Reversible MOF-Based Sensors for the Electrical Detection of Iodine Gas

Leo J. Small,†‡ Ryan C. Hill,†‡ James L. Krumhansl,† Mara E. Schindelholz,† Zhihengyu Chen,‡ Karena W. Chapman,‡ Xinran Zhang,§ Sihai Yang,§ Martin Schröder,§ and Tina M. Nenoff‡†

†Sandia National Laboratories, Albuquerque 87185, New Mexico, United States
‡Department of Chemistry, Stony Brook University, 100 Nicolls Road, New York 11794, United States
§School of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

ABSTRACT: Iodine detection is crucial for nuclear waste clean-up and first responder activities. For ease of use and durability of response, robust active materials that enable the direct electrical detection of I₂ are needed. Herein, a large reversible electrical response is demonstrated as I₂ is controllably and repeatedly adsorbed and desorbed from a series of metal–organic frameworks (MOFs) MFM-300(X), each possessing a different metal center (X = Al, Fe, In, or Sc) bridged by biphenyl-3,3′,5,5′-tetracarboxylate linkers. Impedance spectroscopy is used to evaluate how the different metal centers influence the electrical response upon cycling of I₂ gas, ranging from 10⁻⁶ to 10⁻⁶ decrease in resistance upon I₂ adsorption in air. This large variation in electrical response is attributed not only to the differing structural characteristics of the MOFs but also to differing MOF morphologies and how this influences the degree of reversibility of I₂ adsorption. Interestingly, MFM-300(Al) and MFM-300(Fe) displayed the largest changes in resistance (up to 10⁶ x) yet lost much of their adsorption capacity after five I₂ adsorption cycles in air. On the other hand, MFM-300(Fe) and MFM-300(Sc) revealed more moderate changes in resistance (10⁻⁶–10⁻⁶), maintaining most of their original adsorption capacity after five cycles. This work demonstrates how changes in MOFs can profoundly affect the magnitude and reversibility of the electrical response of sensor materials. Tuning both the intrinsic (resistivity and adsorption capacity) and extrinsic (surface area and particle morphology) properties is necessary to develop highly reversible, large signal-generating MOF materials for direct electrical readout for I₂ sensing.

KEYWORDS: metal–organic framework, MOF, iodine, nanoporous, impedance spectroscopy, sensor

INTRODUCTION

Prompt, reliable fission gas detection is paramount for the safety of the public and first responders during both nuclear accidents and industrial nuclear fuel reprocessing.1 In particular, iodine gas detection is of great concern. The isotopes of iodine have immediate impact to human health and long-term impact to the environment, including ¹³¹I isotope (half life ~8 days) and ¹²⁹I isotope (half life ~17 million years). Commercial I₂ sensors do exist, though they can possess significant drawbacks. Common fuel-cell type I₂ sensors have relatively short lifetimes coupled with susceptibility to fouling. Other solid-oxide-type sensors require temperatures >200 °C for interaction between the gas and oxide surface, limiting applications. Ideally, a compact device easily integrated with modern electronics is desired. For simplicity of design, information output, and device reliability, a direct electrical readout is advantageous.

In an effort to identify materials that enable a compact, reliable, and robust sensor, impedance spectroscopy (IS) is used to monitor series of related materials. IS is a technique that is useful for understanding charge movement in complex materials systems. A small sinusoidal voltage is applied to the sample, and the resulting current is measured, with “impedance” being defined as the ratio of complex voltage to complex current. This measurement is then repeated over a broad frequency range, such as 1 MHz to 10 mHz, to best understand the different components of the system. The use of small sinusoidal voltage about a chosen dc potential enables measurement without necessarily driving a reaction or forcing a net flow of current. IS has been successfully utilized across a variety of systems to understand charge movement in solar cells,5,6 ion-conducting solid electrolytes,5,6 and structures at solid–liquid interfaces.7,8

To develop a sensor based on IS but with high response to I₂ nanoporous materials with the ability to reversibly adsorb I₂ from the environment are necessary. To date, a variety of zeolites and metal–organic frameworks have been shown to selectively adsorb I₂ from complex gas streams,9–12 including ZIF-8,13–16 HKUST-1,17 Zr₆O₄(OH)₄(sdc)₆,18 Zr₂O₃(OH)₄(pez)₆,18 and micro-Cu₄I₄.19

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MOF, Zn$_2$(DL-lac)$_2$pybz)$_2$, CO(bdc)$_1$H$_2$(H$_2$pyz)$_0$.51.-
DMF, TbCu$_4$I$_4$(ina)$_3$(DMF), SBMOF-1 (Ca(sdb)),
silica zeolites, and silver-containing zeolites (e.g., silver-
mordenite) success. Early success was achieved with a thin film of
ZIF-8 as the adsorbent layer on a sensor bed of Pt-
terminated electrodes (IDE). While a large ($>10^4$) change in impedance was observed, the response was largely
irreversible. Subsequent investigation of silver-mordenite, a
widely used zeolite for $^{129}$I capture, revealed a structure stable to gas adsorption and temperature but with
only a modest <5X change in resistance.

In an effort to retain the large electrical response of ZIF-8
MOF but with the stability of silver—mordenite zeolites, sensors
are reported herein from a family of thermally and chemically
robust porous materials MFM-300(X) (X = Al, Fe, In, Sc)
which show exceptional reversible $^{129}$I adsorption capacity.
This high capacity is due to the strong iodine binding sites
(betaine oxide and a site between the ligand phenyl rings).
Furthermore, the triply charged metal cations are
coordinated to a biphenvl-3,3',5,5'-tetracarboxylate linker to
form a porous “wine-rack” structure through which I$_2$
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The materials MFM-300(X) (X = Al, Fe, In, Sc) were
synthesized as powders and individually dropcast onto
platinum IDE, forming a series of sensors capable of detecting
$^{129}$I electrically. IS was used to define the broad electrical
frequency response of these materials. The reversibility of the
electrical response upon repeated $^{129}$I loading (70 °C, 3 h, air)
and unloading (57 °C, 8 h, <1 mTorr) revealed wide
variation between MFM-300(X) as a function of different
metal centers X. These observed changes in electrical
properties were correlated with changes in adsorption capacity,
structural integrity, and morphology and are detailed in depth
below. Importantly, in this work, only the MOF metal centers
were varied in an effort to minimize outside factors interfering
with the impedance of the electrode, such as particle and grain
sizes.

It should be noted that all MFM-300(X) materials exhibited
a similar impedance response, though the magnitude of the
change was variable (see Figure S1–S4). Typical impedance
spectra are provided in Figure 1 for MFM-300(In). The as-
synthesized and dried MFM-300(In) displays a high capacitive
response, with $|Z|_{\text{cap}}$ increasing with decreasing frequency, and
the phase angle is nearly $-90°$ except for the lowest
frequencies. After $I_2$ is adsorbed, the low-frequency impedance
($|Z|_{\text{cap}}$) levels out below 1 Hz, and the phase angle transitions
from $-90°$ to $0°$, indicative of a change in response from
capacitive to resistive. Desorption of $I_2$ from MFM-300(In)
leads to the impedance magnitude and phase angle returning
to nearly their original values. Thus, the reversible adsorption
desorption of $I_2$ from MFM-300(In) is accompanied by a
reversible change in impedance response.
To better quantify the changes in impedance, an equivalent circuit model previously developed for I₂ adsorption in ZIF-8 was used. This circuit, depicted in Figure 2, consists of a series resistance, $R_s$, and two parallel resistor–capacitor networks linked in parallel. The series resistance is dominated by the platinum lines on the IDEs and is typically 400–450 Ω. The first resistor–capacitor network relates the glass substrate resistance, $R_g$ ($\approx 10^{12}$ Ω), and capacitance, $C_g$ ($\approx 40$ pF). Actual values for $R_s$, $R_g$, and $C_g$ were measured on each blank IDE before dropcasting with MFM-300(X). These values were then fixed for subsequent analysis of MFM-300(X) resistance, $R_{\text{MFM}}$, and capacitance, $\text{CPE}_{\text{MFM}}$. Here, a constant phase element is used to describe the inhomogeneity of the response of MFM-300(X). This equivalent circuit analysis was then performed as IDEs containing MFM-300(X) and was cycled through five I₂ loading and unloading cycles.

The resulting changes in $I_2$ adsorption capacity (mass change) and resistance of MFM-300(X) ($R_{\text{MFM}}$) are plotted in Figure 3. Two distinct sets of responses are observed. First, MFM-300(Al) and MFM-300(In) both show a gradual decrease in adsorption capacity, accompanied by an increasing amount of mass retained after desorption. $R_{\text{MFM}}$ was consistently high ($10^{11}$ Ω) across all readings, with MFM-300(In) displaying the overall highest resistance of all tested materials. However, the resistance of I₂-loaded MFM-300(Al) and MFM-300(In) both decreased as cycling continued.

Similar to the two previous members of the series, MFM-300(Fe) and MFM-300(Sc) both display large and consistent $I_2$ adsorption capacities across all five loading cycles. After three cycles, however, a mass increase of 13.6 and 12.0 wt % for MFM-300(Fe) and MFM-300(Sc), respectively, was noted. In contrast to MFM-300(Al) and MFM-300(In), the large, highly reversible adsorption capacities were accompanied by a relatively small change in $R_{\text{MFM}}$ ($10 \times$ and $100 \times$, respectively). MFM-300(Fe) revealed very consistent changes in $R_{\text{MFM}}$ from 550 GΩ unloaded to 55 GΩ when loaded with I₂. MFM-300(Sc) showed similar differences in $R_{\text{MFM}}$, though the unloaded resistance slowly increased with the cycle number.

From these results, it is concluded that a consistent electrical response is indicative of a consistent I₂ adsorption amount. However, large I₂ adsorption capacity is not necessary to create a large change in $R_{\text{MFM}}$. By cycle five, the MFM-300(Al) and (In) devices only adsorbed an additional 28 and 15 wt % I₂, respectively, yet they exhibited changes in $R_{\text{MFM}}$ of $9 \times 10^5$ and $6 \times 10^6$. The fact that $R_{\text{MFM}}$ continuously decreases for the MFM-300(Al) and MFM-300(In) devices suggests that either (i) a chemical or structural change was occurring to the MOF or (ii) relatively small amounts of I₂ were being adsorbed irreversibly into preferential sites in the MOF pore system, decreasing the resistance.

To verify the structural stability of MFM-300(X) materials, XRD was performed on the sensors after each I₂ cycle. Figure 4 compares diffraction patterns for the blank IDE to that loaded.

**Figure 1.** Impedance response and equivalent circuit fits for MFM-300(In). This plot is representative of all MFM-300(X) materials in this work, demonstrating the reversibility of the impedance response as I₂ is added and subsequently removed. For clarity, only every other data point has been plotted.

**Figure 2.** Equivalent circuit fit to impedance data overlaid onto a cross-sectional schematic of the sensor, relating how the circuit elements $R_s$, $R_{\text{MFM}}$, $\text{CPE}_{\text{MFM}}$, $R_g$, and $C_g$ spatially correspond to the materials used. Schematic is not to scale.

**Figure 3.** (Top) I₂ adsorption and (bottom) room-temperature MOF resistance, $R_{\text{MFM}}$, for MFM-300(X) (X = Al, Fe, In, or Sc). Filled symbols denote MFM-300(X) after I₂ sorption at 70 °C for 3 h in air, while open symbols were recorded after desorption at 175 °C for 8 h at <1 mTorr. If not visible, error bars are smaller than the marker.
MFM-300(Fe) retained the least I₂ (10.7 wt %) in the MOF pores after the crystal structure of MFM-300(X) was retained. After desorption of I₂, the diffraction peaks return but with lower intensities. By the fifth desorption, significant differences in peak intensity are observed between the different MFM-300(X) analogues.

These differences are attributed to the amount of I₂ retained in the MOF pores after the fifth desorption cycle. For example, MFM-300(Fe) retained the least I₂ (10.7 ± 0.4 wt %) and showed the most intense diffraction peaks. No additional phases were observed during XRD analysis consistent with MFM-300(Fe) phase stability. Thus, it is concluded that changes in \( R_{\text{MFM}} \) are largely not a result of degradation of the MFM-300 crystal structure.

In contrast, MFM-300(Fe) and MFM-300(Sc) exhibited a wide distribution of orthorhombic particles less than 0.5–25 μm in length, displaying highly variable aspect ratios varying from rods to plates.

EDS was recorded at multiple sites for all powders shown in Figure 5. No significant changes in EDS spectra were observed before versus after I₂ cycling, as shown in Figures S5–S8. For powders before I₂ exposure (Figures S5A–S5G) carbon, oxygen, and the relevant metals were observed. After the fifth I₂ desorption cycle, all powders (Figure S5B,D,F,H) displayed the same framework elements by EDS but also confirmed the presence of additional iodine. This is consistent with the residual (added) masses observed upon desorption (Figure 3).

In conjunction with the previous XRD and SEM data, it is concluded that the residual mass upon I₂ unloading (Figure 3) is predominantly iodine retained in the MFM-300(X) framework and not a secondary species from the environment (e.g., O₂, H₂O, etc.).

**Figure 4.** XRD patterns of IDEs coated with MFM-300(X) (X = Al, Fe, In, or Sc) at different points in the I₂ adsorption/desorption cycle: (A) bare IDE, (B) IDE coated with MFM-300(X) and dried, (C) after the first I₂ sorption, (D) after the first desorption cycle, and (E) after the fifth desorption cycle.

**Figure 5.** SEM images of MFM-300(X) as dried and after the fifth I₂ desorption cycle for (A,B) X = Al, (C,D) X = Fe, (E,F) X = In, and (G,H) X = Sc.
Differences in MFM-300(X) particle morphologies affect bulk adsorption and transport of I$_2$ gas throughout the pores. Furthermore, the differences in electrical responses in MFM-300(X) are due to the differences in the polarization of I$_2$ in the pores, which is likely controlled by the amount and concentration of adsorbed I$_2$, and by the depth of penetration of adsorption in each crystallite. All of these are controlled to a large part by crystallite morphology and nanopore size opening. The crystal structure of MFM-300(X) resembles a “wine rack”, where I$_2$ molecules enter the c-face and diffuse along the c-axis forming a dense network of triple helices when completely packed. Specific differences in adsorption properties between the MFM-300(X) analogues are summarized in Table 1.

Both MFM-300(Fe) and MFM-300(Sc) display wide distribution particle sizes and orientations. Many of these particles are <1 μm, creating a relatively high surface area and encouraging prompt, reversible I$_2$ diffusion. MFM-300(Al) has particles that are highly oriented and, on average, smaller than those of MFM-300(Fe) and MFM-300(Sc). As the c-axis of the MOF lies along the long axis of the particles, the effective surface area and pore opening for I$_2$ to enter the MOF is thus much smaller for MFM-300(Al) than for MFM-300(Fe) and MFM-300(Sc).

This effect is more pronounced for MFM-300(In), where the c-axis is a relatively smaller surface area on the large, long crystallites. The adsorption pathway for I$_2$ is via the small octagonal face with di-axis forming a dense network of triple helices when completely packed. Specific differences in adsorption properties between the MFM-300(X) analogues are summarized in Table 1.

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This effect is more pronounced for MFM-300(In), where the c-axis is a relatively smaller surface area on the large, long crystallites. The adsorption pathway for I$_2$ is via the small octagonal face with di-axis forming a dense network of triple helices when completely packed. Specific differences in adsorption properties between the MFM-300(X) analogues are summarized in Table 1.

It is proposed that I$_2$ adsorbs at key binding sites in the MFM-300(In) structure, enabling the formation of a conductive network. The additional time and temperature provided by subsequent loading/unloading cycles may optimize these adsorption locations in the crystal structure. This hypothesis is consistent with crystallographic data of the preferential adsorption site of I$_2$ at low loadings in other MOFs. Upon desorption, enough of the I$_2$ network may be removed so as to destroy the conduction pathway and create a large increase in resistance, enabling a large sensor response with relatively small addition of I$_2$.

### CONCLUSIONS

Development of robust active sensors for the direct electrical detection of I$_2$ will enable reliable, rapid detection of I$_2$ in critical environments. Herein, the performance of a family of MOFs as reversible selective adsorption materials in an IS-based sensor has been detailed. Interestingly, the responses of these MFM-300(X) materials can be controlled by the choice of X; MFM-300(Al) and MFM-300(In) displayed large (up to ×10$^8$) changes in resistance upon adsorption of I$_2$. While the adsorption capacity of MFM-300(Al) and MFM-300(In) decreased upon successive I$_2$ cycling, the change in resistance increased. On the other hand, MFM-300(Fe) exhibited stable I$_2$ adsorption capacities coupled with relatively stable changes in resistance of about ×23. Differences in electrical properties were attributed to variations in morphology of the MFM-300(X) materials and how this influences I$_2$ diffusion into the crystallites. For MFM-300(In) especially, it is noted that the addition of only a relatively small amount (~15 wt %) of I$_2$ is necessary to generate a large change in resistance. This behavior is attributed to the addition of I$_2$ upon cycling to key adsorption sites, enabling the formation of a conductive I$_2$ network within the pores of the MOF.

More broadly, this work demonstrates how changes in the metal centers of the MOF can profoundly affect the magnitude and reversibility of the electrical response of the sensor materials. Nanoscale tuning of both the intrinsic (resistivity and adsorption capacity) and extrinsic (surface area and particle morphology) properties is necessary to affect the conductivity of the adsorbed I$_2$ gas molecules. This in turn is necessary to produce the conductivity pathway necessary for an electrical response due to gas adsorption. Attention to the nanoscale enabled the development of reversible, highly-specific large signal generation of direct electrical readout I$_2$ sensors. Ongoing research is focused into the enhanced durability of these sensors and the development of related sensors for the targeting of high-impact industrial gases.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b09938.

Impedance spectra for blank IDEs and MFM-300(X) X = Al, Fe, Sc; and EDS of MFM-300(X) (X = Al, Fe, In, and Sc) before and after five I$_2$ exposure cycles (PDF)

#### AUTHOR INFORMATION

**Corresponding Author**

E-mail: tmnenof@sandia.gov. Phone: +1 505 844 0340.

**ORCID**

Leo J. Small: 0000-0003-0404-6287
Karena W. Chapman: 0000-0002-8725-5633
Sihai Yang: 0000-0002-1111-9272
Martin Schröder: 0000-0001-6992-0700
Tina M. Nenoff: 0000-0002-7906-4810

**Notes**

The authors declare no competing financial interest.

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Table 1. Adsorption Properties of MFM-300(X)$^{a}$

| MOF      | BET surface area (m$^2$ g$^{-1}$)$^{b}$ | pore size (Å)$^c$ | pore volume (cm$^3$ g$^{-1}$)$^{d}$ | observed $I_2$ uptake (g g$^{-1}$)$^{e}$ | max. $I_2$ uptake (g g$^{-1}$)$^{f}$ | observed $I_2$ density (g cm$^{-3}$)$^{g}$ |
|----------|---------------------------------------|-----------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|
| MFM-300(Al) | 1370                                  | 6.5             | 0.37                          | 0.869                           | 0.94                           | 2.35                            |
| MFM-300(Fe) | 1192                                  | 7.8             | 0.46                          | 1.11                            | 1.29                           | 2.41                            |
| MFM-300(In)  | 1050                                  | 7.6             | 0.41                          | 0.602                           | 1.16                           | 1.46                            |
| MFM-300(Sc)  | 1250                                  | 8.1             | 0.50                          | 1.18                            | 1.54                           | 2.36                            |

$^{a}$Observed $I_2$ uptake relates the $I_2$ adsorption during the first adsorption cycle (in air), while max $I_2$ uptake describes the maximum observed $I_2$ uptake for the material in ref 30 (in N$_2$). $^{b}$Values from ref 30.
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