

the society for solid-state and electrochemical science and technology

Influence of Adsorption and Catalytic Reaction on Sensing Properties of a Potentiometric La ₂CuO₄?/?YSZ?/?Pt Sensor

Jiho Yoo, Suman Chatterjee, F. Martin Van Assche and Eric D. Wachsman

J. Electrochem. Soc. 2007, Volume 154, Issue 7, Pages J190-J195. doi: 10.1149/1.2731305

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here

To subscribe to *Journal of The Electrochemical Society* go to: http://jes.ecsdl.org/subscriptions

© 2007 ECS - The Electrochemical Society



Influence of Adsorption and Catalytic Reaction on Sensing Properties of a Potentiometric La₂CuO₄/YSZ/Pt Sensor

Jiho Yoo,* Suman Chatterjee, F. Martin Van Assche,* and Eric D. Wachsman^{**,z}

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611-6400, USA

This study describes the gas-sensing properties of a La₂CuO₄/yttria-stabilized zirconia (YSZ)/Pt potentiometric sensor and discusses its sensing mechanism in terms of the adsorptive and catalytic behavior of the electrode materials. The sensor is highly sensitive to NO, CO, and NO₂, but virtually no response is observed for CO₂ and O₂ detection. Optimal NO sensing is obtained at ~450°C. Above 500°C, there is an abrupt decrease in sensitivity. Below 400°C, there is a saturation of the response. The sensor is NO selective against O₂, but its sensitivity is affected significantly by CO₂ and CO. This selectivity behavior is in good agreement with temperature-programmed desorption results, indicating that the NO response is very likely adsorption-related. For example, the NO chemisorption peak disappears in the presence of CO₂, which agrees with the sensor results showing a significant decrease in the NO sensitivity by CO₂ addition even though CO₂ itself shows no sensor response. (© 2007 The Electrochemical Society. [DOI: 10.1149/1.2731305] All rights reserved.

Manuscript submitted October 11, 2006; revised manuscript received February 14, 2007. Available electronically May 9, 2007.

There is a tremendous environmental and industrial need for the monitoring and control of NO_x/CO emissions during combustion processes.^{1,2} Various techniques have been attempted to detect these harmful gases effectively.^{3,4} Among the many sensing devices, solid-state sensors are of particular interest due to their small size, ease of use, and low cost. Specifically, zirconia-based solid-state O_2 sensors have been well proven in harsh combustion exhaust environments. If they are tailored to measure NO_x and CO selectively, this type of sensor can be applied to combustion process optimization, resulting in improved fuel utilization and reduced emissions. Therefore, modification of the conventional O_2 sensor has been attempted repeatedly over the last two decades.⁵

Potentiometric gas sensors assembled by the combination of a metal and semiconducting metal oxide electrode have shown high sensitivity.⁶⁻¹² However, improvement in selectivity, consistency, and stability are still necessary. One of the critical factors determining the gas-sensing properties of the potentiometric sensor is the catalytic activity of the electrodes.^{12,13} La₂CuO₄ is catalytically active for NO reduction by CO as a three-way catalyst but has limited catalytic selectivity in the presence of O₂.¹⁴⁻¹⁷ The catalytic activity of La₂CuO₄ has been attributed to its small bandgap and oxygen defects in the lattice.¹⁸ As we have previously described in our proposed potentiometric sensor mechanism "differential electrode equilibria", the semiconducting behavior of the electrodes also contributes to the potentiometric response.¹⁹ La₂CuO₄ is a semiconducting oxide and has been well established as a semiconducting NO_x sensor material.^{20,21} In this work, the resistivity increased with increasing NO concentration but decreased with increasing NO₂ concentration due to its p-type semiconducting behavior.

The concept of differential electrode equilibria is a comprehensive mechanism wherein, in addition to the generation of an electric potential by the so-called "mixed-potential mechanism", the sensing potential can also be created as a result of a difference in homogeneous gas-phase reaction kinetics and the adsorption of an oxidizing or reducing gas between two asymmetrical electrodes, even when the two electrodes are exposed to the same gas environment.^{19,22} Particularly, the detection of gases can be accomplished by the adsorption of a gaseous species and the accompanying electron transfer into (or from) the semiconducting electrode material via the resultant Fermi level change in the material. Because the electrode is in contact with a solid electrolyte blocking the flow of electronic

^z E-mail: ewach@mse.ufl.edu

charge carriers, the accumulated (or depleted) electrons, via gas adsorption, create an electrical field across the electrolyte.^{13,23}

A key issue that must be addressed for the sensor devices to be useful in combustion exhaust gas is selectivity for discrimination of the target gas. Specifically, the sensors should exhibit a highly selective response to the parts-per-million level of NO_x in the presence of high and varying O_2 , H_2O , CO_2 , CO, and hydrocarbon concentrations. In this work, the sensing properties of an asymmetric potentiometric sensor [La₂CuO₄/yttria-stabilized zirconia (YSZ)/Pt] are reported with an emphasis on the NO selectivity. In addition, gas adsorption on and catalytic reactions by sensor elements of a La₂CuO₄-based potentiometric sensor were investigated using temperature-programmed desorption (TPD) and reaction (TPR). The discussion focuses on how the gas-sensing response is affected by the adsorptive and catalytic behavior of the electrodes.

Experimental

Synthesis and characterization of La_2CuO_4 .— La_2CuO_4 powder was synthesized by the autoignition technique.²⁴ A stoichiometric mixture of $La(NO_3)_3 \cdot 6H_2O$ (Kanto Chemical Co., 99.99%) and $Cu(NO_3)_2 \cdot xH_2O$ (Alfa Aesar, 99.999%) was dissolved in deionized water and subsequently 0.25 mol % citric acid (Alfa Aesar, 99.5%) was added to the mixture. The solution was heated at ~70°C with constant stirring until a precipitate was formed, and then the precipitate was autoignited with further heating at ~90°C. The resulting powder was calcined at 600°C for 10 h.

X-ray powder diffraction [XRD, Philips APD 3720 automated diffractometer (Cu K α radiation, $\lambda = 1.54178$ Å)] was utilized to characterize the phase homogeneity of the La₂CuO₄. Step scans were performed with 2 θ interval = 0.02° and a retention time of 5 s at every step in the 20° $\leq 2\theta \leq 60^{\circ}$ range.

Sensor experiments.— Details of the procedure for the preparation of the sensor electrodes are described elsewhere.^{16,25} La₂CuO₄ slurry for screen-printing was prepared by mixing the powder with polyethylene glycol 400 (PEG-400, Avocado Research Chemicals Ltd.) as a dispersant. Asymmetric planar sensors were fabricated by screen-printing the La₂CuO₄ slurry on one face of an 8 mol % Y₂O₃-doped ZrO₂ substrate (Marketech International Inc., YSZ-8Y, 20 × 12 × 0.1 mm) and platinum paste (Heraeus, Conductor paste CL11-5349) on the other face. The screen-printed sensor was then sintered at 800 °C for 10 h. Micrographs of the electrodes were obtained using a scanning electron microscope (SEM, JEOL JSM 6400 SEM).

Both electrodes of the sensor $[(+) \text{La}_2\text{CuO}_4/\text{YSZ-8Y/Pt} (-)]$ were exposed to the same gas atmosphere. Sensing response was monitored with increasing and then decreasing concentration steps

^{*} Electrochemical Society Student Member.

^{**} Electrochemical Society Active Member.

of sensed gases. The total gas-flow rate was 300 cm³/min and the retention time at every step was 200-300 s. First, the electromotive force (emf) changes were recorded while varying the concentration of NO, CO, NO₂, O₂, and CO₂, at 450°C. Then, the temperature dependence of NO, CO, and NO₂ sensitivity was measured at 350-600°C. Finally, the NO selectivity against O₂ in N₂ balance and against CO₂, CO, H₂O, and NO₂ was investigated in 3% O₂ with N₂ balance.

TPD and TPR experiments.— A brief procedure of the TPD experiments is described below.^{16,26} The TPD was performed to investigate the adsorption characteristics of exhaust gases such as NO, CO, NO₂, O₂, CO₂, and their mixtures on 0.043 g La₂CuO₄ powder [total Brunauer–Emmett–Teller (BET) surface area $\sim 0.15 \text{ m}^2$]. The powder was presintered at 800°C for 10 h before loading in the quartz reactor to prevent microstructural changes during the TPD measurements. The TPD experiments started with adsorption of a gas (or gas mixture) at 300°C for 30 min. The reactor was cooled down to 50°C at 5°C/min and then purged with helium at 50°C. The temperature was increased from 50 to 800°C at 30°C/min under helium while measuring the concentration of effluent gases with a quadrupole mass spectrometer (QMS, Extrel 150-QC). We scanned m/e = 12(C), 14 (N), 28 (CO or N₂), 30 (NO), 32 (O₂), 44 $(CO_2 \text{ or } N_2O)$, and 46 (NO_2) .

In order to determine the catalytic activity of the sensor electrode, gas reactions catalyzed by the La_2CuO_4 thick film on a YSZ-8Y substrate were analyzed using TPR.^{16,26} The same procedure used in the sensor experiments was repeated for the preparation of the TPR sample, except that only one face of the YSZ-8Y substrate was screen-printed. A mixture of a reactant gas (NO₂, NO, CO, O₂, or CO₂) flowed with a flow rate = $30 \text{ cm}^3/\text{min}$ through the reactor at 50°C. When the gas flow was stabilized, temperature was increased from 50 to 800°C at 30°C/min with reactant gas flow while measuring the concentration of effluent gases with the QMS. The same masses were scanned in the TPR as in the TPD measurements.

The present TPR conditions (gas concentration and flow rate) were chosen for experimental convenience and mass spectrometer sensitivity. They are, however, somewhat different from the sensor measurement conditions. In order to compare TPR and sensor results, the TPR experiments were also done under reduced flow rate (matching space velocity) and with 3% O₂ concentration to more closely match the sensor experimental conditions. The difference made by the TPR experimental condition change was found to be within general reproducibility limits for all the TPRs.²⁶

Results and Discussion

Characterization of La_2CuO_4 powder and electrode.— The XRD pattern of the La₂CuO₄ powder is shown in Fig. 1. The



Figure 1. (Color online) XRD pattern of La₂CuO₄ powder calcined at 600°C for 10 h. * indicate peaks due to minor impurity phases.



Figure 2. SEMs of (a) La₂CuO₄ electrode surface and (b) cross section.

K₂NiF₄-type structure corresponding to that of La₂CuO₄ is shown in the powder diffractogram with very weak impurity peaks (asterisks in the figure), due to a minor copper oxide phase.

Figure 2a and b shows scanning electron images of the La₂CuO₄ electrode surface and cross section, respectively, deposited on the YSZ-8Y substrate. The film exhibits a very porous microstructure with 0.1-0.5 µm grains and is 18-25 µm thick. The screen-printed Pt is $\sim 10 \ \mu m$ thick and also has a porous microstructure.

Gas sensitivity.— Response to NO, CO, NO₂, CO₂, and O₂.— The sensitivity to NO, CO, NO₂, and CO₂ was measured in 3% O₂ with N₂ balance, and to O₂ in N₂ balance, at 450°C (Fig. 3). The sensor is highly sensitive to NO, CO, and NO₂, whereas there is virtually no response to O2 and CO2. Values of the emf measured for 650 ppm NO, CO, and NO₂ are approximately 19, 57, and -47 mV, respectively. The slopes are generally linear and the highest slope is obtained in the CO plot.

The direction of the sensor response based on the p-type semiconducting La₂CuO₄ is positive for reducing gases (NO and CO) and negative for oxidizing gas (NO_2) . This is the exact opposite of previous results obtained at 650°C with an n-type semiconducting WO3-based sensor of the same configuration, showing a positive response for NO₂ detection and a negative for NO and CO,²⁵ and is an indication that the sensing mechanism is related to the semiconducting behavior of the oxide electrode.

Temperature dependence of NO sensitivity .-- The temperature dependence of the NO response was investigated in 3% O₂ at 350 < T < 600 °C (Fig. 4). The sensor response is generally rapid at T > 450 °C, with a new steady-state attained within < 70 s and response time becoming more rapid as temperature increases (Fig. 4a). The magnitude of the response increases with decreasing temperature. A linear relationship is obtained in the plot of the emf vs the

60 COSensor EMF (mV) 30 CO₂ NC 0 X)-O -30 NO₂ -60 10^{4} 10^{3} 10^{5} 10^{2} Gas Concentration (ppm)

Figure 3. (Color online) La₂CuO₄-based sensor response to NO, CO, NO₂, and CO_2 in 3% O_2 with N_2 balance and to O_2 in N_2 balance at 450°C.



Figure 4. (Color online) NO sensitivity of La₂CuO₄-based sensor in 3% O₂ with N₂ balance at 350–550°C: (a) plots of sensor emf (mV) vs time (s) and (b) vs NO concentration (ppm). The concentration steps in (a) are 50, 100, 200, 400, and 650 ppm NO at all the temperatures. The lines drawn in (b) are logarithmic fits.

logarithm of NO concentration at $T \ge 400^{\circ}$ C and the slope increases with decreasing temperature (Fig. 4b). Above 500°C, values of the emf are very small; for example, less than 2 mV is produced for 650 ppm NO at 550°C. Nearly no response was observed at 600°C (not shown). At 400°C and below, the response is less stable and saturates in the higher NO concentration region. At 350°C, the sensor response in fact switches to a small and negative slope, indicating a change in mechanism.

Considering response time and sensitivity, optimal sensor response is obtained at ~ 450 °C. Therefore, further measurements (the NO selectivity experiments) were performed at 450 °C, as described in the NO selectivity section. The measurements of the NO sensitivity at 450 °C show good reproducibility between different measurements repeated over 300 h under the same condition, as shown in Fig. 5. The slopes in the plots are similar to each other, but values of the emf are slightly gas-history dependent, most likely due to incomplete desorption of the gaseous species from previous measurement.

We reported¹⁶ that in NO and NO + O₂ TPR experiments of La_2CuO_4 powder, no observable NO or NO₂ concentration changes, associated with homogeneous gas-phase or heterogeneous gas-solid reactions (direct decomposition of NO to N₂ and O₂ or oxidation of NO to NO₂), were observed up to 800°C. Thus, any catalytic mechanism seems to be unlikely and the NO sensitivity due to NO adsorption and the resulting change in Fermi level of the oxide is the more likely mechanism.¹⁹



Figure 5. (Color online) Reproducibility of NO sensitivity measurements repeated over 300 h under the same condition (in $3\% O_2$ at 450°C). The numbers labeled in the figure indicate a sequence of the measurements with elapsed time.



Figure 6. (Color online) TPD of NO over La₂CuO₄ powder.

The NO desorption profile obtained from the NO TPD is shown in Fig. 6. Initially, the powder was exposed to 1000 ppm NO in helium. Nitric oxide is physically (desorption peak max. $\sim 150^{\circ}$ C) and chemically (desorption peak max. $\sim 280^{\circ}$ C) adsorbed onto the oxide surface at $T < 400^{\circ}$ C, thus saturating the surface and sensor response at low temperatures (Fig. 4).

Temperature dependence of CO sensitivity.— The CO sensitivity at $300 < T < 550^{\circ}$ C is presented in Fig. 7. The sensor response is generally rapid, such that even at $T = 350^{\circ}$ C, the response to the CO concentration change is completed within 150 s (Fig. 7a). The CO response time becomes shorter with increasing temperature. The plots of the sensor emf vs the logarithm of CO concentration are generally linear at all the temperatures (Fig. 7b). The CO sensitivity is strongly temperature-dependent and an abrupt decrease in the sensitivity is shown at $T \ge 500^{\circ}$ C; values of the emf corresponding to 100 ppm CO are ~130 mV at 300°C, ~78 mV at 350°C, ~23 mV at 450°C, and ~3 mV at 500°C, and negligible CO response is observed at 550°C.

At 300°C, the sensor shows the highest values of the emf, but the response becomes unstable and varies depending on the direction of the CO concentration change (increasing or decreasing), resulting in an unsymmetrical plot. The sensitivity achieved at temperatures as low as 300°C is surprising in terms of the mixed potential theory, because at this temperature the exchange current is expected to be extremely small. In addition, there are no reported mixed-potential-type potentiometric sensors based on a stabilized zirconia electrolyte working below 400°C.⁶⁻¹¹ These results indicate that CO sensing at



Figure 7. (Color online) CO sensitivity of La₂CuO₄-based sensor in 3% O₂ with N₂ balance at 300–550°C: (a) plots of sensor emf (mV) vs time (s) and (b) vs CO concentration (ppm). The concentration steps in (a) are 50, 100, 200, 400, and 650 ppm CO at all the temperatures. The lines drawn in (b) are logarithmic fits.



Figure 8. (Color online) (a) TPD of CO + O_2 over La₂CuO₄ powder and (b) TPR of CO + O_2 over La₂CuO₄ on YSZ-8Y.

low temperatures is probably not related to electrocatalytic phenomena ("mixed potential") but rather to asymmetric adsorption/ desorption phenomena.

The mechanism and temperature dependence of CO sensing was studied further by TPD of La₂CuO₄ powder and TPR of La₂CuO₄ electrodes on YSZ substrates. The results of the CO + O₂ TPD on the La₂CuO₄ powder are presented in Fig. 8a. For the TPD, an adsorption of 500 ppm CO and 1% O₂ was used. Broad desorption of CO₂ and CO occurs at the same temperature region (150–500°C) with the peak maximum positioned at ~300°C (Fig. 8a). Significantly more CO₂ is desorbed than CO, indicating that either the surface CO is oxidized to CO₂ in the desorption step or exists in an oxidized surface CO_x species. The fact that CO and CO₂ continue to desorb up to 500°C indicates that a CO_x species is strongly bound to the La₂CuO₄ surface. The rapid O₂ evolution above 600°C is due to lattice oxygen and indicates that the La₂CuO₄ surface was not reduced by CO in the presence of O₂ and gives credence to the concept of an oxidized surface CO_x species.

As can be seen in the TPD (Fig. 8a) and both TPRs (Fig. 8b and 9) La_2CuO_4 is highly catalytic for the oxidation of CO

$$\operatorname{CO} + \frac{1}{2} \operatorname{O} \rightleftharpoons \operatorname{CO}_2$$
 [1]

In fact, above $\sim 320^{\circ}$ C the activity of La₂CuO₄ on YSZ-8Y for CO oxidation is higher than that of Pt on YSZ-8Y (Fig. 9).

This would imply a catalytic mechanism; however, at $T \leq 300^{\circ}$ C the relative activity for CO oxidation over La₂CuO₄ on YSZ-8Y is less than Pt on YSZ-8Y (Fig. 9). If the sensing mecha-



Figure 9. (Color online) Comparison of CO + O_2 TPR results between La₂CuO₄ on YSZ-8Y (L + Y) and Pt on YSZ-8Y (Pt + Y).²⁶



Figure 10. (Color online) NO₂ sensitivity of La₂CuO₄-based sensor in 3% O₂ with N₂ balance at 450–600°C: (a) plots of sensor emf (mV) vs time (s) and (b) vs NO₂ concentration (ppm). The concentration steps in (a) are 50, 100, 200, 400, and 650 ppm CO at all the temperatures. The lines drawn in (b) are logarithmic fits.

nism was due to the differential heterogeneous catalytic activity for CO oxidation, resulting in a differential decrease in local pO_2 at the TPB of the two electrodes and a corresponding Nernstian voltage, then the sensor would exhibit a positive emf at one temperature region transitioning to a negative emf at the other, with a zero emf at ~300°C. In fact, an apparent maximum in sensor voltage is obtained at ~300°C, ruling out this mechanism.

Similarly, if the sensing mechanism was electrochemical in nature (e.g., mixed potential) via the anodic reaction 13,26

$$CO_{(gas)} + O^x_{O_{(lattice)}} \rightleftharpoons CO_{2(gas)} + V^{\infty}_{O_{(lattice)}} + 2e^{-}$$
 [2]

then the differential heterogeneous catalytic activity for CO oxidation would result in a differential decrease in local pCO between the TPB of the two electrodes and a corresponding mixed-potential response. Therefore, the sensor would exhibit a positive (mixedpotential) emf at one temperature region transitioning to a negative (mixed-potential) emf at the other, with a zero emf at ~300°C. Due to the apparent maxima in sensor voltage obtained at ~300°C, this does not appear to be the appropriate mechanism.

In addition, a positive CO response at temperatures greater than 300° C cannot be explained based on the difference in the CO oxidation activity (Fig. 9), because according to the catalytic mechanism, the lower CO concentration at the La₂CuO₄ electrode than at the Pt should end up with a negative response, opposite to the experimental results.

Finally, the magnitude of the sensor response increases with decreasing temperature from 550 to 300°C (Fig. 7), which is consistent with the CO/CO₂ TPD profiles (Fig. 8a) that show a desorption maximum at 300°C and extended but decreasing CO_x coverage up to ~550°C. This appears to indicate that CO sensing is adsorption-related, similar to NO sensing.

Temperature dependence of NO_2 sensitivity.— The temperature dependence of the NO_2 sensitivity was studied, as shown in Fig. 10. The NO_2 response at $T \ge 500^{\circ}$ C is fast enough to attain a new steady state in less than 100 s and is symmetrical between increasing and decreasing NO_2 concentration steps. However, the response at 450°C, while significantly greater, becomes slow and varies depending on whether the measurements were obtained with increasing or decreasing concentration steps (Fig. 10a). As stated previously, this is probably due to the difference between adsorption and desorption kinetics.²⁵

At $T \le 400$ °C, the sensor response is so unstable and saturated that no meaningful reading is achieved (not shown). The NO₂ response, as with NO and CO, is strongly temperature dependent, with both magnitude and slope decreasing with increasing measurement temperature. The emf value obtained for 650 ppm NO₂ is approximately -47 mV at 450 °C and -3 mV at 600 °C (Fig. 10b).

The desorption profiles obtained in the NO_2 TPD over La_2CuO_4 powder show significant, strong surface adsorption (Fig. 11a). Not only does NO_2 exhibit strong chemisorption but it involves multiple



Figure 11. (Color online) (a) TPD of NO_2 over La_2CuO_4 powder and (b) TPR of $NO_2 + O_2$ over La_2CuO_4 on YSZ-8Y.

adsorbed NO_x surface species. NO₂ begins desorption at ~230°C with a peak max ~280°C. Further, the NO₂ desorption peak is concomitant with an even larger NO desorption peak. A second NO desorption peak at ~400°C is concomitant with an O₂ desorption peak, indicating decomposition of a surface nitrate species. Thus, a series of complex reaction steps occur on the surface of La₂CuO₄ at the lower end of the temperature range, where it is most sensitive to NO₂. Further, at the upper end (T > 600°C) lattice oxygen is emitted, which would dramatically alter the sensing mechanism.

The NO₂ + O₂ TPR results over the La₂CuO₄ on YSZ-8Y show that above 350°C, NO₂ is decomposed to NO (Eq. 3), with a steep slope at 400 < T < 500°C, and by 600°C, NO₂ is almost completely decomposed (Fig. 11b).

$$NO_2 \Rightarrow NO + \frac{1}{2}O$$
 [3]

Interestingly, the NO₂ decomposition activity of the La₂CuO₄ on YSZ-8Y is identical (within experimental error) to that of the Pt on YSZ-8Y (Fig. 12).²⁶ This similarity rules out NO₂ sensing due to a catalytic difference for Eq. 3 between the electrodes creating any differential pNO₂ or pO₂ between the electrodes.

The TPD desorption profiles (Fig. 11a) show strongly adsorbed NO_x species to just beyond ~450°C, with a trailing NO shoulder extending to almost ~600°C. At 450°C the sensor exhibits a large but asymmetric signal. This is probably due to the nonequilibrium associated with desorption kinetics that are relatively slow as compared to the rate of adsorption. This nonequilibrium becomes more



Figure 12. (Color online) Comparison of $NO_2 + O_2$ TPR results between La_2CuO_4 on YSZ-8Y and Pt on YSZ-8Y.²⁶ L + Y and Pt + Y correspond to La_2CuO_4 on YSZ-8Y and Pt on YSZ-8Y, respectively.



Figure 13. (Color online) Effect of O_2 , CO_2 , CO_1 , H_2O_2 , and NO_2 on the NO response at 450°C: (a) O_2 effect (3–30%), (b) CO_2 effect (0–16%), (c) CO effect (0–200 ppm), (d) H_2O effect (0–3%), and (e) NO_2 effect (0–400 ppm), measured in N_2 balance for (a) and in 3% O_2 with N_2 balance for (b–e).

severe below 400 °C, and therefore, meaningful sensor results were not achieved, most likely due to surface saturation.

Above ~450°C faster desorption rates would allow attainment of equilibria with adsorption. Because La₂CuO₄ exhibits a p-type semiconducting sensor response to NO and NO₂, a corresponding change in Fermi level could explain the potentiometric sensor mechanism in this temperature range. In addition, differential electrocatalytic reactions such as Eq. 4 may also contribute to symmetric NO₂ sensing

$$NO_{2(gas)} + V_{O_{(lattice)}}^{\circ\circ} + 2e^{-} \Longrightarrow NO_{(gas)} + O_{O_{(lattice)}}^{x}$$
[4]

NO selectivity against O₂, H₂O, CO₂, CO, and NO₂.— The NO selectivity of the sensor was studied at 450°C against O2 in N2 and against CO₂, CO, H₂O, and NO₂ in 3% O₂ (Fig. 13). The NO sensitivity is not significantly affected by 3-30% O2 concentration change (Fig. 13a). The difference in the emf values made by the O_2 change is always small (at most 2 mV) at the same NO concentration steps. The NO desorption profile obtained from the NO + O_2 TPD over the La₂CuO₄ powder after exposing to 1000 ppm NO and 1% O₂ for adsorption is presented in Fig. 14a. Two well-defined NO desorption peaks in the NO + O_2 TPD profiles are attained at same the temperatures (~150 and ~ 280° C) where the desorption peaks are obtained in the NO TPD (Fig. 6). Additionally, the magnitude of the two desorption peaks shown in the NO + O_2 TPD is very similar to that in the NO TPD. These results indicate that the NO adsorption on the La_2CuO_4 is not affected by the addition of O_2 . Therefore, the idea that the NO sensitivity is adsorptive in nature (Gas sensitivity section) seems reasonable, because the NO adsorption is not influenced by the presence of O2, consistent with the selective NO detection against pO_2 change. In contrast, the gas sensitivity at higher temperatures, where gas adsorption is negligible due to fast desorption kinetics and the catalytic behavior is believed to be dominant, is strongly affected by a change in the pO_2 .^{25,27,28}



Figure 14. (Color online) TPD over La2CuO4 powder: (a) TPD of NO + O_2 and (b) TPD of NO + CO_2 .

Even though the sensor shows no response to CO_2 (Fig. 3), the effect of CO₂ on the NO sensitivity is significant, reducing the sensor signal and reversing the direction of response by adding 16% CO_2 (Fig. 13b). This coincides with the results of the NO + CO_2 TPD (Fig. 14b). When NO and CO₂ coexist, a broad and intense CO₂ peak replaced the NO chemisorption peak observed in the NO-related TPD (Fig. 6 and 14a), and only the weaker NO physisorption peak remains at ~ 150 °C.¹⁶ Therefore, the decrement in the NO sensitivity, by nonsensed CO₂ (Fig. 3), occurs due to elimination of NO chemisorption by CO₂. In contrast, potentiometric sensors based on different oxide electrodes (WO₃) are capable of detecting NO selectively against CO2 in the regime of catalysis control $(T > 600^{\circ} \text{C})$.²

Addition of CO (30-200 ppm) decreases the slope (i.e., the NO sensitivity) gradually but increases the emf values (Fig. 13c). This is surprising, because the response of the sensor to NO and CO are both positive. Thus, one would expect an additive response. We find by TPD (Fig. 15a) that the presence of CO enhances NO adsorption, so that NO continues to desorb up to 800°C (compare Fig. 15a and ¹⁶ Thus, the decrease in sensitivity with CO addition can be 14a). described in terms of the surface saturation that is exhibited for the NO response alone below 400°C (Fig. 4). The intense CO₂ desorption peak at 200–500 °C in the NO + CO + O_2 TPD probably forms by the surface reactions of CO with adsorbed oxygen or lattice oxygen. During the NO + CO + O_2 TPR, formation of CO₂ (Eq. 1) is shown over the La₂CuO₄ on the YSZ-8Y, with a corresponding decrease of CO and O₂ concentration at T > 200 °C but without a clear change of NO concentration (Fig. 15b).²⁶ A different CO effect was observed at high temperature (650°C) with the WO₃-based potentiometric sensor, where the sensor showed a negative NO response and, by CO addition, the emf response increased, but without a significant change of slope.²

Values of the emf are reduced by 1-6 mV in the presence of 3% H_2O with a decrease in the slope (Fig. 13d). Figure 13e shows that the NO sensitivity plots are shifted downward gradually with an increase in NO₂ concentration (50-400 ppm). The sensitivity (slope)



Figure 15. (Color online) (a) TPD of NO + CO + O_2 over La_2CuO_4 powder and (b) TPR of NO + CO + O_2 over La₂CuO₄ on YSZ-8Y.

increases noticeably by 50 ppm NO₂ addition, but among the plots obtained with 50-400 ppm NO₂ the slopes are similar.

Conclusions

The sensing behavior of a potentiometric sensor built using a combination of La2CuO4 and Pt electrodes is demonstrated. The sensor shows relatively high sensitivity to NO, CO, and NO₂ at 450°C but no sensitivity to O₂ or CO₂. The NO sensitivity increases with decreasing temperature from 600 to 400°C. However, sensor operation is limited to T > 400 °C, because NO does not fully desorb from the surface of the metal oxide below 400°C, resulting in a saturation of the sensor response. The NO selectivity results support the idea that the NO sensitivity is adsorptive in nature. The NO adsorption is not influenced by the presence of O₂, which is consistent with the selective NO sensing against pO₂ change. Removal of the NO chemisorption peak by CO2 addition agrees with the sensor results, showing a significant decrease in the NO sensitivity by CO₂. Moreover, by CO addition, the sensor emf values for NO detection increase, but with a decrease in the slope (NO sensitivity), which seems to be due to surface saturation caused by the enhanced NO adsorption in the presence of CO.

Acknowledgment

This work was supported by the DOE under contract no. DE-FG26-02NT41533 and DE-FC26-03NT41614.

University of Florida assisted in meeting the publication costs of this article.

References

- 1. H. Oshima, M. Tatemichi, and T. Sawa, Arch. Biochem. Biophys., 417, 3 (2003).
- F. Ménil, V. Coillard, and C. Lucat, Sens. Actuators B, 67, 1 (2000). 2.
- M. Ruao, M. Costa, and M. Carvalho, Fuel, 78, 1283 (1999).
- L. Whalley, A. Lewis, J. McQuaid, R. Purvis, J. Lee, K. Stemmler, C. Zellweger, and P. Ridgeon, J. Environ. Monit., 6, 234 (2004).
- 5. M. J. Madou and S. R. Morrison, Chemical Sensing with Solid State Devices, Academic Press, New York (1989)
- 6. E. Di Bartolomeo, N. Kaabbuathong, M. L. Grilli, and E. Traversa, Solid State Ionics, 171, 173 (2004)
- 7. E. Traversa, A. Bearzotti, M. Miyayama, and H. Yanagita, J. Eur. Ceram. Soc., 18, 621 (1998). 8.
- N. Miura, T. Raisen, G. Lu, and N. Yamazoe, Sens. Actuators B, 47, 84 (1998). G. Lu, N. Miura, and N. Yamazoe, Sens. Actuators B, 65, 125 (2000).
- J. Yoo, H. Yoon, and E. D. Wachsman, J. Electrochem. Soc., 153, H217 (2006). 10.
- 11. F. H. Garzon, R. Mukundan, and E. L. Brosha, Solid State Ionics, 136-137, 633 (2000).
- 12. E. D. Wachsman, K. Swider-Lyons, M. F. Carolan, F. H. Garson, M. Lia, and J. R. Setter, in Solid State Ionic Devices III, Solid-State Sensors, PV 2002-26, pp. 215-221, The Electrochemical Society Proceedings Series, Pennington, NJ (2003).
- 13. W. Weppner, Ionics 7, 404 (2001)
- 14. S. Peter, É. Garbowski, V. Perrichon, and M. Primet, C. R. Chim., 7, 57 (2004).
- Y. Teraoka, K. Nakano, W. Shangguan, and S. Kagawa, Catal. Today, 27, 107 15. (1996)
- 16. F. Van Assche, J. Yoo, S. Chatterjee, and E. Wachsman, ECS Trans., 1-7, 185 (2006).
- 17. E. D. Wachsman, P. Jayaweera, G. Krishnan, and A. Sanjurjo, Solid State Ionics, 136-137, 775 (2000).
- K. Ramanujachary, N. Kameswari, and C. Swamy, J. Catal., 86, 121 (1984).
- E. D. Wachsman and P. Jayaweera, in Solid State Electrode Devices VI, Ceramic 19. Sensors, E. D. Wachsman, W. Weppner, E. Traversa, M. Liu, P. Vanysek, and N. Yamazoe, Editors, PV 2000-32, pp. 298–304, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- X. Zhau, Q. Cao, Y. Hu, J. Gao, and Y. Xu, Sens. Actuators B, 77, 443 (2001). 20
- 21. T. Morita, M. Miyayama, J. Motegi, and H. Yanagida, in Chemical Sensors II, M. Butler, A. Ricco, and N. Yamazoe, Editors, PV 93-7, pp. 450-455, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
- 22. M. L. Grilli, E. Di Bartolomeo, and E. Traversa, J. Electrochem. Soc., 148, H98 (2001).
- P. T. Moseley, Meas. Sci. Technol., 8, 223 (1997). 23
- 24
- S. Roy, W. Sigmund, and F. Aldinger, J. Mater. Res., 14, 1524 (1999). J. Yoo, S. Chatterjee, and E. D. Wachsman, Sens. Actuators B, 22, 644 (2007) 25 26. J. Yoo, F. M. Van Assche, and E. D. Wachsman, J. Electrochem. Soc., 153, H115
- (2006). 27
- J. Yoo and E. D. Wachsman, ECS Trans., 1-7, 173 (2006).
- 28. D. L. West, F. C. Montgomery, and T. R. Amstrong, Sens. Actuators B, 106, 758 (2005)