectivity, sensitivity, CO sensing

Detection of low levels of oxidizing and reducing gases is essential for the monitoring and control of combustion processes, toxic gas detection and alarming, and pollution control. Surface-effect semiconductor gas sensors are often used in such applications as a result of their high sensitivity and relatively low cost. The mechanism of gas detection in such sensors is a result of the interaction of a reducing gas with adsorbed oxygen on the surface of the semiconducting oxide host material. Such adsorbed oxygen traps carriers from the semiconductor, resulting in the formation of a depletion region at the surface and grain boundaries of the sensor under ambient conditions. These depleted regions are highly resistive relative to the bulk of the material. Small amounts of reducing gas can react with adsorbed oxygen, thereby liberating charge carriers and increasing the overall conductivity of the sensor. The most common semiconducting oxide used in such applications is tin dioxide. Unfortunately, the selectivity of such sensors is often inadequate. Exposure to any reducing gas results in a decrease in the resistance of the sensor. As a result, detection of one gas in the presence of another is rather difficult.

Several schemes have been utilized in order to increase the sensitivity of semiconductor gas sensor devices, including catalytic treatments, selective filtering,

temperature scanning, and arrays of multiple sensor elements [1, 2]. At the heart of the problem, however, is the fact that relatively little can be done to alter the adsorption of different gases on the surface of the semiconducting oxide. Tin oxide, for instance is an  $n$ -type semiconductor with limited flexibility when it comes to changing the chemistry of the surface. Dopants can be added to change the overall conductivity [3], the grain size can be controlled through various processing techniques [4, 5], porosity can be introduced to expose more active surface area [6], but the surface remains largely the same composition.

Praseodymium doped cerium oxide (PCO), on the other hand, offers a wide range of flexibility in electrical properties as a function of praseodymium concentration, degree of nonstoichiometry, and high temperature thermal/ $p\text{O}_2$  history [7]. Both cerium and praseodymium oxide are known to be catalytic to redox reactions at low temperatures [8, 9], also making the solid solution a suitable candidate material for a surface-effect gas sensing device. The purpose of this study is a preliminary examination of PCO as a semiconducting gas sensor host material. The defect chemistry of the material at relatively high temperatures (600–850°C) has previously been examined [7]. A  $p\text{O}_2$  dependent ionic conductivity has been observed at high

$pO_2$ 's and impurity band electronic hopping conductivity contributes significantly to the total conductivity of the material at high  $pO_2$ 's in samples containing between 10 and 20% Pr.

## Experimental

Powders of PCO were prepared using a chemical coprecipitation route. Metal nitrate solutions mixed in the appropriate cation ratios were dripped into excess oxalic acid, forming insoluble Ce/Pr oxalates. These oxalates were calcined at 700°C to yield homogeneous PCO powders. These were isostatically pressed into pellets at 275 MPa and fired at 1425°C for 10 hours. The resulting pellets were dense (>90% in all cases, >95% for all but the 20% sample) and no secondary phases were observed. Rectangular bar samples were cut from these pellets and electroded with platinum ink for four point DC resistance measurements. The samples were placed in a large tube furnace and conductivity data were collected between 600–850°C over a wide range of  $pO_2$ 's. A defect model consistent with the observed results was devised [7]. The same samples were used to collect the sensor response data presented in this work. 10%  $O_2$  in a balance of  $N_2$  was used as a background gas, and small concentrations of  $H_2$  and CO were flowed into the furnace in order to determine sensing response at temperatures between 250°C and 350°C. While dense, bulk samples are not optimized for achieving high sensitivity and fast response times, the sensing behavior examined here is a valuable first step in determining the utility of PCO as a gas sensing material.

## Results and Discussion

At temperatures greater than 600°C, the bulk defect equilibria of PCO change as a function of  $pO_2$  and Pr content. The ratio of  $Pr^{3+}$  to  $Pr^{4+}$ , the concentration of electronic carriers, and the nonstoichiometry are not frozen in. Introduction of a reducing gas affects the bulk conductivity of the material and is not confined to surfaces and grain boundaries. In order to observe stable sensitivity to low levels of reducing gas within an oxidizing background (i.e. air), the operating temperature must be dropped to freeze in all but the defect species at the surfaces and accessible interfaces. Figure 1 shows the conductivity of 5, 10, and 20% PCO as

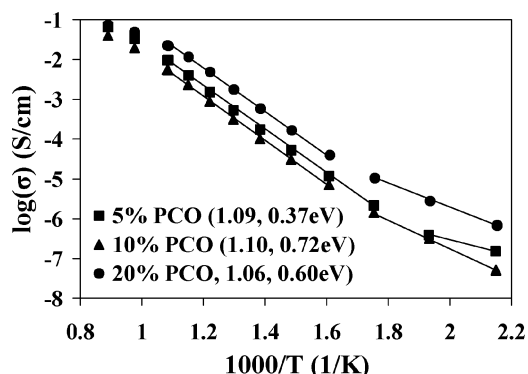


Fig. 1. Conductivity of PCO in 10%  $O_2$  as a function of temperature. Activation energies in the legend correspond to the high and low temperature regimes for each sample.

a function of temperature from 850 to 200°C in 10%  $O_2$ /90%  $N_2$ . All compositions exhibit a marked decrease in activation energy near 300–350°C. At this stage, the oxygen vacancy concentration is expected to be frozen in. As oxygen can no longer diffuse through the bulk of the material, gas reactions are confined to adsorption/desorption at all accessible surfaces.

Small amounts of test gas were introduced to the system at temperatures between 250 and 350°C. The resistance of the PCO samples was monitored as the gas exchanged and the overall sensing response was determined. As the resistance of the system decreases with additions of reducing gas, a convenient measure of the overall change in electrical response is the ratio of the original resistance to the resistance in the presence of the test gas, which is mathematically equivalent to the ratio of the conductance of the sample in a test gas to the conductance in the ambient atmosphere. Such response data is plotted as a function of time in CO concentrations ranging from 0–1000 ppm at 300°C in Fig. 2. The response is characteristic of the response of an  $n$ -type semiconducting gas sensor (i.e.; the conductance increases in the presence of a reducing gas). The response of the 5 and 10% PCO samples is smooth, reproducible, and fully reversible. The conductivity changes by a factor of 2.5 in 1000 ppm CO. The response times are very long, though as noted, the volume of the test chamber used is very large and response times are likely more a characteristic of the experimental apparatus than of the PCO sensing elements. While the initial magnitude of the response is larger in 20% PCO, the response is not stable. An initial large increase in conductance is followed by a decay of the response, and the total response

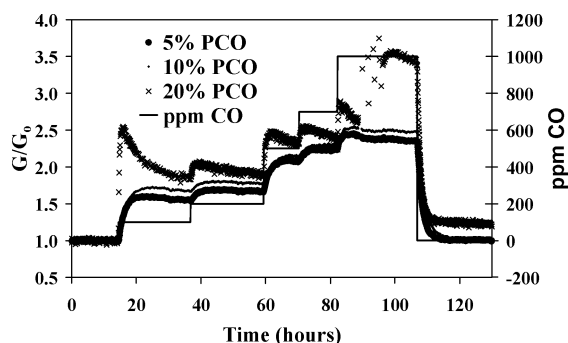


Fig. 2. Sensor response data for 5, 10, and 20%  $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$  samples at 300°C in CO. Solid line represents the set CO concentration.

is not fully reversible when the system is returned to the 10%  $\text{O}_2$  ambient. This suggests that the bulk defect structure of the 20% sample may not be fully fixed at 300°C. Additions of reducing gas may indeed react with adsorbed oxygen species at the surface, but then oxygen defects can interact with the newly established equilibrium  $p\text{O}_2$  at the surface, diffuse through the material, and establish a new bulk conductivity. The observed decrease in conductivity as the oxygen content of the grains is reduced would be consistent with a decrease in the impurity band conductivity observed at low temperatures in PCO [7].

The response to  $\text{H}_2$  additions is similar to that of CO, but the overall response is significantly lower, as shown in Fig. 3. The response of the 10% PCO sample is shown for both CO and  $\text{H}_2$  at 300°C. The maximum response in CO (at 1000 ppm) is a factor of 2.5 change in conductance; for  $\text{H}_2$  the maximum change is only a factor of 1.3. The steady state response of each composition of PCO at 300°C in CO and  $\text{H}_2$  is shown in

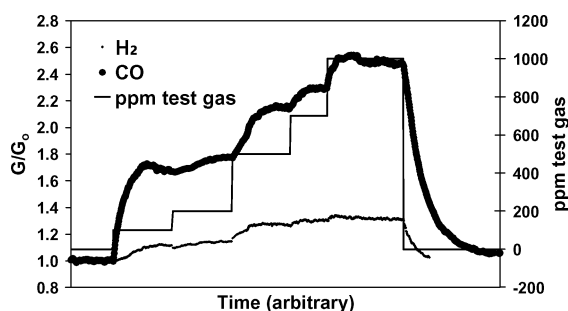
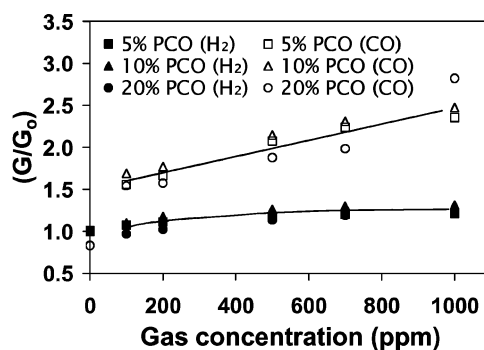
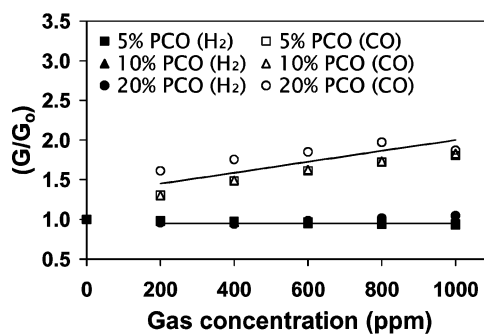


Fig. 3. Response of 10% PCO to CO and  $\text{H}_2$  at 300°C. Solid line represents the set analyte gas concentration.



(a)



(b)

Fig. 4. Steady state sensor response for PCO in CO and  $\text{H}_2$  at (a) 300°C and (b) 350°C. Dashed lines are included to emphasize trends and do not represent data fits.

Fig. 4(a). For all compositions at all CO concentrations, the response to CO is higher than the response to  $\text{H}_2$ . The response to CO is relatively linear as a function of concentration, whereas the weak response to  $\text{H}_2$  appears to saturate at concentrations approaching 1000 ppm. Figure 4(b) shows sensor response at 350°C. The response to both CO and  $\text{H}_2$  is lower overall, but the response to  $\text{H}_2$  at 350°C is nearly zero. Note that the dashed lines drawn in Fig. 4 are not best fits and are only provided to emphasize the observed trends.

PCO demonstrates selectivity towards CO over  $\text{H}_2$ . Since  $\text{H}_2$  is stronger reductant than CO, this result was not anticipated. Praseodymium is known to be a catalytic material, however. It is possible that the praseodymium in the system catalyzes the CO oxidation reaction more strongly than the  $\text{H}_2$  oxidation reaction, providing a natural, internal selection mechanism towards CO detection.

The selectivity possible in the system is very interesting and deserves further attention. The samples and

experimental apparatus used in this study were not optimized. Porous, thin film samples with closely spaced (or perhaps interdigitated) electrodes should be produced and the response of such samples should be examined in a low volume gas flow system such that the response time measured is characteristic of the sensors rather than the experimental test setup. The results presented here indicate that PCO is selective towards CO detection over H<sub>2</sub> detection, but mixtures of the two gases should be examined in order to determine cross-effects and verify selectivity toward one gas over the other.

### Summary

Preliminary studies of praseodymium doped cerium oxide show that the material can be successfully used as a semiconducting gas sensor element. The operating temperature for the  $x = 0.05$  and  $0.10$  PCO sensor elements must be held below approximately 350°C in order to ensure that the defect structure of the bulk material remains fixed. The response of the  $x = 0.20$  PCO sensors to ppm levels of reducing gas is not stable at temperatures of 300 or 350°C, indicating that the bulk defect structure of the material may not be frozen in at these temperatures. At 300°C in 10% O<sub>2</sub>/90% N<sub>2</sub>, a factor of 2.5 change in conductance is observed in a  $x = 0.10$  PCO sensing element upon the introduction of 1000 ppm CO. Response to H<sub>2</sub> is significantly lower than that of CO. At 300°C, H<sub>2</sub> response appears to saturate at concentrations approaching 1000 ppm, whereas response to CO is relatively linear. At 350°C, response to both CO and to H<sub>2</sub> is reduced, but H<sub>2</sub> response is reduced to nearly zero, indicating a high selectivity towards CO over H<sub>2</sub>. Further studies are required to optimize the microstructure of the devices and to establish the source of selectivity of CO over that of H<sub>2</sub>.

### Acknowledgments

This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD19-01-1-0566 and initially by the National Science Foundation under grant DMR-9701699.

### Addendum

Subsequent analysis of the "5% PCO" sample by wavelength dispersive spectroscopy showed that the specimen actually had 10% substitution of Pr for Ce rather than 5%. This correction has no impact on the conclusions of the manuscript.

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