

Examination of Conducting Metal Oxides for Low Temperature Gas Sensing Applications

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Abstract

The subject matter of this presentation involves a class of resistive based electrochemical gas sensors that includes ruthenium and vanadium oxides. In illustrating the potential of this class of metal oxide gas sensors, carbon monoxide and nitric oxide are used as examples. The fabrication of the devices, their synthesis, performance and sensing mechanisms are the focus of this study. For these ambient temperature devices, electrochemical measurements are rapidly and readily made by simple electronics, and integration into mobile electronic devices can lead to mHealth and mEnvironmental applications.

Key words: mobile sensors, health, environmental, carbon monoxide, nitrogen oxides.

Introduction

A vision for the next generation of air quality and biomedical sensors are devices that are ubiquitous, mobile with precise position determination, wireless transmission capabilities and tied into an intelligent network. The platform for such technology is readily available in the form of cell phones. Thus, if gas sensors can be developed that can be integrated with the cell phone platform, extensive information of air quality as well as point of care health monitoring becomes possible. In order to accomplish this vision, several developments need to occur. These include

- Development of sensor technology for gases adaptable with cell phone platforms
- Integration of sensors into cell phones
- Information technology development for data manipulation, data transfer and interpolation techniques to develop pollution maps, visualization and alerts

The focus of our study is to develop sensors for CO and NO. There are numerous reports on detection of these gases, though none integrated into cell phones. To be compatible with a cell phone platform, there are stringent requirements, including size, selectivity, and power. Solid-state electrochemical sensors meet the size, selectivity requirement, but operate at elevated temperatures. We are examining conducting metal oxides for gas sensing, which are nominally metallic under ambient conditions (making possible ambient electrical measurements), and also ensuring

that these oxides have metals with multiple accessible oxidation states.

Experimental Section

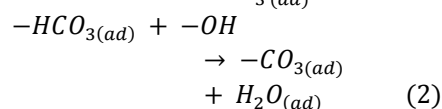
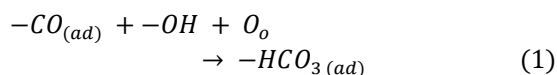
Hydrated ruthenium oxide was prepared by a precipitation method [1]. To a stirred 0.1M aqueous solution of ruthenium chloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ Sigma Aldrich), 0.3M sodium hydroxide (Mallinckrodt 98.7%) solution was added drop-wise until pH 7. The resulting precipitate was washed several times until chloride free (tested with AgNO_3), and dried in air at room temperature. Vanadium pentoxide used in all the experiments was obtained from Alfa Aesar (99.9 % metals basis). Nanocrystalline vanadium dioxide was synthesized by previously established methods [2]. A 1.81g of Vanadium oxide (V_2O_5) was dispersed in 30ml of 37% formaldehyde by stirring for 2 hours. This resulted in the formation of a yellow suspension. The resulting suspension was placed in two Paar bombs and hydrothermally treated for 2 days at 180°C. After 2 days the bombs were cooled to room temperature, the resulting blue-black metastable powder was washed with two 10 mL aliquots of water, ethanol and diethyl ether and dried overnight at 70°C in a vacuum oven. A final heat treatment was done by heating the metastable sample in argon at 700 °C for 1 hr. Alumina substrates (15 mm X 10 mm) with interdigitated gold lines of 0.25mm spacing were obtained from Case Western Reserve University Electronics Design Center. Gold lead wires (Alfa Aesar, 99.99%) were connected with gold paste (Heraeus). The electrodes were heat treated at 600°C for 3 hours in order to remove

organic binders from the gold paste. The metal oxide particles were suspended in water (5% by weight) by sonication for 1 hr. The suspension was drop coated onto the electrodes and allowed to dry in air for 4-6 hrs. All tests were done with a quartz tube housed in a temperature programmable furnace (Lindberg Blue, TF55035A). Measurement protocol consisted of flowing various volumes of certified mixtures of gases whose concentrations were varied with a Sierra Side-Trak[®] model 840 analog gas mass flow controller, controlled by a National instruments card (NI- 6703) and operated by a Labview program. Resistance measurements were made with a HP34970A at a scan rate of 0.1Hz. Tests were carried out at 25°C with a gas flow rate of 100 cc/min for all experiments.

Results and Discussion

CO sensor : Figure 1 shows the changes in resistance of a thick film of $\text{RuO}_x(\text{OH})_y$ upon repeated exposure to 250 ppm CO at 25°C in a background of dry 21% O_2 (the rest is N_2). There is an increase in resistance with CO, and a decrease as the CO is turned off in the gas stream over the film. This cycle can be repeated numerous times (~100) with an average relative resistance change, R/R_0 (R/R_0 , where R is the resistance in the presence of the CO and R_0 is the resistance in the background gas) of 2.5. The change in resistance of $\text{RuO}_x(\text{OH})_y$ with CO provides an opportunity for developing a solid state electrochemical ambient CO sensor. Response times and recovery times for the 1000 ppm CO were calculated to be 6 and 11 minutes (time taken to reach 90% of the steady state signal). Figure 2 depicts the normalized resistance (R/R_0) to 2000 ppm CO_2 , 1000 ppm methane and propane, 150 ppm ammonia, 15 ppm NO and NO_2 , indicating that the device is selective towards CO.

We propose the following reactions on $\text{RuO}_x(\text{OH})_y$ to explain the sensing response.



The reaction with O_o (lattice oxygen) on the $\text{RuO}_x(\text{OH})_y$ leads to reduction in the metal. It has been noted that redox active metal oxides such as iron oxide [3] and cobalt oxide [4] are more active in CO oxidation. CO oxidation on iron oxide is shown to occur by abstraction of lattice oxygen from Fe_2O_3 (Fe(III)) to form

Fe_3O_4 , (Fe(II,III)). In the instance of cobalt oxide, CO oxidation is proposed to occur by an initial CO adsorption event on a lower oxidation state of cobalt Co(II), which interacts with a neighboring oxygen bound to a higher oxidation state cobalt Co(III), to form carbon dioxide. The oxygen lost in these reactions is then replaced by the oxygen present in the gas mixture. Evidence for the reduction in ruthenium also comes from the CO chemisorbed band at 2003 cm^{-1} , which is in the frequency $\sim 2000\text{ cm}^{-1}$ range assigned to CO adsorbed on oxygen vacancies [5]. Overall, CO oxidation is leading to a reduction of the $\text{RuO}_x(\text{OH})_y$ surface, formation of CO_2 leading to carbonate/bicarbonate formation involving the OH groups of $\text{RuO}_x(\text{OH})_y$ and the oxygen vacancies are being occupied by CO. The adsorbed water is formed by reaction of bicarbonate with $-\text{OH}$.

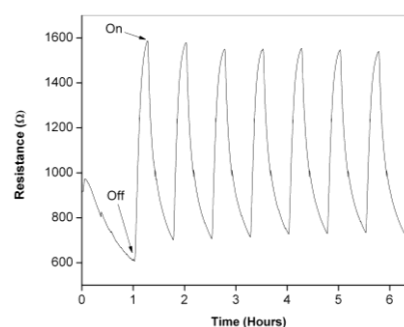


Fig. 1. Change in resistance of $\text{RuO}_x(\text{OH})_y$ upon repeated exposure to 250 ppm CO at 25°C in a background of dry 21% O_2 .

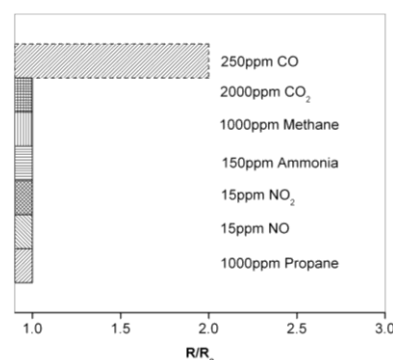
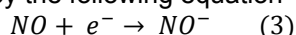


Fig. 2. Normalized resistance (R/R_0) to CO_2 , methane and propane, ammonia, NO and NO_2 ,

NO Sensor : Figure 3 shows the change in resistance of the V_2O_5 sample to 15ppm NO in an air background. There is initially slight decrease in the background resistance with air. Upon introduction of 15ppm NO at point (A), there is an increase in the resistance until point (B). Upon turning off the 15ppm NO at point

(C), the resistance decreases again. The cycle of air on/off and 15ppm NO on/off is repeated a total of three times until point (E). After the fourth exposure to air (E), the concentration of the analyte gas is then changed to 500ppm NO. An initial increase from the baseline resistance is observed in the change from point (E) to (F). Then there is a slight decrease in the resistance as shown in point (F) to (G), which then increases slightly until the 500 ppm NO is turned off at point (H). Once the 500ppm NO is switched off (H), and the V_2O_5 sample is exposed to air, the resistance continues to increase and stabilizes until point (I). The sample is then exposed to another cycle of 500ppm NO and the resistance decreases rapidly to point (J) and stabilizes to point (K), then it is exposed to air and the resistance increases again and stabilizes. This is repeated one more time to make a total of three cycles with 500ppm NO. These surface interactions at room temperature for 15ppm NO can be described by the following equation



Higher concentrations lead to increased NO^- formation, leading to greater depletion of the surface of electrons (dominant charge carriers). We propose that the increased NO chemisorption results in the formation of an

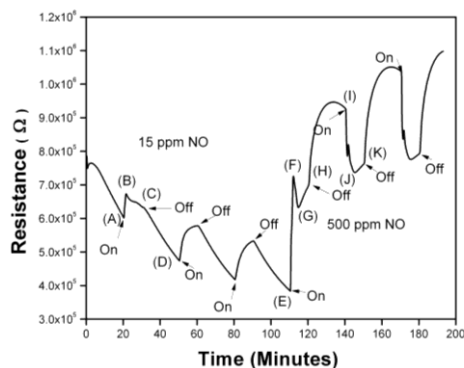


Fig. 3. Resistance change of the V_2O_5 sample to 15 and 500 ppm NO.

inversion layer with holes becoming the majority charge carrier (p-type). Thus, switching between low and high concentration of NO has led to switch from n- to p-type conductivity. The electrical resistivity changes are determined by the bulk donor density. With high bulk donor density, n-type behavior is expected, whereas with low bulk density, p-type behavior is expected. At intermediate donor densities, $n \rightarrow p$ or $p \rightarrow n$ transitions can be expected, depending on the amount and donor/acceptor properties of the adsorbing gas. It has been recognized that the $n \rightarrow p$ or $p \rightarrow n$ transition can be brought about by changes in the

elemental composition (e.g. valence) as well as by altering the extent of chemisorption by an adsorbed gas, the latter phenomenon being observed here.

Resistance changes to other gases were also tested at 25°C and the results are summarized in Figure 4. Vanadium pentoxide is exposed to 500ppm nitrogen dioxide, 1000ppm carbon monoxide, 1000 ppm propane, 150 ppm ammonia and 2.5ppm acetone. As observed there is an increase and decrease in the R/R_0 dependent on the analyte gas with 500ppm nitrogen dioxide showing the greatest change after nitrogen oxide.

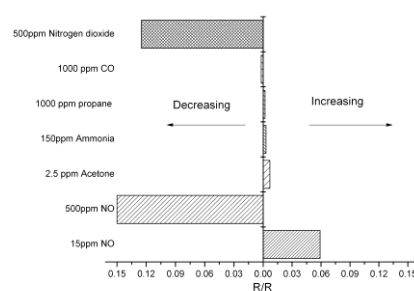


Fig. 4 Resistance changes of vanadium pentoxide with a series of gases.

Results with VO_2 were distinct from that of V_2O_5 , in that the 15 ppm NO exhibited an increase of resistance as shown in Figure 3, and also with 500 ppm NO, there was an increase, showing no n to p conversion.

Conclusions

The sensing tests show that the selectivity and detection limits have the potential to make $RuO_x(OH)_y$ a practical CO detector for low power application, and V_2O_5/VO_2 for ambient temperature detection of NO. It is interesting to contrast the CO sensor using RuO_x and NO sensor using V_2O_5 . In the former case, it is a chemical reaction catalyzed by the Ru that results in the sensing response, whereas for the latter, it is chemisorption that is controlling the response. However, in both cases, the presence of lower oxidation states of the metal are relevant. For the CO, it facilitates the oxidation, whereas with NO, it promotes the conductivity and provides the electrons involved in the chemisorption.

Acknowledgments

We acknowledge funding by NASA.

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