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Tunable Impedance Spectroscopy Sensors via Selective Nanoporous Materials

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Abstract

Impedance spectroscopy was leveraged to directly detect the sorption of I_2 by selective adsorption into nanoporous metal organic frameworks (MOF). Films of three different types of MOF frameworks, respectively, were drop cast onto platinum interdigitated electrodes, dried, and exposed to gaseous I_2 at 25, 40, or 70 °C. The MOF frameworks varied in topology from small pores (equivalent to I_2 diameter) to large pore frameworks. The combination of the chemistry of the framework and pore size dictated quantity and kinetics of I_2 adsorption. Air, argon, methanol, and water were found to produce minimal changes in ZIF-8 impedance. Independent of MOF framework characteristics, all resultant sensors showed high response to I_2 in air. As an example of sensor output, I_2 was readily detected at 25 °C in air within 720 s of exposure, using an un-optimized sensor geometry with a small pored MOF. Further optimization of sensor geometry, decreasing MOF film thicknesses and maximizing sensor capacitance, will enable faster detection of trace I_2.

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1. INTRODUCTION

Concerns with increased worldwide energy demands, balanced with the need to reduce greenhouse gas emissions, have fueled research on clean, safe, and responsible nuclear energy.[1] Safety remains a main issue of concern for nuclear energy. Of particular interest is the monitoring and detection of escaping volatile gaseous fission products from nuclear fuel reprocessing or inadvertent/accidental environmental release. These radionuclides include ^{129}I and ^{131}I, ^{3}H, $^{14}CO_2$, and ^{85}Kr. Of these, radiological iodine poses exceptional issues. Iodine (I_2) is a highly mobile gas whose individual isotopes present unique exposure problems: ^{129}I is a particularly long-lived isotope (half-life of 1.57 x 10^7 years) that must be captured and reliably stored while it decays, whereas the ^{131}I isotope is short-lived (half-life of 8.02 days) but requires immediate detection and/or capture because it directly affects human metabolic processes. The development of reliable sensors for the detection of iodine gas under ambient conditions (in the presence of air components including water) is necessary.

In this short term Express LDRD, we studied the development of iodine specific sensors. We drew together separate technologies (impedance spectroscopy (IS), nanoporous materials, and selective iodine adsorption) to create a MOF-based I_2 sensor with broad ($10^5\times$) electrical response and reasonable performance at ambient conditions. Interestingly, these strong results were obtained using non-optimized sensor geometry, facile fabrication techniques, and only commercially available materials.

2. RESULTS AND DISCUSSION

Utilizing metal organic frameworks (MOFs) that have been shown to have selectivity for iodine gas by Nenoff, et.al.,[2-5] we utilized MOFs and commercial interdigitated electrodes in the successful developed, building and testing of an impedance spectroscopy sensor for I_2 gas.

During this project, we were successful in achieving all of our milestones. First steps included the purchase and testing (confirmation of signal) of interdigitated electrodes (IDEs; Pt on silica glass) for the study. Then, the down select of three unique MOF structures to utilize in the sensor was performed; the MOFs chosen ranged from small pored (approximately I_2 sized pore opening) to large pores with highly active metal centers for bonding to the I_2.

Next, IDEs were coated with a specific MOF using a simple dropcasting technique. This procedure consistently deposited a film thickness on the order of 35 μm, as measured by profilometer. The sensors were subsequently exposed to I_2 at 25, 40, or 70 °C for 30 minutes, followed by heating at 70 °C in air to desorb bulk-surface adsorbed I_2. The MOF film was deposited so that covered the entire active area of the IDE. The white film acquired an orange-brown hue upon exposure to I_2.

To ensure reliability of the IS data, materials characterization of the MOF films and impedance spectroscopy signal interpretation were performed pre- and post- I_2 adsorption at all temperatures. Impedance spectra were recorded with a Solartron 1260 Frequency Response Analyzer connected in series with Solartron 1296 Dielectric Interface, utilizing the internal reference capacitors for measurements. Materials characterization included: Powder X-ray diffraction performed on the films using a Bruker D2 Phaser system set in the traditional Bragg-Brentano geometry with Cu Kα radiation, and infrared (IR) spectra recorded on a Thermo Scientific Nicolet 6700 spectrometer using the diffuse reflectance attachment set to an incident angle of 30° from substrate normal (128 scans were averaged at a resolution of 1 cm^{-1}).

One exemplar of this LDRD is a sensor developed using the small pored MOF. The results showed that the as-received sensor had very high impedance ($|Z| > 10^{11}\ \Omega$ at 10 mHz) and highly capacitive character ($\theta \approx -90°$), as expected for metal lines on a glass substrate. Upon addition of the small pored MOF film, the low frequency impedance decreased slightly, and the phase angle rose slightly, consistent with reports on the high resistivity of many MOFs.[6,7] Exposing the sensor to I_2, however, created a large change in both impedance and phase angle at low frequencies. A $>10^5\times$ decrease in ZIF-8 resistance, R_Z was observed when 116 wt% of I_2 was sorbed by the MOF at 70 °C in air. It is believed that the decrease in resistance is related to new conduction pathways unlocked upon irreversible loss of long-range crystal structure during I_2 sorption.

3. CONCLUSION

One of the most attractive aspects of using MOFs for chemical sensors is the chemical tunability of the structures and how these influence the selective sorption of various species, minimizing interfering responses. The results from this project demonstrate how highly selective gas adsorption in MOFs can be leveraged to create large ($>10^5$) changes in impedance response. Furthermore, this enables the direct electrical sensing and detection of fission off gases under ambient conditions from nuclear reprocessing or accident conditions, with the use of impedance spectroscopy techniques.

The details of this research can be found in reference 8:

8) Small, L. J.; Nenoff, T. M. "Direct Electrical Detection of Iodine Sorption by a Metal Organic Framework Sensor", *ACS Applied Materials & Interfaces*, 2017, in preparation.

REFERENCES

1) Kintisch, E. *Science* **2005**, *310*, 1406.

2) Sava, D.F.; Rodriguez, M.A.; Chapman, K.W.; Chupas, P.J.; Greathouse, J. A.; Crozier, P.S.; Nenoff, T.M. "Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8", *J. Amer. Chem. Soc.*, **2011**, *133* (32), 12398–12401.

3) Sava, D.F.; Chapman, K.W.; Rodriguez, M. A.; Greathouse, J. A.; Crozier, P. S.; Zhao, H.; Chupas, P. J.; Nenoff, T.M. "Competitive I_2 Sorption in Cu-BTC from Humid Gas Streams", *Chem. Mater.*, **2013**, *25* (13), 2591–2596.

4) Hughes, J.T.; Sava, D.F.; Nenoff, T. M.; Navrotsky, A. "Thermochemical Evidence for Strong Iodine Chemisorption by ZIF-8", *J. Amer. Chem. Soc.*, **2013**, 135(44), 16256-16259.

5) Sava Gallis, D. F.; Ermanoski, I.; Greathouse, J.A.; Chapman, K. W.; Nenoff, T.M. "Iodine Gas Adsorption in Nanoporous Materials: a Combined Experiment-Modeling Study", *Ind. Eng. Chem. Res.*, **2017**, 56(8), 2331-2338.

6) Achmann, S.; Hagen, G.; Kita, J.; Malkowsky, I.; Kiener, C.; Moos, R. Metal-Organic Frameworks for Sensing Applications in the Gas Phase. *Sensors* **2009**, *9*, 1574–1589.

7) Talin, A.; Centrone, A.; Ford, A.; Foster, M.; Stavila, V.; Haney, P.; Kinney, R.; Szalai, V.; Gabaly, F.; Yoon, H.; Leonard, F.; Allendorf, M. Tunable Electrical Conductivity in Metal-Organic Framework Thin-Film Devices. *Science* **2014**, *343*, 66–69.

8) Small, L. J.; Nenoff, T. M. "Direct Electrical Detection of Iodine Sorption by a Metal Organic Framework Sensor", *ACS Applied Materials & Interfaces*, **2017**, in preparation.

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