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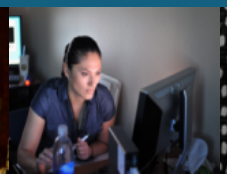
Sandia National Laboratories

Nanoporous-Based Sensors for Impedance Spectroscopy -Based Detection of Gaseous Pollutants



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ACS Spring 2022, Chemistry of Materials: Metal Organic Frameworks

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Introduction

- The ability to sense and identify individual gaseous pollutants from the complexity of the environment requires highly selective materials

  Avoidance of interference from real-world air components

  - Current conductivity-based devices generally fall into two categories:
    - Solid state – (oxide based) require higher temperatures (>200°C) for interaction of the gas with the surface oxides; heating devices are needed
    - Fuel cell – room temperature liquid electrolyte, easily fouled, short lifetime
  - Electrical metal organic framework (MOF) based sensors have previously been used for direct electrical sensing of gases; however, none for NO_2 have been reported in open literature
  - By tuning the composition of MOFs, selective chemical adsorption and/or catalysis can be achieved
  - Typical sensors for this application are hard-wired or require frequent battery replacement–nanoporous MOFs allows for “near-zero” long lived sensing in a wider range of environments

Direct Electrical Readout Sensors Combined with Nanoporous Adsorption Materials

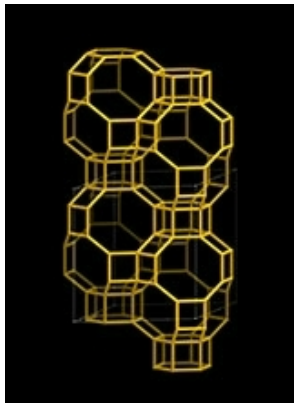
- Composed of **Pt interdigitated electrodes (IDEs) with a nanoporous adsorbent layer**
- Nanoporous adsorption materials chosen for **ability to selectively adsorb target** gas molecules
- Electrical readout sensor of this design:
  - Decreased power consumption
  - Ability to interrogate for specified gases selectively in real-time or as an integrating sensor for delayed/later testing

- Design of an integrated sensor:
  - Record whether any **degradation product was ever present** during the sensor's lifetime
- Integrated sensor is **useful** in cases where degradation products may:
  - Subsequently **react** with other components,
  - Gradually **leak out** of the system

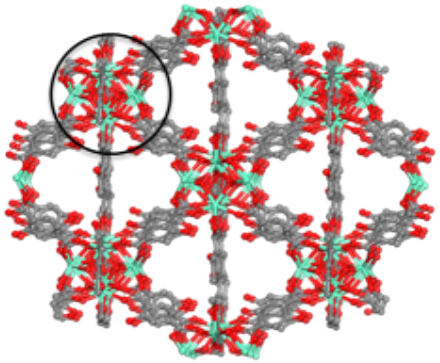
Nanoporous Materials Targeted for the Selective Adsorption of NO_x

Durable nanoporous adsorbents with selectivity for NO_x at low temperatures (near ambient)

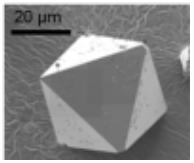
- Zeolites are aluminosilicates with high temperature durability. Specific metals give rise to NO_x selectivity
- Metal-organic frameworks (MOFs) are metal nodes with organic linkers with selectivity to NO_x designed by incorporating NO_x –friendly metals into the framework

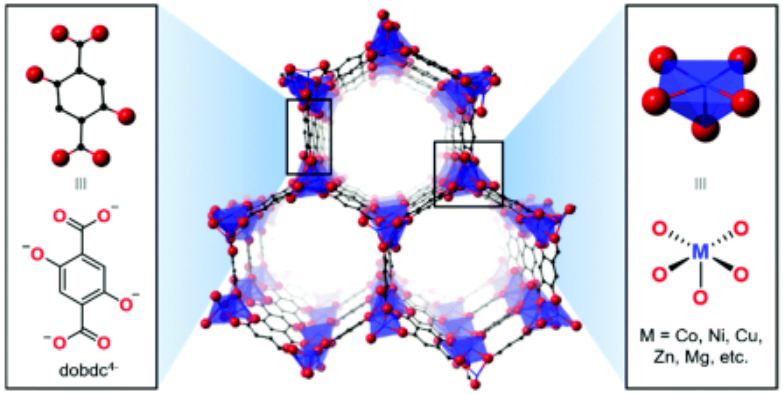


Zeolite SSZ-13 (CHA)



Metal-organic framework M-DOBDC (M = Y, Yb, Eu, Tb)

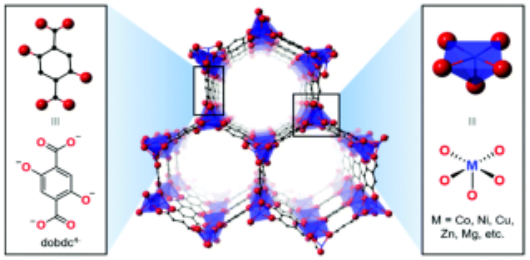


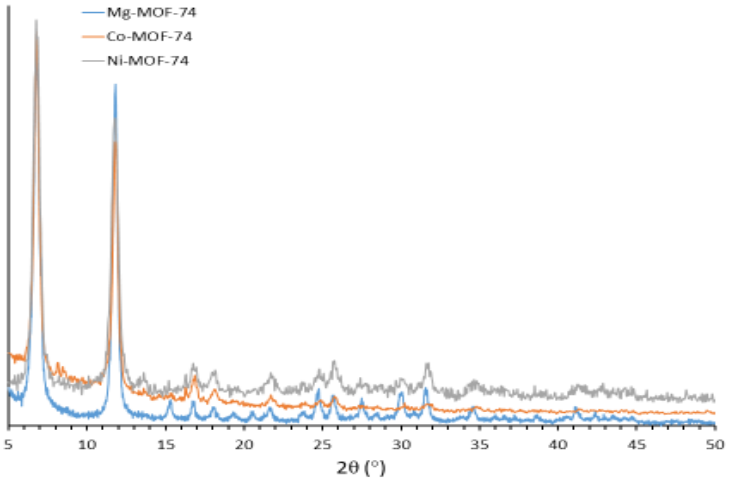


M-MOF-74 (M = Co, Mg, Ni)

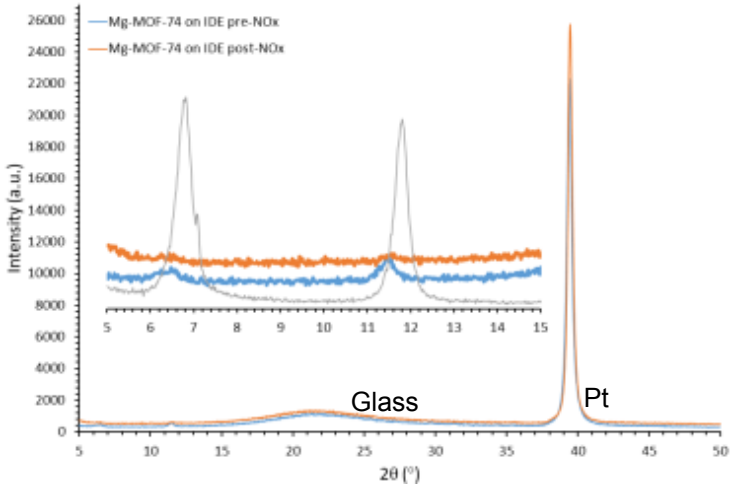
M-MOF-74-Based Sensors for the Selective Adsorption of NO_x

- M-MOF-74 (M= Co, Mg, Ni) was targeted for its selectivity to NO_2
- MOF-74 materials were synthesized and investigated as bulk materials and dropcast onto an interdigitated electrode (IDE)
- Each powder pattern highlighted two primary diffraction peaks corresponding to the MOF pore (intensities reduced for dropcast samples, with the large peak corresponding to the platinum IDE)





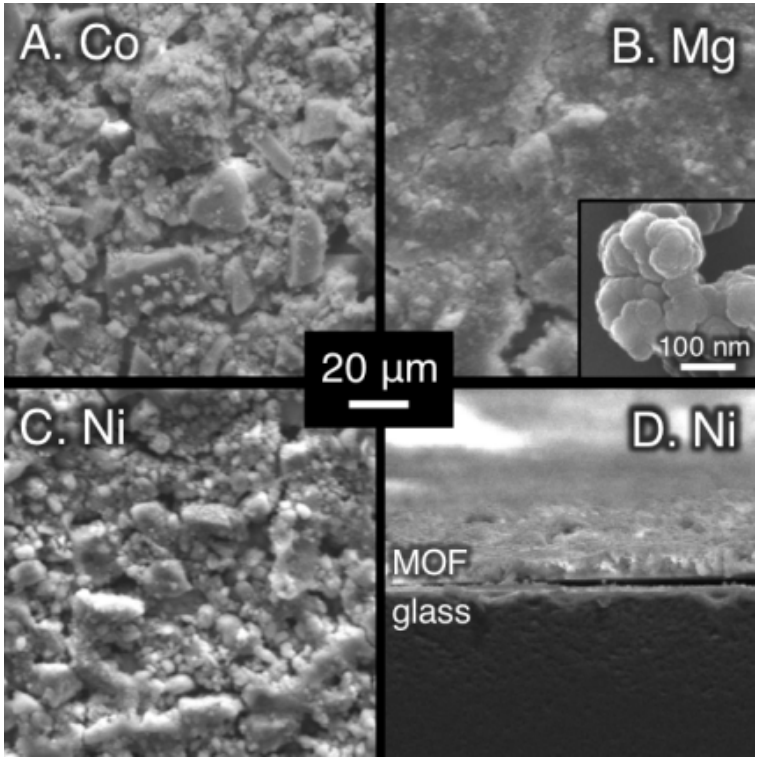
Powder XRD patterns for as-synthesized MOF-74 in the bulk phase.



Powder XRD patterns for Mg-MOF-74 dropcast onto IDE pre-NO_2 (blue) and post-NO_2 (orange). Inset: zoomed in region compared to bulk powder Mg-MOF-74.

Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,**

SEM Characterization of Dropcast M-MOF-74 Films



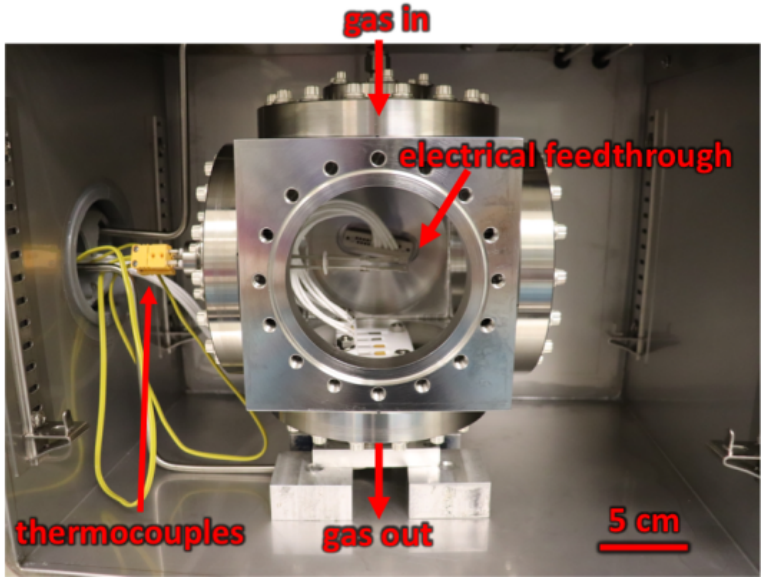
Plan-view SEM micrographs of (A) Co-MOF-74, (B) Mg-MOF-74, (C) Ni-MOF-74 powders dropcast onto IDEs. (D) Cross-sectional micrograph of Ni-MOF-74 film from (C).

- Co- and Ni-MOF-74 contained a wide range of crystallite sizes, from 100's of µm to 100 nm
- Mg-MOF-74 crystallites were on the order of 100 nm
- Film thickness was ~ 10 µm

Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,**

NO_x Exposure and In Situ Electrical Testing

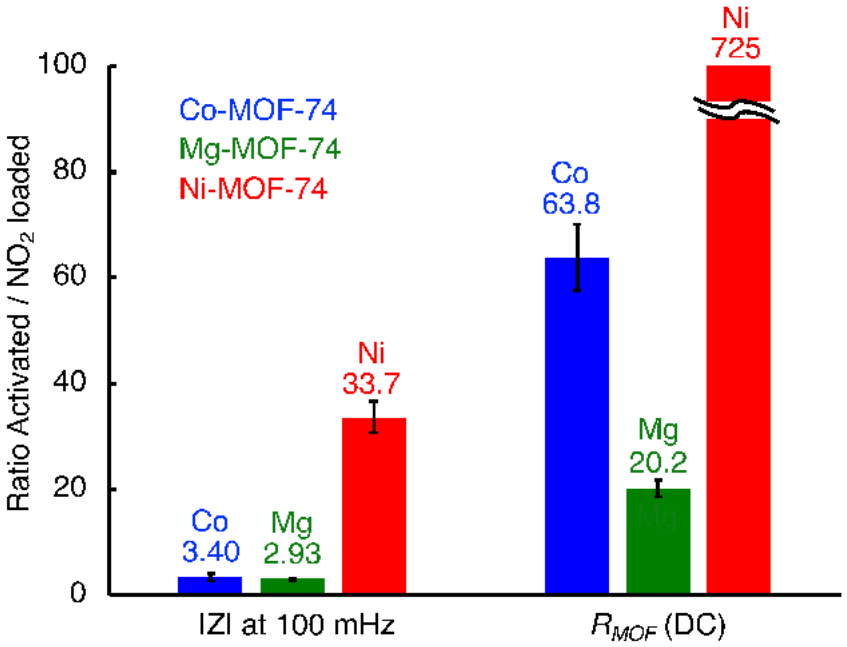
- Custom- built NO_x exposure chamber enabled MOF activation and subsequent in situ electrical testing under varying NO_2 concentrations without exposure to lab atmospheres
- Variable NO_2 concentrations (0.5-5 ppm) were achieved by diluting 5 ppm NO_2 gas stream with pure UHP N_2 at 500 sccm total gas flow
- Impedance spectra recorded at 0 V DC and 100 mV (RMS) AC over 1 MHz - 10 mHz
- All electrical measurements and NO_2 exposures occurred at 50°C



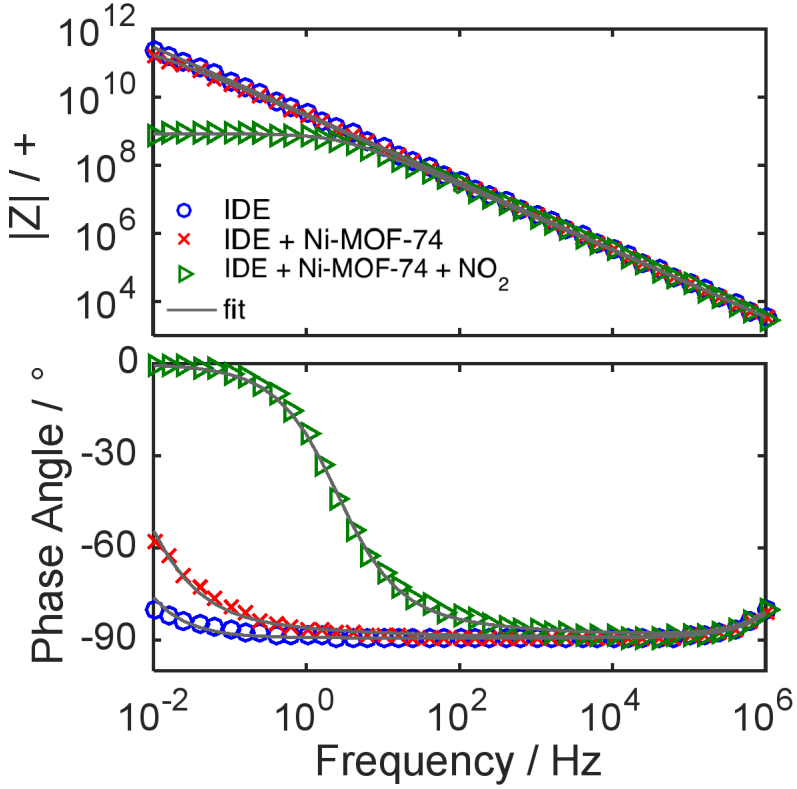
Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,**

Typical Impedance Responses of M-MOF-74-Based Sensors

Exposed M-MOF-74-based sensors to 5 ppm NO_2 for 8 h at 50°C.



Ratio of response as-activated to NO_2-exposed for (1) impedance magnitude ($|Z_{activated}|/|Z_{NO2}|$) at 100 mHz and (2) MOF DC film resistance ($R_{activated}/R_{NO2}$) for IDEs coated with M-MOF-74 (M= Co, Mg, Ni).

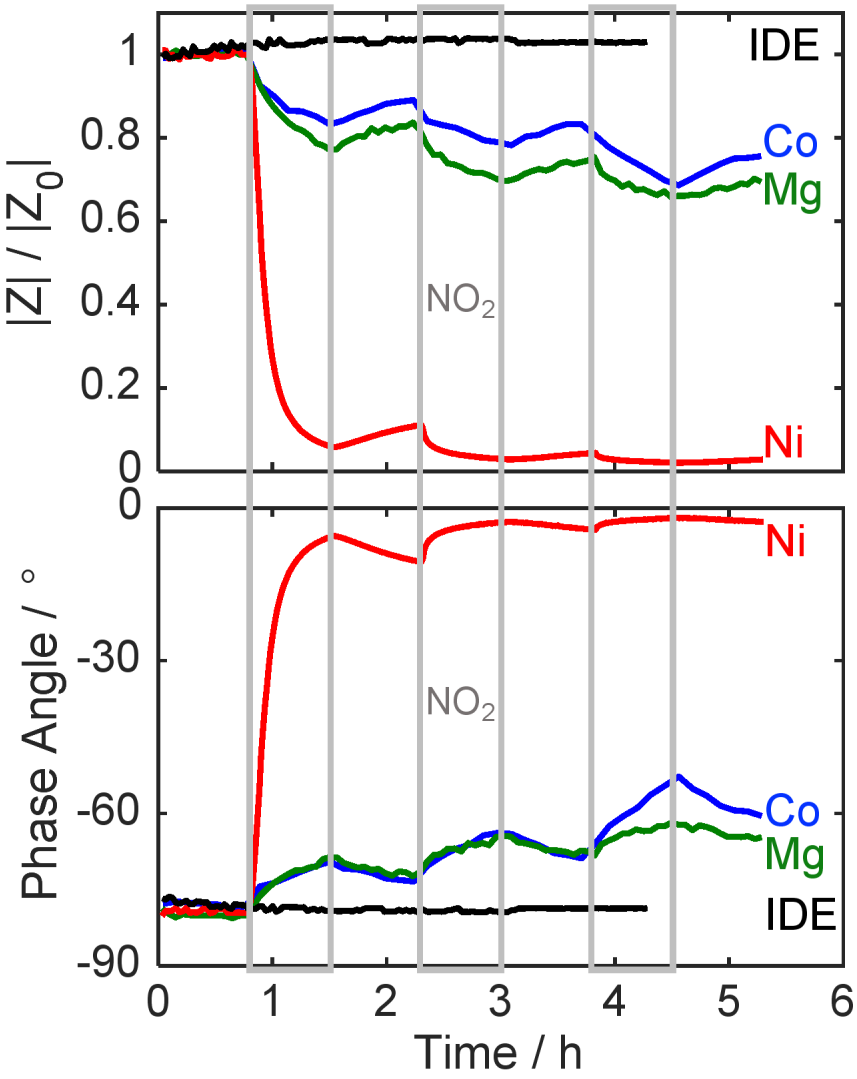


Example impedance spectra for Ni-MOF-74-based sensor

Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,** 2006598.

Impedance Responses as a Function of NO_2 Concentration

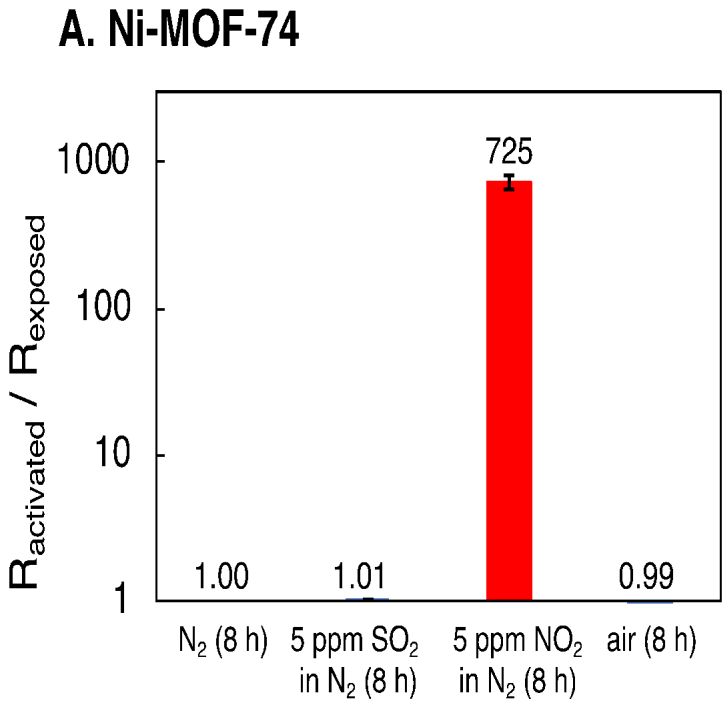
- Blank IDEs and IDEs coated in M-MOF-74 (M= Co, Mg, Ni) were activated and exposed to alternating 0.75 h flows of pure N_2 or N_2 containing trace NO_2, while impedance was constantly measured at 100 mHz
- Magnitude of electrical response is ordered Ni > Co > Mg
  - Explained by each variant's NO_2 adsorption capacity and specific chemical interaction
- Use of Ni-MOF-74 provided the highest sensitivity to NO_2, with a 725× decrease in resistance at 5 ppm NO_2 and a NO_2 detection limit <0.5 ppm

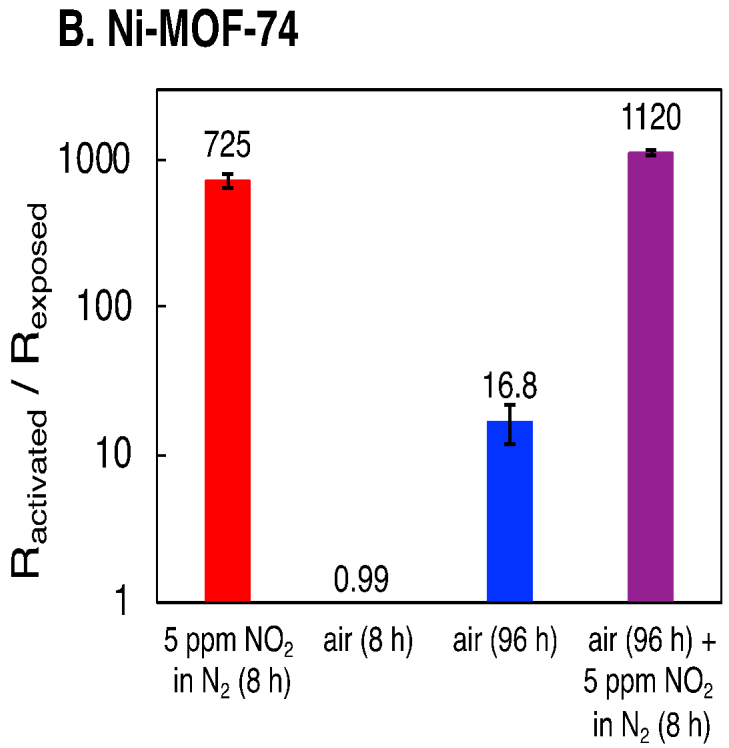


Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,** 2006598.

NO_2 Selectivity for a Ni-MOF-74-Based Sensor

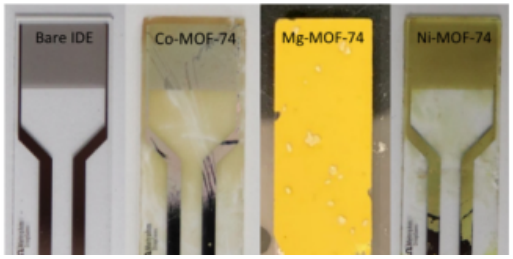
- A Ni-MOF-74-based sensor was activated and exposed to 5 ppm SO_2 in N_2, and ambient air (25 °C, 50% RH, 400 pm CO_2) heated to 50 °C, and its response compared to previous exposures to 5 ppm NO_2 in N_2
- An extended air exposure (96 hours) followed by subsequent NO_2 exposure was also performed
- The Ni-MOF-74-based sensor demonstrated selectivity to NO_2 versus N_2, SO_2, and air.





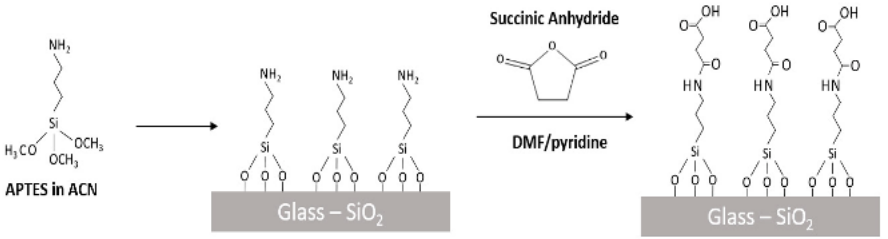
Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat., 50,* **2020,** 2006598.

Enhanced Sensitivity of Nanoporous-Based Sensors Using MOF Thin Film Membranes

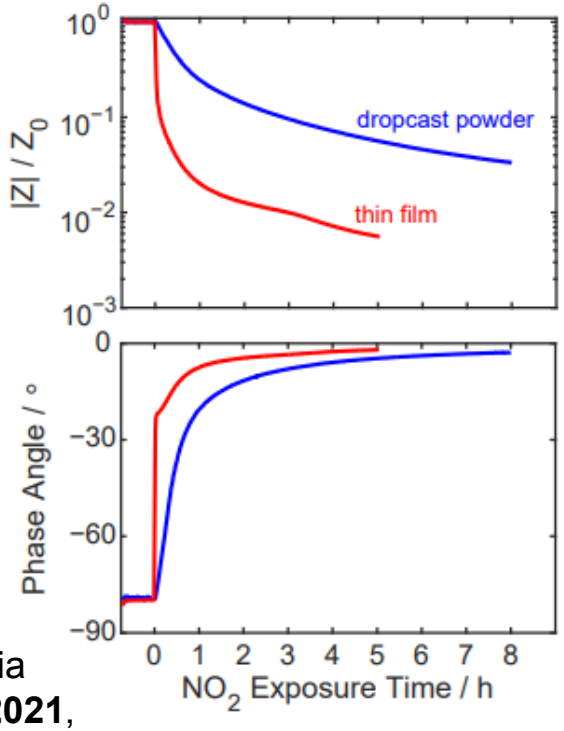


- M-MOF-74 (M=Co, Mg, Ni) MOFs synthesized as crystalline thin films on functionalized IDEs

  Two step functionalization procedure:
  - Reacted IDE with aminosilanes, followed by ring opening of succinic anhydride
  - Functionalization allowed for binding of metal cation and further growth of 3-D MOF



- Ni-MOF-74 boasted a continuous thin film and used in a comparison study vs. a dropcast powder
- Thin film passed a modified ASTM D3359 test for durability
- Demonstrated an increased response rate and larger total change in impedance



Henkelis, S. E., et al., "Continuous MOF Membrane-Based Sensors via Functionalization of Interdigitated Electrodes", INVITED: *Membranes* **2021**,

Conclusions

- M-MOF-74 (M = Co, Mg, Ni)-based sensors for selective detection of trace (0.5–5 ppm) NO_2 were successfully demonstrated
- Ni-MOF-74-based sensor exhibited a superior electrical response in its selectivity to NO_2 over interfering gases such as N_2, SO_2, and ambient air
- Differences in electrical response to NO_2 between the M-MOF-74 analogues were attributed to both the adsorption capacity and chemical interactions between the NO_2 and MOF
- The magnitude of the electrical response observed is ordered Ni > Co > Mg, with Ni-MOF-74 providing 725× decrease in resistance at 5 ppm NO_2 and a NO_2 detection limit <0.5 ppm
- The high impedance of these materials enables applications requiring an ultralow power sensor or dosimeter, with the active material dissipating <15 pW, despite being a macroscale device
- Thin film Ni-MOF-74-based sensors demonstrated an increased response rate and larger change in impedance than a dropcast Ni-MOF-74 sensor

Future Work

- Investigations are underway:
  - To further understand sensor response with potential interfering and/or secondary off-gases
  - To evaluate sensor response/stability over a range of environmental conditions (temp., humidity, NO_x) as a function of time (e.g., 24 hours to >1 year)