Polymer-Based Carbon Monoxide Sensors

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Abstract— **Polymer-based sensors have been used primarily to detect volatile organics and inorganics; they are not usually used for smaller, gas phase molecules. We report the development and use of two types of polymer-based sensors for the detection of carbon monoxide. Further understanding of the experimental results is also obtained by performing molecular modeling studies to investigate the polymer-carbon monoxide interactions. The first type is a carbon-black-polymer composite that is comprised of a non-conducting polymer base that has been impregnated with carbon black to make it conducting. These chemiresistor sensors show good response to carbon monoxide but do not have a long lifetime. The second type of sensor has a non-conducting polymer base but includes both a porphyrin-functionalized polypyrrole and carbon black. These sensors show good, repeatable and reversible response to carbon monoxide at room temperature.**

I. INTRODUCTION

The detection and monitoring of post-fire constituents in air is important for crew health and safety on space vehicles. One scenario of a combustion event occurring in space vehicle may be failure of electrical wires after prolonged use under high load conditions (voltage or temperature). The post-fire air constituents that are of interest to NASA include carbon monoxide (CO) and some acid gases (HCl and HCN). Because CO is also a precursor to fire we have selected that as our target molecule. Carbon monoxide is a small, gaseous molecule that is odorless, colorless and tasteless as well as toxic to humans. NASA's Constellation Program Human-Systems Integration Requirements [1] ask for CO detection from 5-500 parts-per-million (ppm) and the 7-day Space Craft Maximum Allowable Concentration (SMAC) is 10 ppm. This makes it an important molecule for air monitoring in human habitats.

We are interested in expanding our Jet Propulsion Laboratory (JPL) Electronic Nose (ENose) array capabilities to monitor these post-fire constituents. The JPL ENose is designed to run continuously and autonomously to monitor for the presence of selected chemical species in the air at parts-per-million (ppm) to parts-per-billion (ppb) concentrations. The JPL ENose has been developed to monitor spacecraft cabin air for anomalous events such as leaks and spills of solvents, coolants or other fluids with near-real-time analysis [2-6]. The Third Generation JPL ENose recently completed more than 6 months of continuous operation as a Technology Demonstration in the US Lab Destiny, on the International Space Station (ISS). For this ISS technology demonstration, the JPL ENose was designed to detect, identify and quantify eleven chemical species (analytes), consisting of eight organic compounds as well as ammonia, mercury and sulfur dioxide [5,6]. The Third Generation JPL ENose used an array of 32 semi-selective sensing materials, primarily polymer-carbon composite films, but also included inorganic and carbon nanotube sensors.

As for CO detection, many of the sensors found in the literature (as described below) show excellent response, but we need sensors that can be incorporated into our existing ENose sensing array architecture. Our requirements include, the CO sensor needs to be a low-power chemiresistor that operates at room temperature; the sensor fabrication techniques must be compatible with our ceramic substrates. Based on our requirements, polymer based sesnors are attractive candidates for these applications.

In the following sections, we will discuss sensor development and testing for carbon monoxide and present results for several polymer-based sensors that have been tested for carbon monoxide response. We have also performed molecular simulations to understand the interactions between these polymer based sensors and CO, to further understand our experimental results.

II. LITERATURE REVIEW

Sensors for carbon monoxide detection has been widely researched and investigated. There are many different techniques used for sensing carbon monoxide, including optical [7,8,9], amperometric [10,11] and electrical conductivity [12,13,14,15]. Some of the optical techniques included monitoring the reflectance or plasmon resonances of the sensing materials; direct optical absorption of CO can also measured, but with a sensitivity around 5000 ppm [8]. Some of these techniques employ different sensing materials including multi-walled nanotubes [10], a polyaniline-zeolite

composite [12], TiO_2 nanofibers [13], mesostructured cobalt oxide [14], and conducting polymers [15,16]. The carbon nanotube sensor is part of an electrochemical cell that is exposed to the gas using a permeable membrane and measured CO down to 10 ppm [10]. The TiO_2 nanofibers are operated at 200 °C and showed good response to CO down to 1ppm [16]. The mesostructured cobalt oxide are operated at 200 °C and showed good response to CO down to 10 ppm [14].

III. SENSOR DEVELOPMENT FOR CARBON MONIXIDE DETECTION

A. Polymer-Carbon Black Sensors

We considered four different non-conducting polymers: Ethylene-propylene-diene-terpolymer, Polyepichlorohydrin Poly (4-vinylpryridine) and Polyethylene oxide (PEO). Conductivity is imparted to these polymers by adding carbon black to make a polymer-carbon composite. The carbon black used for the composite films was Black Pearls 2000 (Cabot Corporation). Polymers and carbon black were used as received.

These polymer-carbon-black sensing films are made by dissolving the polymer in a solvent (1.0-1.3% polymer/solution wt.), sonicating the carbon black in the same solvent to get a good dispersion and then mixing the polymer and carbon black solutions to obtain the sensor solution. Table I shows the solvent used for each polymer-carbon black dispersion. The polymer weights are in 1.0-1.5 wt% (of total solution) range and the carbon black weights are in the 10-20 wt% range (of polymer-carbon black weight).

TABLE I. SOLVENTS FOR POLYMER-CARBON BLACK SENSORS

Polymer	Solvent
Polyepichlorohydrin	Dioxolane
Polyethylene oxide 600K MW	Dioxolane
Poly (4-vinylpryridine)	2-Propanol
Ethylene-propylene-diene-terpolymer	toluene

B. Polypyrrole Functionalized with Iron Porphyrin Sensors

The heme group is the moiety in the blood that binds oxygen and/or carbon monoxide and consists of an iron ion at the center of a porphyrin or heterocyclic ring. This strong but reversible binding of carbon monoxide makes iron porphyrins an excellent candidate for CO sensing. Paul *et al* [16]. functionalized a polypyrrole with an iron porphyrin to make conducting CO sensors that operate at room temperature with a sensitivity down to 100 ppm.

We tested two types of sensors made from a polypyrrole functionalized with an iron porphyrin. The first sensing films are made from a mixture of non-conducting polymer and a functionalized conducting polymer. The second sensing film incorporates carbon black in to the film.

First, pyrrole was polymerized in a ferric chloride/iron porphyrin solution in methanol. The iron porphyrin is 5, 10, 15, 20-Tetraphenyl-21H, 23H-porphine iron (III) chloride. This creates a polypyrrole that is functionalized with the porphyrin. After the synthesis, we made sensors from the functionalized polypyrrole by binding it with a small amount of polyethylene oxide (600 MW). This composite made films that were too resistive (>3 MΩ) to be measured in our device.

Subsequently, we added carbon black to the composite to bring the sensing film resistivity within a measurable range. We created a suspension in methanol using the functionalized polypyrrole (90% by weight), polyethylene oxide (600,000 MW, 5% by weight) and carbon black (5% by weight).

The sensing films for the above polymer based sensors described in sections *A* and *B* were casted on a sensor substrate [2,3]. The sensor substrate has 8 Au-Pd electrodes; covering an area of 2 mm x 1 mm. The sensor substrate is heated using resistive heaters embedded in the substrate, and the temperature feedback loop is closed using a thermistor that is surface mounted on the back of the substrate. More detailed descriptions of the sensor chip can be found elsewhere [2-6]. The sensing films were solution cast onto the Au-Pd electrodes on the ceramic substrates. After deposition, the films were dried in a vacuum oven for four hours at 60 °C.

IV. SENSOR TESTING FOR CARBON MONIXIDE DETECTION

We used a gas handling system built in our laboratory to deliver clean air as well as analytes to the sensors for testing. The gas handling system is run on house air that is filtered to clean and dehumidify it. The flow of the air is controlled by a series of mass flow controllers, valves, and check valves. The air delivered to the sensors can then be humidity controlled: a fraction of the air is bubbled through water and remixed with dry air. The entire system is computer controlled using a LabVIEW program. All of these experiments were performed using air with 10,000 ppm of water in air. Carbon monoxide in dry air (1014 ppm) is purchased and that mixture is connected to a mass flow controller and further diluted to desired concentrations.

The sensors were placed in our test chamber and were exposed, alternately, to clean humidified air and humidified air containing CO. After allowing the sensors to equilibrate in clean humidified air, the sensor exposures alternate between 30 minutes of carbon monoxide at varying concentrations and 60 minutes of clean air. All of the tests were run with a water background of 10,000 ppm H_2O. The sensor substrates were held at 28°C. Our testing chamber and device electronics can test 32 sensors concurrently: 3 substrates with 8 Au-Pd electrodes each and 1 substrate with 8 microhotplates. More detailed descriptions of the device operation can be found elsewhere [2-6].

Sensor data is measured as resistance versus time and the data is plotted as the normalized change in resistance, $\Delta R/R_0$,

where ΔR is (R_t-R_0), R_0 is the resistance at the start of an experiment and R_t is the resistance at time t.

V. RESULTS AND DISCUSSION

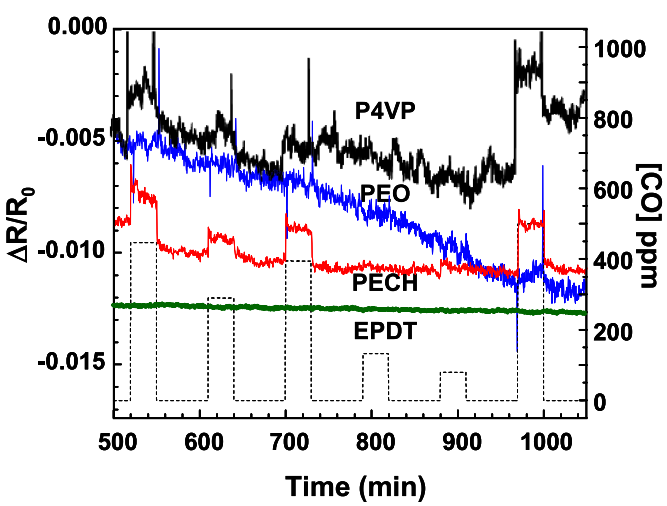
A. Sensor Testing

The response of several polymer-carbon black sensors and the pyrrole-porphyrin based sensors to varying concentrations of CO is discussed below.

1) Polymer-Carbon Black Sensors

Figure 1 shows the response of the four polymer-carbon black sensors to varying concentrations of CO (80-500 ppm). The CO concentration is represented by the dotted line traces. The noisy spikes on sensor are from humidity spikes and are an artifact of the gas handling system. Neither the polyethylene oxide (PEO) nor the ethylene-propylene-diene terpolymer (EPDT) show any response to CO. The Poly (4-vinylpryridine) sensor is noisy and detects CO above 200 ppm only. The polyepichlorohydrin (EPCH) sensor is less noisy and shows good response down to 100 ppm and is the best responding among the these four polymers considered. EPCH based sensor shows a linear response in the 100-500 ppm concentration range and do not have a long life time.

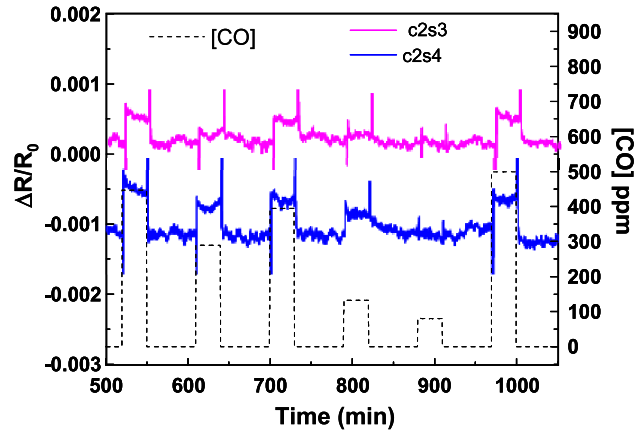
Figure 1. Polymer-carbon black sensor response to CO concentrations ranging from 80-500 ppm, at 26 °C. Sensor is a polymer-carbon composites of Ethylene-propylene-diene-terpolymer (EPDT), Polyepichlorohydrin (EPCH), Poly (4-vinylpryridine), and Polyethylene oxide (PEO) polymers. The CO concnetration is represented by the dotted line traces.



2) Polypyrrole Functionalized with Iron Porphyrin

The porphyrin-functionalized polypyrrole films, with PEO and carbon black were tested under the same conditions as the polymer-carbon black films. As described previously, PEO was tested, separately, as a polymer-carbon black film and did not show any response to CO. Figure 2 shows the response to CO for two of the PEO-porphyrin-functionalized polypyrrole films. The films in this figure show some drift; this is a temporary response due to rehydration and relaxation of the films after the initial vacuum bake. All of the PEO-porphyrin-functionalized polypyrrole films show good response to CO. The lowest limit for CO detection in these films is currently just over 150 ppm. In addition, these films are reversible and have not demonstrated any degradation.

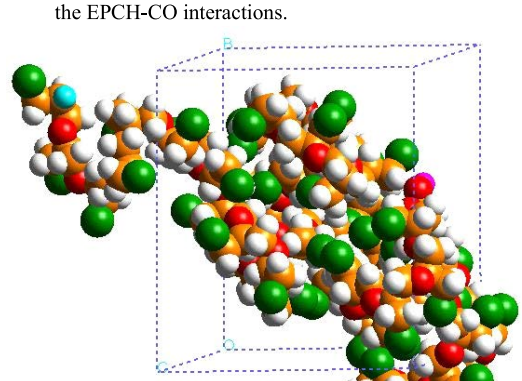
Figure 2. Polypyrrole functionalized with Iron Porphyrin sensor response to CO concentrations ranging from 80-500 ppm, at 26 °C. The sensor is a composite of polyethylene oxide, porphyrin-functionalized polypyrrole and carbon black. Seen are responses from two sensors.



B. Molecular Modeling of polymer-CO interactions

In order to understand these trends in the polymer-carbon composite response to CO, we investigated the polymer-CO interactions using molecular modeling tools [17,18]. The polymers are modeled using its basic monomer unit. A polymer box containing a polymer chain of about 50 monomer units was created. Charges on the monomer and carbon monoxide atoms were assigned by the charge equilibration method (Q_{eq}) [19]. The Dreiding force field[20] was used for polymer and analyte molecules. Energy equilibration of the polymer box was achieved by molecular mechanics and then by molecular dynamics simulations at 300K. The polymer box developed using the above procedure was used to calculate the interaction energy between the polymer chain and the CO molecule. The polymers considered for modeling are Polyepichlorohydrin (EPCH), Poly (4-vinylpryridine), and Polyethylene oxide (PEO). A representative EPCH polymer box is shown in Figure 3.

Figure 3. Polyepichlorohydrin (EPCH) polymer box used for claculating the EPCH-CO interactions.



Molecular simulations to calculate the polymer-CO interaction energy were carried with one CO molecule interacting with the polymer chain. The interaction energy values calculated includes the van der Waals and electrostatic energy contributions when CO molecule interacts with the polymer chain. All described modeling and simulations were carried out using the Cerius[2] software [21].

TABLE II. POLYMER-CARBON MONOXIDE INTERACTION ENERGY

Polymer	Interaction energy kcal/mol
Polyepichlorohydrin	-11.3
Polyethylene oxide	0
Poly (4-vinylpryridine)	-4.7

Table II, shows the results for the CO interactions with the three polymers Polyepichlorohydrin (EPCH), Poly (4-vinylpryridine), and Polyethylene oxide (PEO). It can be seen that PEO shows zero interaction energy and would not respond to CO. Polymers, EPCH and PVPY do interact with CO, with EPCH showing the strongest interaction. When comparing to the experimental results, the modeling results show similar trends in the interaction energy values as the experimental response. The strongest interaction energy corresponds to strong response, as reflected in the experimental results ; EPCH is the best responder in the polymer-carbon black sensor category.

VI. CONCLUSIONS

We have developed and tested two types of polymer-based sensors capable of detecting 80-500ppm concentrations of carbon monoxide at room temperature conditions. Both the polymer-carbon black sensors and the porphyrin-functionalized polypyrrole films show good, reversible response to carbon monoxide. In the case of PECH, the preliminary data show that the sensor response to CO is linear. The data on the PEO-porphyrin-functionalized polypyrrole films show good response and reversibility upon exposure to carbon monoxide. Work is in progress to increase the sensitivity of these sensors to carbon monoxide for use to NASA applications.

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REFERENCES

[1] NASA Document No: CxP 70024, Revision A, Change 001, “Constellation Program Human-Systems Integration Requirements,” (Release Date 10/30/2007).

[2] M. A. Ryan, M. L.Homer, H. Zhou, K. S.Manatt, V. S. Ryan and S. P. Jackson, "Operation of an Electronic Nose Aboard the Space Shuttle and Directions for Research for a Second Generation Device," *Proceedings of International Conference on Environmental Systems* 2000, 00ICES-259, Toulouse, France.

[3] M. A. Ryan, H. Zhou, M. G. Buehler, K. S. Manatt, V. S. Mowrey, S. R. Jackson, A. K. Kisor, A. V. Shevade and M. L Homer, "Monitoring Space Shuttle Air Quality Using the Jet Propulsion Laboratory Electronic Nose," *IEEE Sensors Journal*, Vol. 4, No. 3, 2004, pp. 337-347.

[4] M. A. Ryan, M. L.Homer, H. Zhou, K. Manatt and A. Manfreda, "Toward a Second Generation Electronic Nose at JPL: Sensing Film Optimization Studies," *Proceedings of International Conference on Environmental Systems* 2001, 2001-01-2308, Orlando FL, USA.

[5] M. A. Ryan, M. L. Homer, H. Zhou, K. Manatt, A. Manfreda, A. Kisor, A. Shevade and S.P.S.,Yen, "Expanding the Capabilities of the JPL Electronic Nose for an International Space Station Technology Demonstration" *Journal of Aerospace, SAE Transactions* 2006, *2006-01,* 225-210.

[6] M. A. Ryan, K. S. Manatt, S. Gluck, A. V. Shevade, A. K. Kisor, H. Zhou, L. M. Lara and M.L. Homer, “Operation of the Third Generation JPL Electronic Nose on the International Space Station,” *Proc. 39th International Conference on Environmental Systems* 2009-01-2522, SAE (2009).

[7] M. Ando, "Recent Advances in Optochemical Sensors for the Detection of H-2, O-2, O-3, CO, CO2 and H2O in Air," *Trac-Trends in Analytical Chemistry*, Vol. 25, No. 10, 2006, pp. 937-948.

[8] J. P. Dakin, M. J. Gunning, P. Chambers and Z. J. Xin, "Detection of Gases by Correlation Spectroscopy," *Sensors and Actuators B-Chemical*, Vol. 90, No. 1-3, 2003, pp. 124-131.

[9] U. Liebl, L. Bouzhir-Sima, L. Kiger, M. C. Marden, J. C. Lambry, M. Negrerie and M. H. Vos, "Ligand Binding Dynamics to the Heme Domain of the Oxygen Sensor Dos From Escherichia Coli," *Biochemistry*, Vol. 42, No. 21, 2003, pp. 6527-6535.

[10] P. Santhosh, K. M. Manesh, A. Gopalan and K. P. Lee, "Novel Amperometric Carbon Monoxide Sensor Based on Multi-Wall Carbon Nanotubes Grafted With Polydiphenylamine - Fabrication and Performance," *Sensors and Actuators B-Chemical*, Vol. 125, No. 1, 2007, pp. 92-99.

[11] M. E. Tess and J. A. Cox, "Humidity-Independent Solid-State Amperometric Sensor for Carbon Monoxide Based on an Electrolyte Prepared by Sol-Gel Chemistry," *Analytical Chemistry*, Vol. 70, No. 1, 1998, pp. 187-190.

[12] N. Densakulprasert, L. Wannatong, D. Chotpattananont, P. Hiamtup, A. Sirivat and J. Schwank, "Electrical Conductivity of Polyaniline/ Zeolite Composites and Synergetic Interaction With Co," *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, Vol. 117, No. 3, 2005, pp. 276-282

[13] J. A. Park, J. Moon, S. J. Lee, S. H. Kim, T. Zyung and H. Y. Chu, "Structure and Co Gas Sensing Properties of Electrospun TiO_2 Nanofibers," *Materials Letters*, Vol. 64, No. 3, 2010, pp. 255-257.

[14] C. Y. Liu, C. F. Chen and J. P. Leu, "Fabrication of Mesostructured Cobalt Oxide Sensor and Its Application for Co Detector,"

Electrochemical and Solid State Letters, Vol. 12, No. 4, 2009, pp. J40-J43.

[15] S. Javadpour, A. Gharavi, A. Feizpour, A. Khanehzar and F. Panahi, "Morpholine Doped Poly(3,4-Ethylenedioxy) Thiophene-Poly(Styrenesulfonate) as a Low Temperature and Quick Carbon Monoxide Sensor," *Sensors and Actuators B-Chemical*, Vol. 142, No. 1, 2009, pp. 152-158.

[16] S. Paul, F. Amalraj and S.Radhakrishnan, "CO Sensor Based on Polypyrrole Functionalized With Iron Porphyrin," *Synthetic Metals*, Vol. 159, No. 11, 2009, pp. 1019-1023.

[17] A. V. Shevade, M. A. Ryan, M. L. Homer, A. M. Manfreda, H. Zhou and K. Manatt, "Molecular modeling of polymer composite-analyte interactions in electronic nose sensors," *Sens. and Actuat. B: Chemical* 2003, 93, 84-91.

[18] A. V. Shevade, M. A. Ryan, M. L. Homer and H. Zhou *et al.*, "Chemical Sensor Array Response Modeling Using Quantitative Structure-Activity Relationships," in *Computational Methods for Sensor Material Selection* (Integrated Microanalytical Systems), M.A. Ryan, A.V. Shevade, C.J. Taylor, M.L. Homer, M. Blanco, J.R. Stetter, eds., Springer, New York, 2009, Chaps 8.

[19] A. K. Rappe and W.A.,Goddard, "Charge equilibration for Molecular-dynamics simulations, "*J. Phys. Chem.* 1991, 95(8), 3358-3363.

[20] S. L. Mayo, B. D. Olafson and W. A. Goddard, "Dreiding - A generic force-field for molecular simulations," *J. Phys. Chem.* 1990, 94(26), 8897-8909.

[21] Cerius^2 v 4.2, Accelrys Inc., San Diego, California, USA.