La$_2$CuO$_4$ sensing electrode configuration influence on sensitivity and selectivity for a multifunctional potentiometric gas sensor

Eric R. Macam[a,b], Briggs M. White[a,b], Bryan M. Blackburn[d], Elisabetta Di Bartolomeo[b], Enrico Traversa[b,c], Eric D. Wachsman[d,*]

[a] Florida Institute for Sustainable Energy, University of Florida, Gainesville, FL 32611-6400, USA
[b] Dip. di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133 Rome, Italy
[c] International Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan
[d] University of Maryland Energy Research Center, University of Maryland, College Park, MD 20742-2115, USA

ABSTRACT

The effects of electrical contact configuration for La$_2$CuO$_4$ sensing electrodes for a planar-based potentiometric gas sensor were studied in order to further quantify the effects of processing on sensor performance. Five configurations of La$_2$CuO$_4$ were used for the sensing electrode. The La$_2$CuO$_4$ sensing electrode was screen printed opposite a Pt counter electrode on a tape cast YSZ electrolyte. Three sensors were prepared for each configuration to test repeatability. Each sensor was tested at temperatures from 400 to 700 °C at various concentrations of NO$_2$, NO, and CO in an environment of 3% O$_2$ with a balance of N$_2$. Results show that these sensors exhibit suitable sensitivity to all the gases tested. More importantly, it was shown that the sensitivity, selectivity/cross-sensitivity, and repeatability of these sensors are dependent on the sensing electrode configuration.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Since the development of the oxygen lambda sensor [1] many have attempted to develop similar sensors for other gases, such as NO$_x$, CO, and H$_2$. Gas sensors are essential for controlling gas emissions, especially with the increasing regulations on automobile emissions. Gas sensors are vital for energy efficiency; they help balance the air to fuel ratio in automobiles, as well as provide a way to regulate gas emissions in developing lean burn engines.

Much attention has been given to gas sensors, which are based on solid state electrolytes combined with metal oxide sensing electrodes. Thus far, they are the most stable materials at high temperatures and in harsh environments. Although many have reported on the development and performance of these sensors, no one has been able to develop a sensor suitable for commercialization, such as the oxygen lambda sensor. One reason is the failure to make sensors that have adequate shelf lives and produce consistent results. Some attribute the lack of repeatability to the fabrication process [2], however few have attempted to quantify or rectify this problem.

La$_2$CuO$_4$ electrodes for non-Nernstian potentiometric sensors have been studied in previous works including the effect of the sensing electrode microstructure/grain size [3], thickness [4], and area on the response of the potentiometric sensor [5]. In this current work, the effect of electrical contact configuration for the La$_2$CuO$_4$ sensing electrodes on the sensor response is investigated. Although this design aspect is often overlooked, it proved to have an effect on sensor sensitivity, selectivity/cross sensitivity, and repeatability.

2. Experimental

2.1. Powder synthesis

La$_2$CuO$_4$ was selected as the candidate for the sensing electrode in this research because of its p-type semiconducting response upon NO$_x$ adsorption. In addition, it is non-catalytic for the reduction of NO [6] and highly catalytic for the reduction of NO$_2$ and oxidation of CO [7]. La$_2$CuO$_4$ powders were synthesized via an amorphous citrate gel combustion method [8]. Solutions of nitrates of La and Cu were prepared. The concentrations of these solutions were determined using Inductively Coupled Plasma Spectroscopy (ICPS, Perkin-Elmer Plasma 3200).

Appropriate amounts of the solution were mixed with citric acid in order to obtain the stochiometric ratio of La ions to Cu ions and a molar ratio of citric acid to nitrate ions equal to 0.22.

* Corresponding author. Tel.: +1 301 405 8193; fax: +1 301 314 8514.
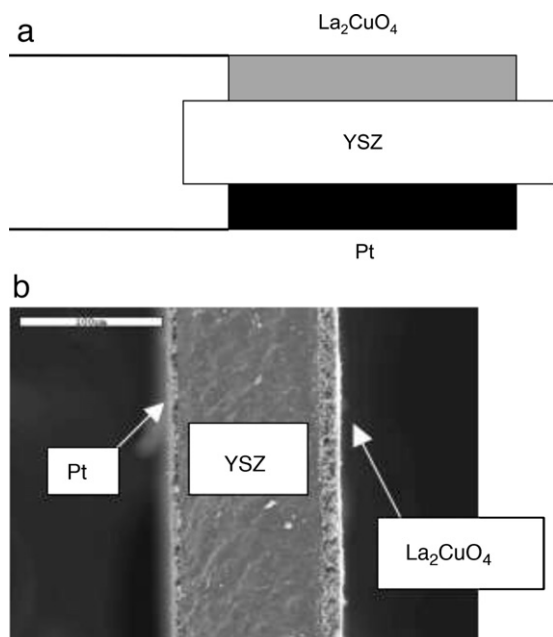*E-mail address:* ewach@umd.edu (E.D. Wachsman).

Fig. 1. (a) Schematic of sensor and (b) SEM cross section of sensor.

The mixture was heated to 100 °C until most of the water in the solution evaporated, leaving behind a gel. This gel was calcined for 10 h at 650 °C. X-ray diffraction (XRD) analysis was used for structural characterization of the resulting powder.

2.2. Sensor fabrication

Each sensor was composed of a commercially purchased 8 mol% yttria-stablized zirconia (YSZ) electrolyte (Marketech). These electrolytes had dimensions of 13 mm × 20 mm × 0.1 mm. To fabricate the sensing electrode, a screen-printable slurry was prepared by mixing La_2CuO_4 powder (17.5% solids loading) with polyethylene glycol and ethanol. This slurry was used to screen print an 8 mm × 8 mm electrode on one side of a YSZ electrolyte. The electrode was dried at 120 °C, followed by a 1 h burnout at 400 °C, and then sintered at 800 °C for 10 h. This procedure was repeated on 14 additional YSZ electrolytes.

An 8 mm × 8 mm Pt counter electrode was screen printed on the opposite side of each of the YSZ electrolytes using commercial a Pt Paste (Heraeus) in direct alignment with the La_2CuO_4 electrode. The Pt electrodes were burned out for 1 h at 400 °C and then fired at 750 °C for 4 h. Fig. 1 shows a schematic of the sensors with a SEM micrograph of the sensor cross section.

The 15 samples were then separated into 5 groups of 3 to prepare the different configurations of the sensing electrode. The differences in the 5 different configurations are described below and shown in Fig. 2. After Pt or La_2CuO_4 ink was used to attach Pt wire to the respective electrodes, the sensors were again fired at 750 °C for 1 h.
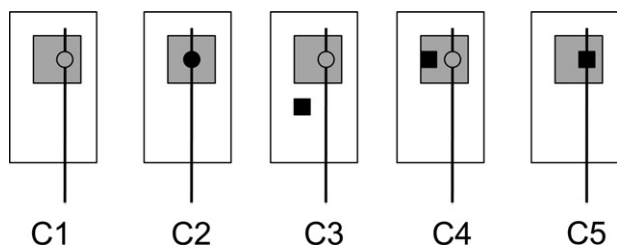

Fig. 2. Schematic of the different La_2CuO_4 electrode configurations.

2.2.1. Configuration 1
Pt ink was used to attach a Pt wire to the Pt counter electrode while the La_2CuO_4 slurry was used to attach a Pt wire to the La_2CuO_4 electrode.

2.2.2. Configuration 2
Pt ink was used to attach Pt wires to both the Pt counter electrode and La_2CuO_4 sensing electrode.

2.2.3. Configuration 3
Configuration 3 is identical to Configuration 1 except that it has an additional 4 mm × 4 mm Pt electrode screen printed on the YSZ electrolyte adjacent to the La_2CuO_4 sensing electrode.

2.2.4. Configuration 4
Configuration 4 is identical to Configuration 1 except that it has an additional 4 mm × 4 mm Pt electrode screen printed on top of the La_2CuO_4 sensing electrode without making contact with the Pt wire.

2.2.5. Configuration 5
A 4 mm × 4 mm Pt electrode was screen printed on top of the La_2CuO_4 electrode. A Pt wire was attached to the 4 mm × 4 mm Pt electrode using Pt ink. The counter electrode is identical to that used in Configuration 1.

2.3. Testing parameters

Sensor experiments were conducted in a gas-flow apparatus. Gas environments were controlled using mass flow controllers. A custom LabView program was used which allowed temperatures and gas-flow rates to be automatically controlled by a computer. Sensors were exposed to 3% O_2 balanced by N_2. The total flow rate was set at a constant 300 sccm. NO_2, NO, and CO each were exposed to the sensors in the following concentrations: 0, 50, 100, 200, 400, and 650 ppm, holding each concentration for 200 s. The gas concentrations were stepped for each gas in two hysteresis type loops at each temperature between 400 and 700 °C at 50 °C increments.

The voltage between the sensing and counter electrode was measured during the step changes using a Keithley Multimeter. For each sensor, the sensing electrode was connected to the positive terminal of the multimeter while the counter electrode was connected to the negative terminal. The design of the testing apparatus allowed for two sensors to be tested simultaneously. Thus, the first two samples of each configuration were tested together. For each configuration, the third sample was then tested along with the first sensor. Testing one sensor twice from each configuration allowed one to look at the sensor's behavior based on gas history. Furthermore, it should be noted that all electrodes from both sensors were in the same gas atmosphere, with no reference gas used.

3. Results and discussion

3.1. Powder characterization

Fig. 3 displays the XRD plot obtained from the La_2CuO_4 powder. The figure also displays the angles for the four strongest intensities for CuO and La_2O_3 which could not be identified in the XRD plot. This displays that phase pure La_2CuO_4 is obtained from the amorphous citrate gel combustion synthesis route.

3.2. Sensor response

The typical sensor response (Configuration 2 at 600 °C) for all three different gases (NO_2, NO, and CO) can be seen in Fig. 4(a). It shows the change in voltage (measured between the sensing
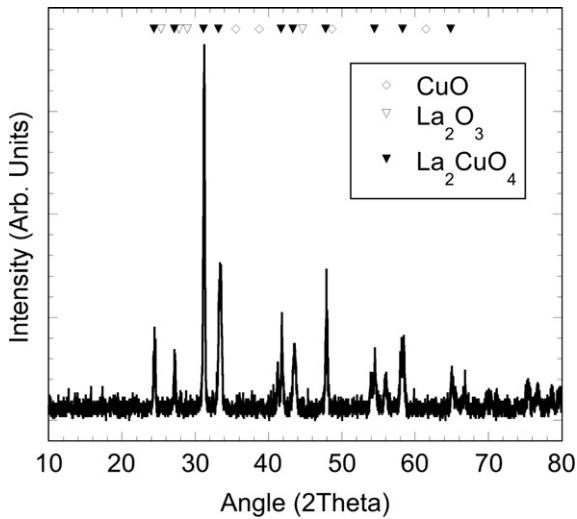
Fig. 3. XRD Plot of La$_2$CuO$_4$.

Fig. 5. NO$_2$ Sensitivity of "Sensor 1" for each configuration at 550, 600, and 650 °C.

electrode and counter electrode) with time as the gas concentration varied. Fig. 4(b) is a plot of the sensor voltages versus gas concentration on a logarithmic scale. The sensitivities of the sensors are defined as the slope of the linear relationship between sensor voltage and log(gas concentration) and were recorded
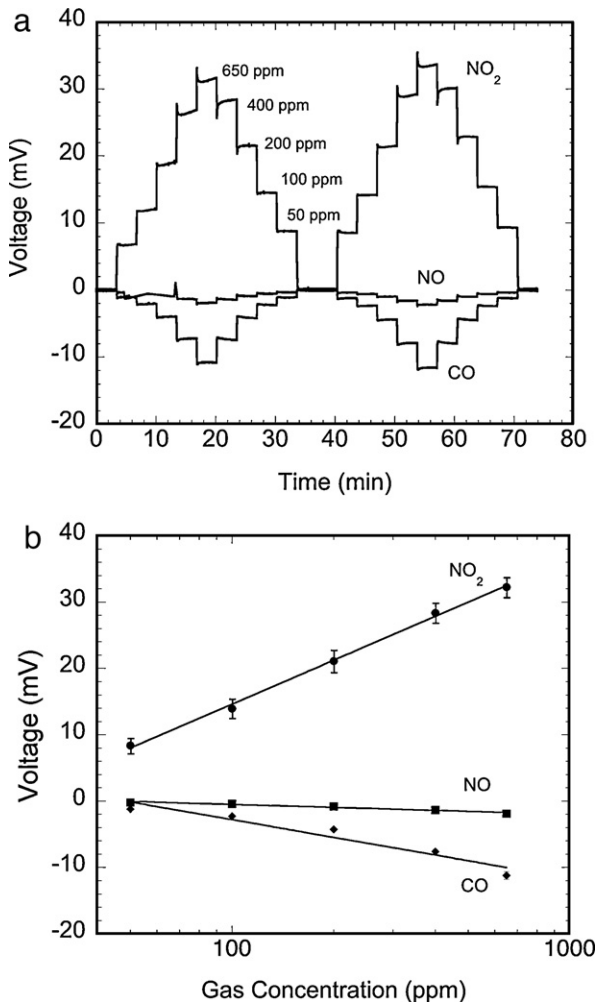
for each configuration in the range of 550–650 °C. This is the temperature range that each sensor of each configuration had a stable response for each gas tested.

3.2.1. Sensitivity

For each temperature one can make sensitivity comparisons for the different configurations. This is seen in the NO$_2$, NO, and CO sensitivity versus temperature plots (Figs. 5–7) for the first sensor out of the three made for each configuration (i.e., Sensor 1). In each of these figures, the slope describes the change of sensitivity with change of temperature. For example, if the sensitivity is positive, a positive slope indicates that the sensitivity increases with increasing temperature while a negative slope corresponds to a decrease in sensitivity with increasing temperature. The opposite is observed for sensors with a negative sensitivity.

Depending on the configuration, the change in NO$_2$ sensitivity with temperature, as seen in Fig. 5, displays both positive and negative changes in slope. The simplest case, Configuration 1 (C1), shows a negative slope with the increase in temperature. This decrease in sensitivity is usually seen in most solid state sensors with metal oxide sensing electrodes. C2, C4, and C5 display a positive slope between 550 and 600 °C and a negative slope between 600 and 650 °C. Each of these configurations have some type of Pt/La$_2$CuO$_4$ interface in addition to the Pt wire/sensing electrode interface present in each of the configurations. C3, the most distinct configuration with an additional area of Pt screen printed adjacent

Fig. 4. (a) Voltage versus time plot and (b) voltage versus log(gas concentration).

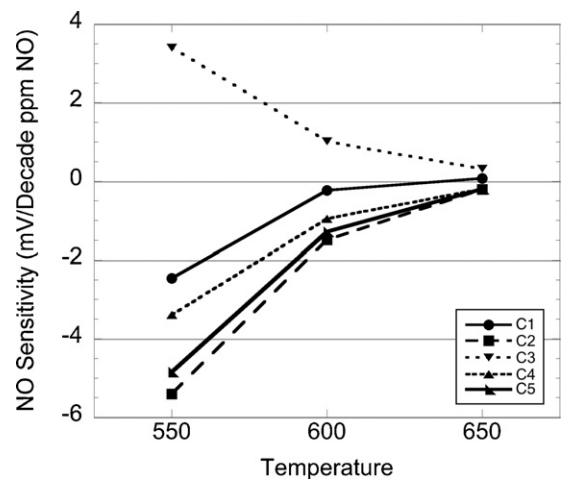Fig. 6. NO Sensitivity of "Sensor 1" for each configuration at 550, 600, and 650 °C.

Fig. 7. CO Sensitivity of "Sensor 1" for each configuration at 550, 600, and 650 °C.
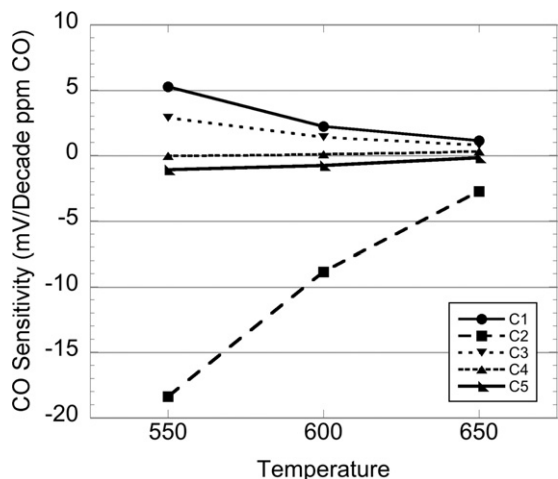
Fig. 9. NO$_2$ selectivity with respect to CO at 550, 600, and 650 °C.

to the sensing electrode, deviated the most from the rest of the configurations in that it produced a negative sensitivity (with a positive slope). The differences in sensitivity for NO$_2$ are most likely due to the more complex nature of NO$_2$ interaction with La$_2$CuO$_4$. This will be discussed further in the analysis section.

The slopes for NO and CO sensitivity, Figs. 6 and 7, indicate a decrease in sensitivity with increasing temperature. This suggests that the sensor configuration plays a less significant role in affecting sensitivity at higher temperatures. As in the case for NO$_2$, C3 deviates from the rest of the configurations having a NO sensitivity of opposite sign to the other configurations. According to semiconductor theory [9–11], one would expect NO$_2$ to have a sensitivity of the opposite polarity than that of NO, as was the case for all configurations. In the case of CO, the configuration that deviated the most from the rest was C2.

3.2.2. Selectivity/cross sensitivity

A gas sensor is selective if it responds to a particular gas but not to others. One may need to detect NO$_2$ without its sensitivity being affected by changes in another gas, such as CO. The issue of selectivity is particularly important for NO$_x$ since NO is found in much larger concentrations than NO$_2$ in combustion engines.

The selectivity is quantitatively described as the ratio of the sensor sensitivity for one gas to the sensitivity of another. Figs. 8–10 show how electrode configuration alters sensor selectivity for NO$_2$, NO, and CO. 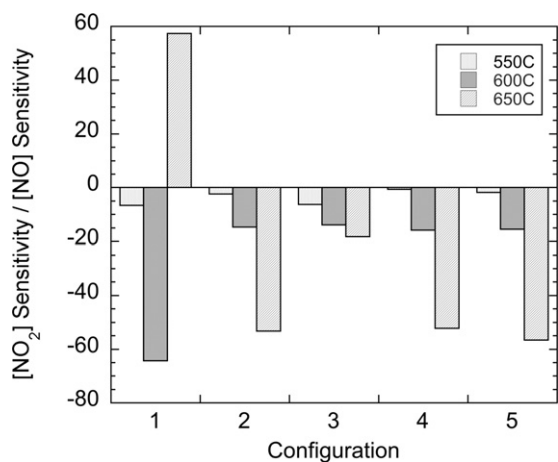A negative ratio simply indicates that the sensitivity for each gas was opposite in polarity. Fig. 8 shows that all configurations show good selectivity towards NO$_2$ with respect to NO, particularly at 650 °C where all configurations showed little sensitivity towards NO. The data follows a similar trend for all configurations except at 650 °C where the ratio is positive for C1. At this temperature, the NO sensitivity switches to a very small positive value. These results suggest that when using La$_2$CuO$_4$ as a sensing electrode, operation temperature can be used as a parameter to control sensor selectivity between NO$_2$ and NO. This principle has been demonstrated in a multifunctional sensor array [12].

The results in Figs. 9 and 10 imply that the presence of a Pt electrode on top of the La$_2$CuO$_4$ electrode (C4 and C5) improves the selectivity for NO$_x$ in the presence of CO. Configurations C1, C2, and C3 show some NO$_2$ to CO selectivity, but not as high as C4 and C5. While the Pt layer does not drastically improve NO$_x$ sensitivity, it effectively makes the sensor insensitive to CO resulting in the high NO$_x$ selectivity. Although the CO sensitivity is low for C4, the response switches direction between 550 and 600 °C causing the switch in the sign of the NO$_x$ selectivity at these temperatures.

3.2.3. Repeatability

Another important parameter, particularly in regards to commercializing sensor technology, is repeatability. Repeatability can refer to two aspects: ability for one sensor to produce similar results after repeated testing (run to run) and the ability to manufacture multiple sensors that give similar results to each other (sample to
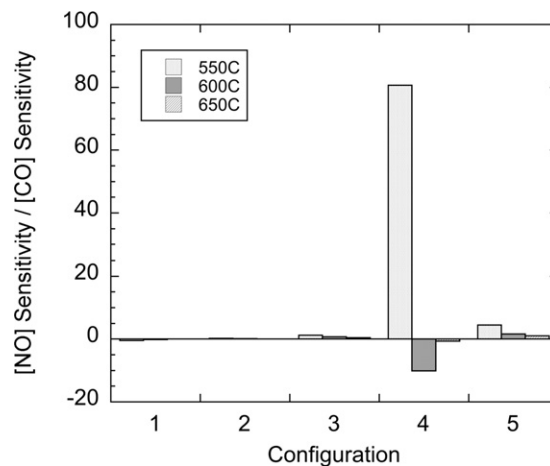

Fig. 8. NO$_2$ selectivity with respect to NO at 550, 600, and 650 °C.

Fig. 10. NO selectivity with respect to CO at 550, 600, 650 °C.

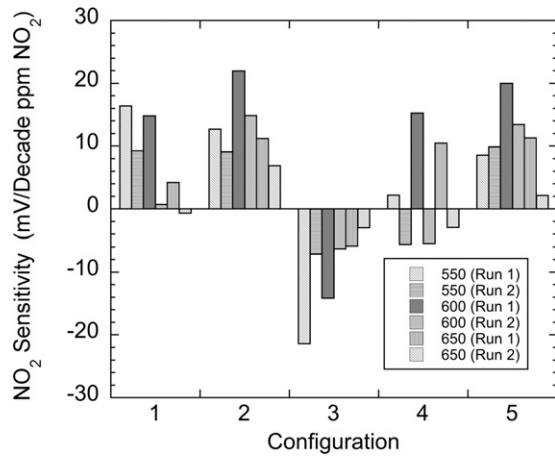**Fig. 11.** NO_2 sensitivity comparisons between Run 1 and Run 2 at 550, 600, and 650 °C.
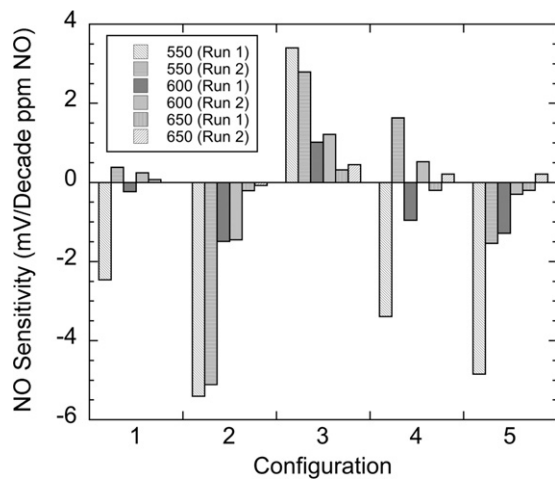

Fig. 12. NO sensitivity comparisons between Run 1 and Run 2 at 550, 600, and 650 °C.

sample). If sensitivity can be related to the accuracy of the sensor, repeatability should then be related to the precision.

Figs. 11–13 show how testing each sensor a second time affected the sensitivity. One general trend is that the sensitivity for each gas usually decreases upon the repeated tests. In several instances, the direction of the response even switched. This is especially true for
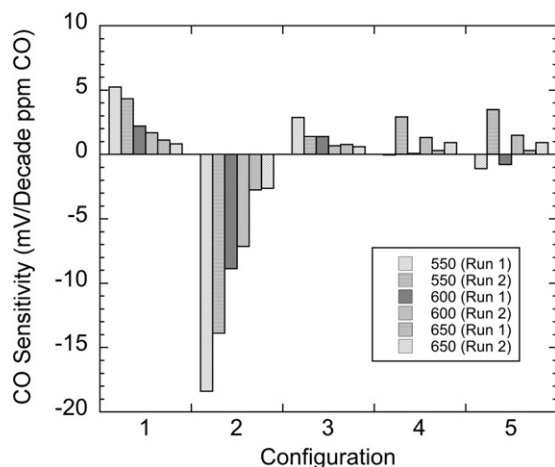

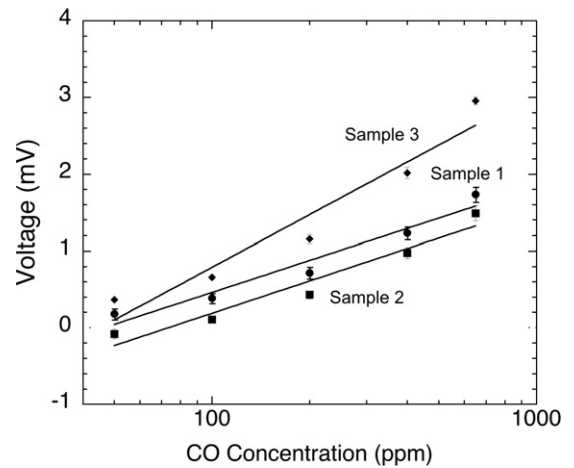**Fig. 13.** CO sensitivity comparisons between Run 1 and Run 2 at 550, 600, and 650 °C.

Fig. 14. Comparison of CO sensitivity for 3 samples of Configuration 3 at 600 °C.

C4, which changed direction at each temperature for NO_2 and NO. Nevertheless, C2 and C3 have the best repeatability-performance in terms of having the least degradation in sensitivity, without changing response direction for a particular gas. On the other hand, C4 and C5 show the worst repeatable performance. In their work, Penza et al. [13] noted that long term stability was an issue for the WO_3 electrodes which had a Pt layer on top of them.

The two additional samples from each configuration were also tested in the same conditions as the first sensor in order to test sample to sample repeatability. Results showed that two additional sensors within a given configuration produced similar, but not identical, results to the first sensor as shown in Fig. 14 for the CO response for sensors of C3 at 600 °C. This is an example of the best sample-to-sample repeatability. While all configurations did not show this level of repeatability at least two sensors from each configurations showed similar behavior for each gas. However, the variations were not dependent on the gas tested. Thus, further improvement and control in sensor fabrication is needed to ensure sample-to-sample repeatability before these sensors can be made for large scale commercialization.
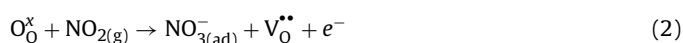
3.3. Sensor mechanism

Some insight into the sensor behavior in this work may be drawn from understanding the concept of "Differential Electrode Equilibria" [6]. This concept explains that the signal generated by the sensor is the difference in potential between the sensing electrode and counter electrode. The potential on each electrode is affected by gas/electrode interaction processes like electrochemical reactions, electrocatalytic activities, and/or changes in semi-conducting properties due to gas adsorption [14]. Since La_2CuO_4 is a p-type semiconductor with some catalytic activity towards CO oxidation and NO_2 reduction, all these processes must be taken into consideration. In general, each of these processes occurs at specific temperatures for each sensing material; however, at a given temperature more than one can contribute to each electrode potential. The potential difference arises from having two electrodes with some form of asymmetry, in most cases a difference in material.

The difference in sensor electrode configuration could further contribute to asymmetry, and thus the sensor signal. In order to rationalize the effects of configuration, one must remember the inherent properties of La_2CuO_4 mentioned above and except for C1 the contributions due to the addition of Pt, which also shows catalytic activity.

The sensor mechanism for La_2CuO_4 based NO_x and CO potentiometric sensors has previously been investigated via temperature

programmed reactions (TPR) and temperature programmed desorption (TPD) experiments [15]. In addition, the composition of the NO_x adsorbates on La_2CuO_4 and the mechanism of oxygen exchange between NO_x and La_2CuO_4 have been studied extensively using Infrared/X-ray Photoemission Spectroscopy [16] and TPR/TPD experiments with isotopically labeled O_2 [17], respectively. NO sensitivity was attributed to NO adsorption and the associated change of potential with respect to the Fermi Energy level at the surface. This change is caused by the removal of electrons from the La_2CuO_4 bulk when the adsorbed NO interacts with lattice oxygen to form the nitrite complex (NO_2^-) on the surface. The same can be said about NO sensitivity in this work. The nature of NO_2 is more complicated. NO_2 begins to reduce to NO over La_2CuO_4 at 350 °C and completely decomposes by 600 °C. However, NO_2 behaves similarly over Pt. Thus, the sensing mechanism cannot be attributed to a catalytic difference between electrodes of Pt and La_2CuO_4. Rather, NO_2 is adsorbed onto the surface of La_2CuO_4 similarly as NO, also resulting in a change of potential with respect to the in Fermi Energy level. However, when a nitrite is formed with NO_2 adsorption electron holes are produced with no La_2CuO_4 lattice oxygen exchange. Thus as expected, the response of NO_2 is positive and opposite to that of the NO response. NO_2 adsorbates can also further form a nitrate complex (NO_3^-). Depending on the reaction pathway of nitrate formation (Eqs. (1) and (2)), the surface conductivity of La_2CuO_4 can either increase or decrease. The overall voltage is thus dependent on the relative amount of nitrite and nitrate formation. This complexity helps explain the behavior seen in Fig. 5.

$$NO_{2(g)} + O_{(ad)} \rightarrow NO_{3(ad)}^- + h^\bullet \tag{1}$$

$$O_O^x + NO_{2(g)} \rightarrow NO_{3(ad)}^- + V_O^{\bullet\bullet} + e^- \tag{2}$$

CO shows both adsorption/desorption behavior as well as oxidation to CO_2 over La_2CuO_4 above 300 °C. Pt also oxidizes CO, but the relative conversion compared to La_2CuO_4 depends on temperature. Thus, the resulting sensitivity could be attributed to both a difference in local pO_2 (and a corresponding Nernstian voltage) in addition to a change in energy levels due to surface adsorption. This makes CO sensitivity more difficult to explain and could give an explanation as to why in some cases a sensor responds in opposite directions for NO and CO, although both are reducing gases.

An additional contribution that must be considered is the interaction between a catalyst and semiconductor present in C2, C4, and C5. It was previously shown that the presence of Pt (as well as other additive catalysts like Pd) on a semiconducting oxide (e.g., InO_x and SnO_2) can affect the electrochemical state of the oxide [18,19]. There are two proposed mechanisms of how the electrochemical state is altered. One is a "spill over" mechanism in which species adsorb onto the additive surface, where it then reacts. This reacted species subsequently spills over to the semiconductor, causing a change in its resistance. In the second mechanism, adsorption of a species onto the additive results in an electron exchange. This exchange continues in the semiconductor, also resulting in a change in semiconductor resistance.

The Pt/La_2CuO_4 interaction plays a role for each gas tested. For NO_2, the sensors with a Pt interface on La_2CuO_4 (C2, C4, and C5) have the lowest sensitivity (in terms of absolute magnitude) at 550 °C, and the highest sensitivity at 650 °C. While the amount of Pt affects the sensitivity at lower temperatures, the effect on NO_2 sensitivity is independent of the amount of Pt at 650 °C. The interaction also causes an increase in NO sensitivity between 550 and 650 °C, with the effect less prominent above 600 °C. The catalyst/semiconductor interaction plays the greatest role with CO sensitivity. A small amount of Pt (as in C2) increased the sensitivity significantly, while sensors with larger amounts of Pt (as in C4 and C5) had very little CO sensitivity at 550–650 °C.

The results for C3 are perhaps the most difficult to understand. There are no Pt/La_2CuO_4 interfaces present, but an additional screen printed Pt area next to the La_2CuO_4 electrode. Although it might be assumed that this configuration would behave similarly to C1, its behavior towards NO_2 and NO deviates the most from the other configurations. While producing large sensitivities, Configuration 3 has responses of opposite polarity than the others: a negative response for NO_2 and positive for NO. As far as CO, C3 behaves similarly to C1. Thus, the presence of interfaces proves to affect sensitivity, but it cannot be clearly attributed to either of the two catalyst-semiconductor interfacial phenomena.

4. Conclusions

The sensor fabrication process and design is often overlooked in terms of understanding gas sensor behavior. This work has attempted to show how sensor design, in particular sensing electrode configuration can affect sensitivity, selectivity, and repeatability for gases such as NO_x and CO. Sensors with five different configurations of the sensing electrode were tested. The sensors responded best in the temperature range of 550–650 °C. The differences in configuration proved to change, and sometimes improve, sensitivity and selectivity and also affected the run to run repeatability. In particular, depositing Pt on top of the La_2CuO_4 sensing electrode enhanced sensor selectivity towards NO_x with respect to CO. However, the sensors with the Pt electrode on top of the sensing electrode proved to be the least stable in terms of run to run repeatability. Thus, long term stability must still be addressed.

References

[1] W.J. Fleming, Physical principles governing nonideal behavior of the zirconia oxygen sensor, J. Electrochem. Soc. 124 (1) (1977) 21–28.
[2] N.F. Szabo, P.K. Dutta, Correlation of sensing behavior of mixed potential sensors with chemical and electrochemical properties of electrodes, Solid State Ionics 171 (2004) 183–190.
[3] B. White, S. Chatterjee, E. Macam, E. Wachsman, Effect of electrode microstructure on the sensitivity and response time of potentiometric NO_x, J. Am. Ceram. Soc. 91 (6) (2008) 2024–2031.
[4] E. Macam, B. Blackburn, E.D. Wachsman, The effect of La_2CuO_4 sensing electrode thickness on potentiometric NO_x sensor response, Sens. Actuators B: Chem. 157 (2011) 353–360.
[5] E. Macam, B. Blackburn, E.D. Wachsman, Effect of La_2CuO_4 electrode area on potentiometric NO_x sensor response and its implications on sensing mechanism, Sens. Actuators B: Chem. 158 (2011) 304–312.
[6] E. Wachsman, P. Jaiyaweera, Selective detection of NO_x by differential electrode equilibria, in: W. Weppner, E. Traversa, M. Liu, P. Vanysek, N. Yamazoe (Eds.), Solid State Ionic Devices II – Ceramic Sensors, Vol. PV 2000-32. The Electrochemical Proceedings Series, Pennington, NJ, 2000, pp. 298–304.
[7] J. Yoo, S. Chatterjee, F.M.V. Assche, E.D. Wachsman, Influence of adsorption and catalytic reaction on sensing properties of a potentiometric La_2CuO_4/YSZ/Pt sensor, J. Electrochem. Soc. 154 (7) (2007) J190–J195.
[8] S. Roy, W. Sigmund, F. Aldinger, Nanostructured yttria powders via gel combustion, J. Mater. Res. 14 (1999) 1524–1531.
[9] A. Azad, S. Akbar, S. Mhaisalkbar, L. Birkefed, K. Goto, Solid state gas sensors: a review, J. Electrochem. Soc. 129 (12) (1992) 3690–3704.
[10] E. Di Bartolomeo, M.L. Grilli, E. Traversa, Sensing mechanism of potentiometric gas sensors based on stabilized zirconia with oxide electrodes: is it always mixed potential? J. Electrochem. Soc. 151 (5) (2004) H133–H139.
[11] R.E. Hummel, Electronic Properties of Materials, 3rd Edition, Springer, New York, 2001.

[12] B. Blackburn, E. Wachsman, Multifunctional gas sensor array with improved selectivity through local thermal modification, ECS Trans. 11 (33) (2008) 141–153.

[13] M. Penza, C. Martucci, G. Cassano, NO_x gas sensing characteristics of WO_3 thin films activated by noble metals (Pd, Pt, Au) layers, Sens. Actuators B Chem. 50 (1998) 52–59.

[14] L. Chevallier, E. Di Bartolomeo, M.L. Grilli, M. Mainas, B. White, E. Wachsman, E. Traversa, Non-Nernstian planar sensors based on YSZ with a Nb_2O_5 electrode, Sens. Actuators B Chem. 129 (2008) 591–598.

[15] J. Yoo, F.M.V. Assche, E.D. Wachsman, Temperature-programmed reaction and desorption of the sensor elements of a WO_3/YSZ/Pt potentiometric sensor, J. Electrochem. Soc. 153 (6) (2006) H115–H121.

[16] F.M.V. Assche, J.C. Nino, E.D. Wachsman, Infrared and X-ray photoemission spectroscopy of adsorbates on La_2CuO_4 to determine potentiometric NO_x sensor response mechanism, J. Electrochem. Soc. 155 (7) (2008) J198–J204.

[17] F.M.V. Assche, E.D. Wachsman, Isotopically labeled oxygen studies of the NO_x exchange behavior of La_2CuO_4 to determine potentiometric sensor response mechanism, Solid State Ionics 179 (2008) 2225–2233.

[18] S. Morrison, Selectivity in semiconductor gas sensors, Sens. Actuators 12 (1987) 425–440.

[19] D. Vlachos, C. Papadopoulos, J. Avaritsiotis, Characterisation of the catalyst-semiconductor interaction mechanism in metal-oxide gas sensors, Sens. Actuators B Chem. 44 (1997) 458–461.

Biographies

Eric R. Macam received a BS in Materials Science and Engineering (MSE) from the University of Florida (UF) in 2004, an MS in MSE from UF in 2006, and a PhD in MSE from UF and the University of Rome Tor Vergata in 2010. His research includes the processing and development of ceramic electrochemical devices such as sensors and solid oxide fuel cells.

Briggs M. White is a project manager for the National Energy Technology Laboratory where he provides technical and managerial support to the United States Department of Energy's Solid-State Energy Conversion Alliance (SECA) program on solid oxide fuel cells. He received a BS in Materials Science and Engineering (MSE) from the New York State College of Ceramics at Alfred University in 2002, an MS in MSE from the University of Florida in 2004 and a PhD in MSE from the University of Florida and the University of Rome Tor Vergata in 2007. His technical interests are focused on high temperature electrochemical devices such as solid-state pollutant sensors and solid oxide fuel cells.

Bryan M. Blackburn received his BS in Electrical Engineering and BA in Business Administration in 2005, and MS and PhD degrees in Materials Science and Engineering in 2006 and 2009, all from the University of Florida. He has since worked at the University of Maryland and then as an entrepreneur driving the commercialization of clean technology such as solid-state gas sensors and solid oxide fuel cells for cleaner energy, improved efficiency, and reduced pollution. His professional interests include the investigation, innovation, and development of electrochemical and electronic devices. He is also interested in electron processes during catalytic and electrocatalytic reactions.

Elisabetta Di Bartolomeo is Assistant Professor in Materials Science and Engineering, Faculty of Engineering, University of Rome Tor Vergata. She received her Laurea in Physics from the University of Rome La Sapienza in 1994 and her Ph.D. in Materials Engineering from the University of Rome Tor Vergata in 2000. Her research interest focuses on synthesis, design and characterization of functional ceramic materials for chemical sensors and solid oxide fuel cells (SOFCs) at high and intermediate temperatures.

Enrico Traversa received his "Laurea" (Italian doctoral degree, 1986) in Chemical Engineering from the University of Rome La Sapienza. In 1988, he joined the University of Rome Tor Vergata where he is currently Professor of Materials Science and Technology. Since 2009 he has been Principal Investigator at the International Research Center for Materials Nanoarchitectonics (MANA), at the National Institute for Materials Science (NIMS), Tsukuba, Japan. Traversa's research interests are in nanostructured materials for environment, energy, and healthcare, with special attention to fuel cells, chemical sensors, and tissue engineering.

Eric D. Wachsman, Director of the University of Maryland Energy Research Center, received his PhD in Materials Science and Engineering from Stanford University, and his B.S. in Chemical Engineering from the U.C. Berkeley. He is a Fellow of The Electrochemical Society (ECS), formerly Chair of the High Temperature Materials Division of ECS, Editor-in-Chief of *Ionics*, Editor of *Energy Systems*, and formerly an Associate Editor of *Journal of the American Ceramic Society*. He has more than 190 publications and 8 patents on ionic and electronic transport in ceramics, their catalytic properties, and device performance.