SAND2022-8632C

Sandia National Laboratories

Near-Zero Power Zeolite and MOF based Sensors for NO_2 Detection

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IZC 2022, Valencia, Spain. July 8, 2022

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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

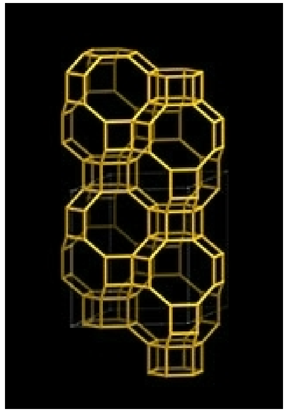
We have a wide study of sensors for target gases:

ACS Applied Mater. Interfaces, **2017**, *9*, 44649
Micro. Meso. Mater. **2019**, *280*, 82
ACS Applied Mater. Interfaces, **2019**, *11*, 27982
Adv. Func. Mater. **2020**, *1407*, 2006598
Membranes **2021**, *11*, 176
I&ECR **2021**, *60*, 21, 7998
I&ECR, **2021**, *60*, 40, 14371
Chem. Soc. Rev. **2022**, *51*, 324

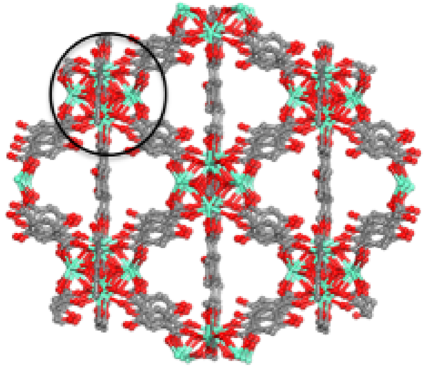
Nanoporous Materials Targeted for the Selective Adsorption of NO_x

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

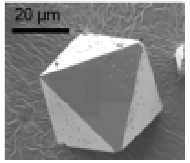
- Zeolites are aluminosilicates with high temperature durability. Specific metals give rise to NO_x selectivity
- Metal-organic frameworks (MOFs) are metal nodes with organic linkers with selectivity to NO_x designed by incorporating NO_x –friendly metals into the framework

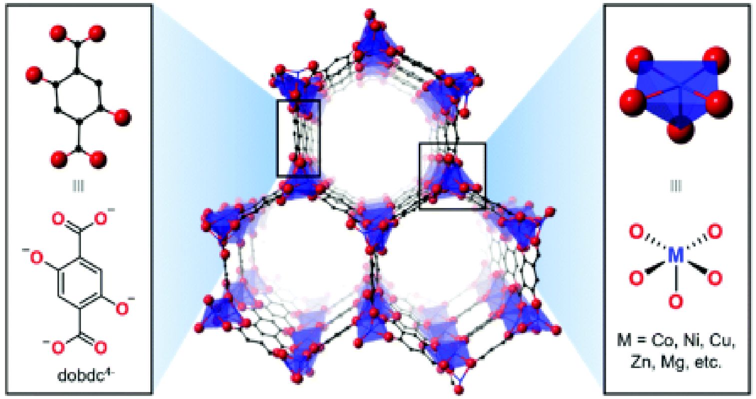


Zeolite SSZ-13 (CHA)



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



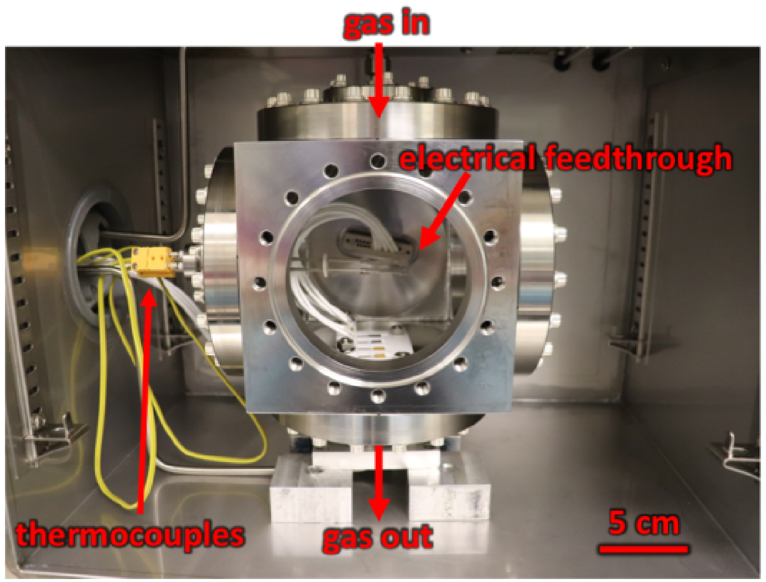


M-MOF-74 (M = Co, Mg, Ni)

Small, Schindelholz, Nenoff, *Perspective:* "Hold on Tight: MOF-Based Irreversible Gas Sensors" *I&ECR*, **2021**, *60*, 21, 7998

NO_x Exposure and In Situ Electrical Testing

- Custom- built NO_x exposure chamber enabled Zeolite, 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



A.

blank IDE

B.

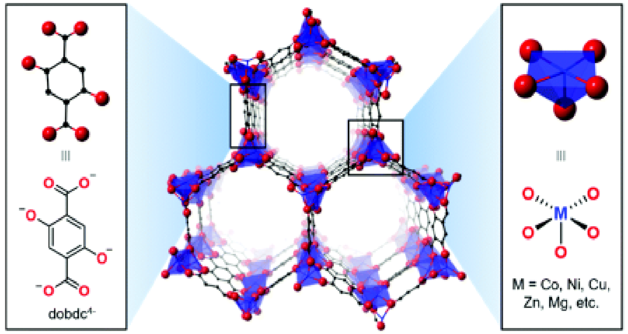
IDE + Ni-MOF-74

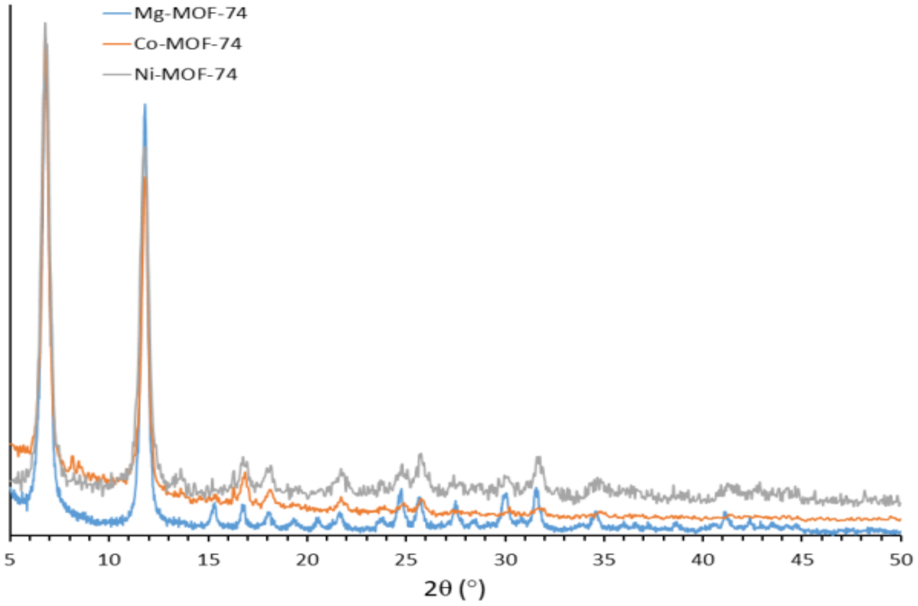
C.

IDE + Ni-MOF-74
Exposed to 5ppm NO_2
8 h 50 °C

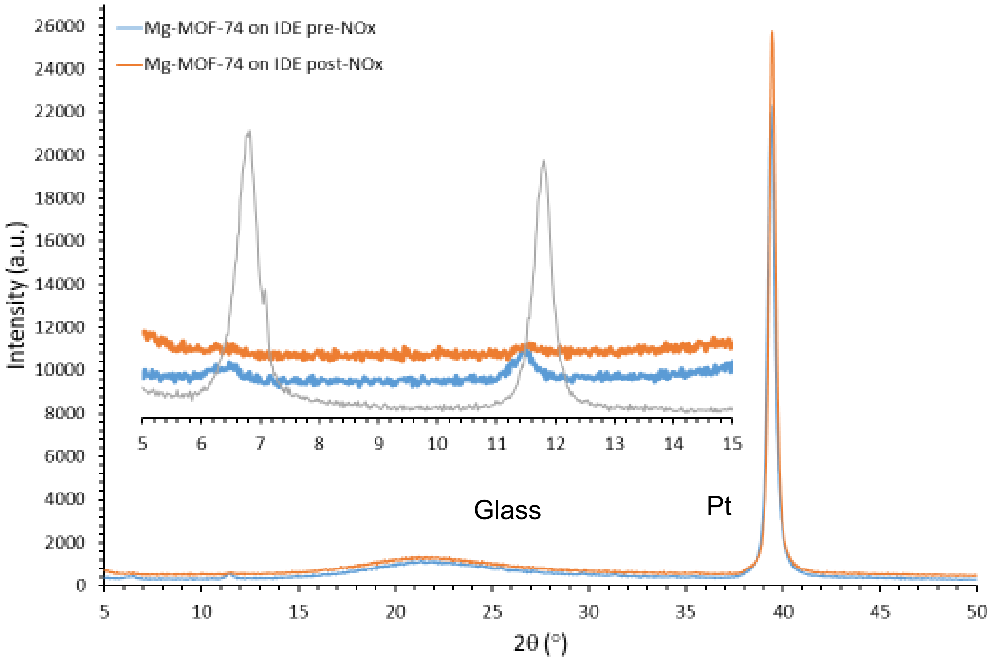
M-MOF-74-Based Sensors for the Selective Adsorption of NO_x

- 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)





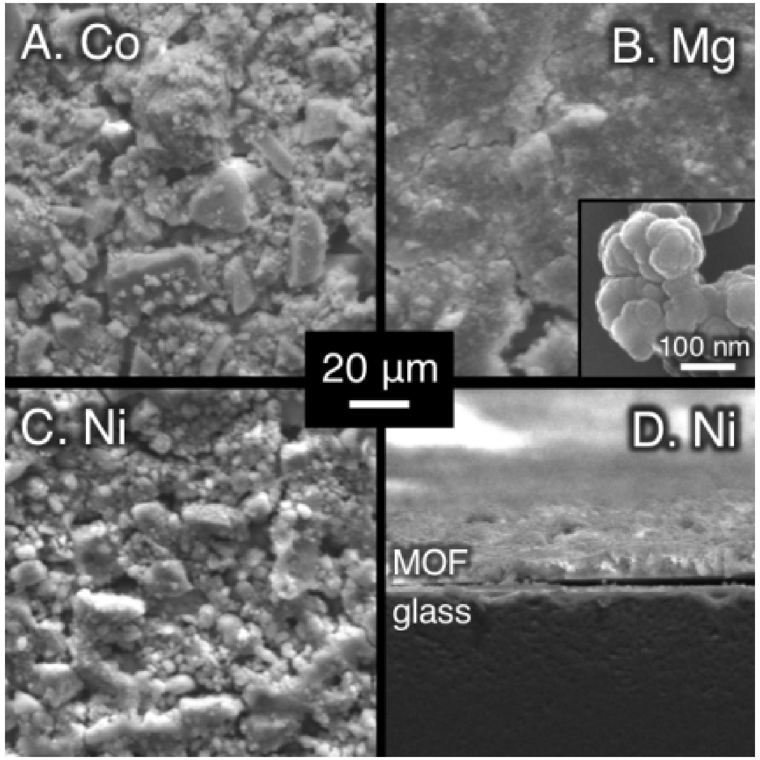
Powder XRD patterns for as-synthesized MOF-74 in the bulk phase.



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.*, **2020,** *50,* 2006598

SEM Characterization of Dropcast M-MOF-74 Films

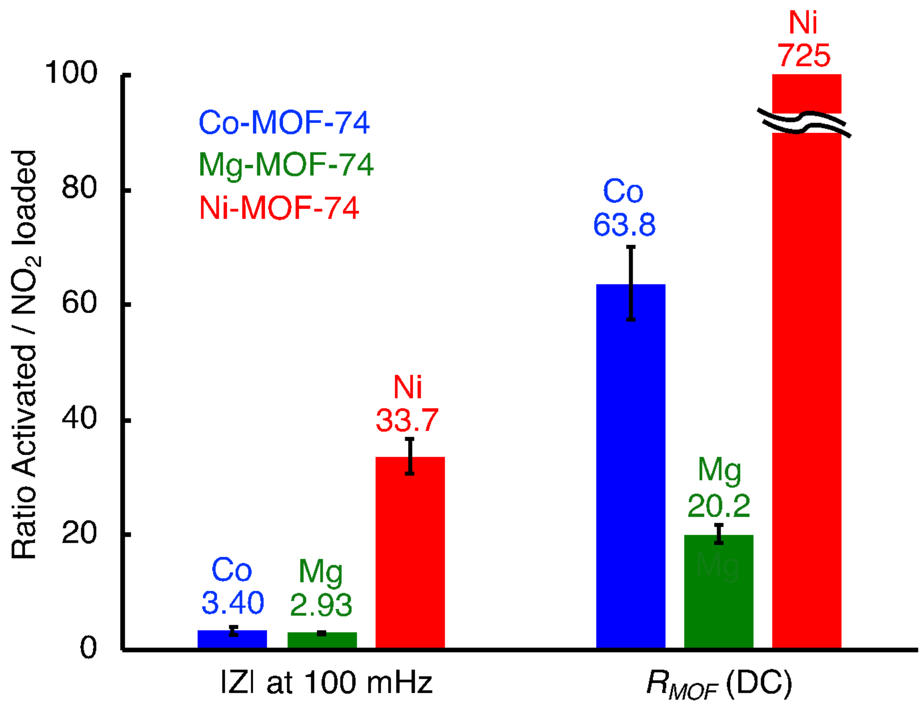


Plan-view SEM micrographs of (A) Co-MOF-74, (B) Mg-MOF-74, (C) Ni-MOF-74 powders dropcast onto IDEs. (D) Cross-sectional micrograph of Ni-MOF-74 film from (C).

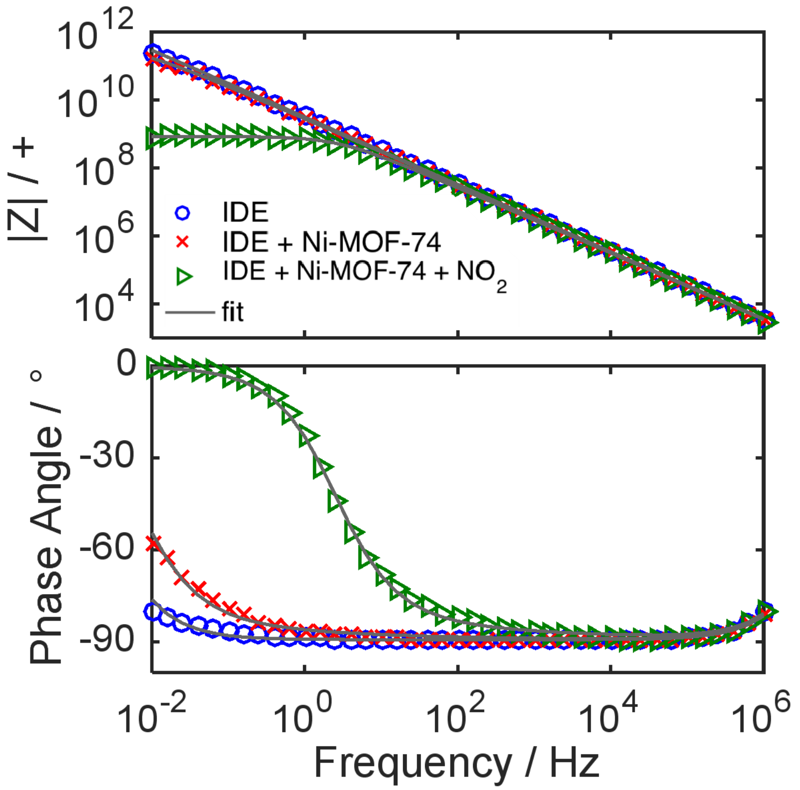
- Co- and Ni-MOF-74 contained a wide range of crystallite sizes, from 100's of µm to 100 nm
- Mg-MOF-74 crystallites were on the order of 100 nm
- Film thickness was ~ 10 µm

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.



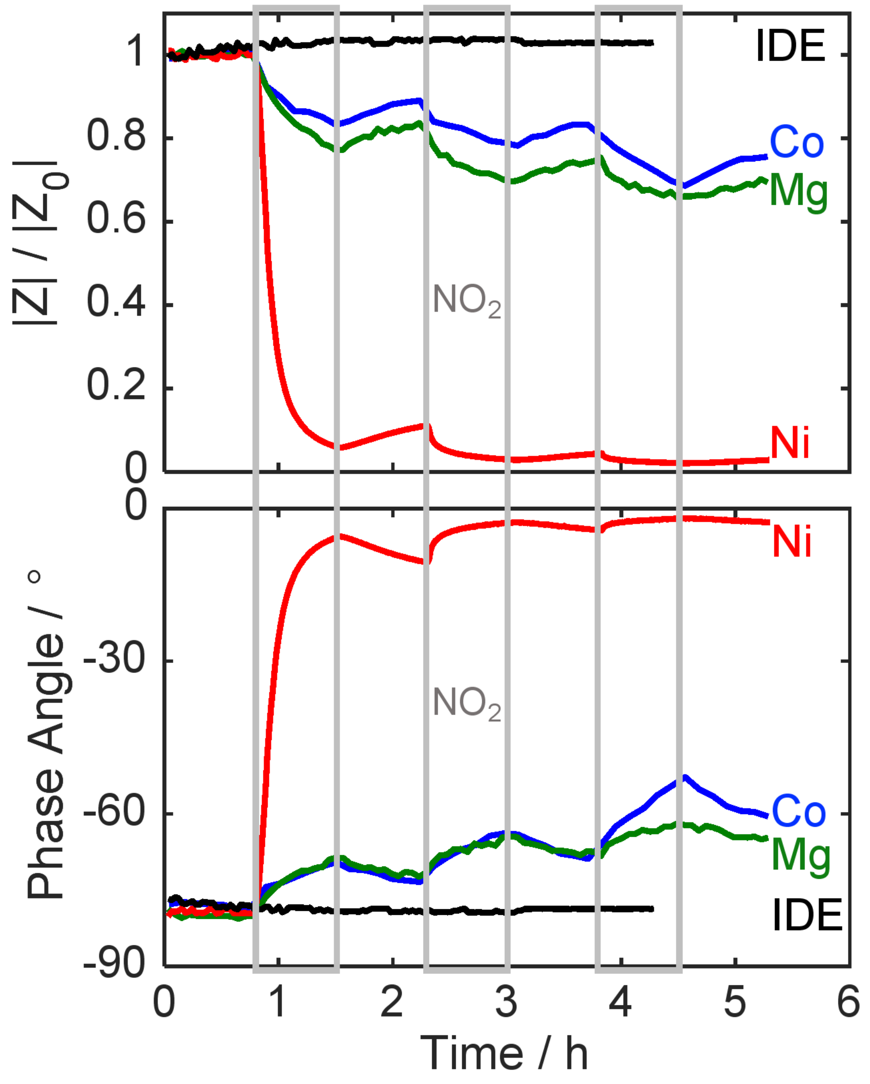
Ratio of response as-activated to NO_2-exposed for (1) impedance magnitude ($|Z_{activated}|/|Z_{NO2}|$) at 100 mHz and (2) MOF DC film resistance ($R_{activated}/R_{NO2}$) for IDEs coated with M-MOF-74 (M= Co, Mg, Ni).



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

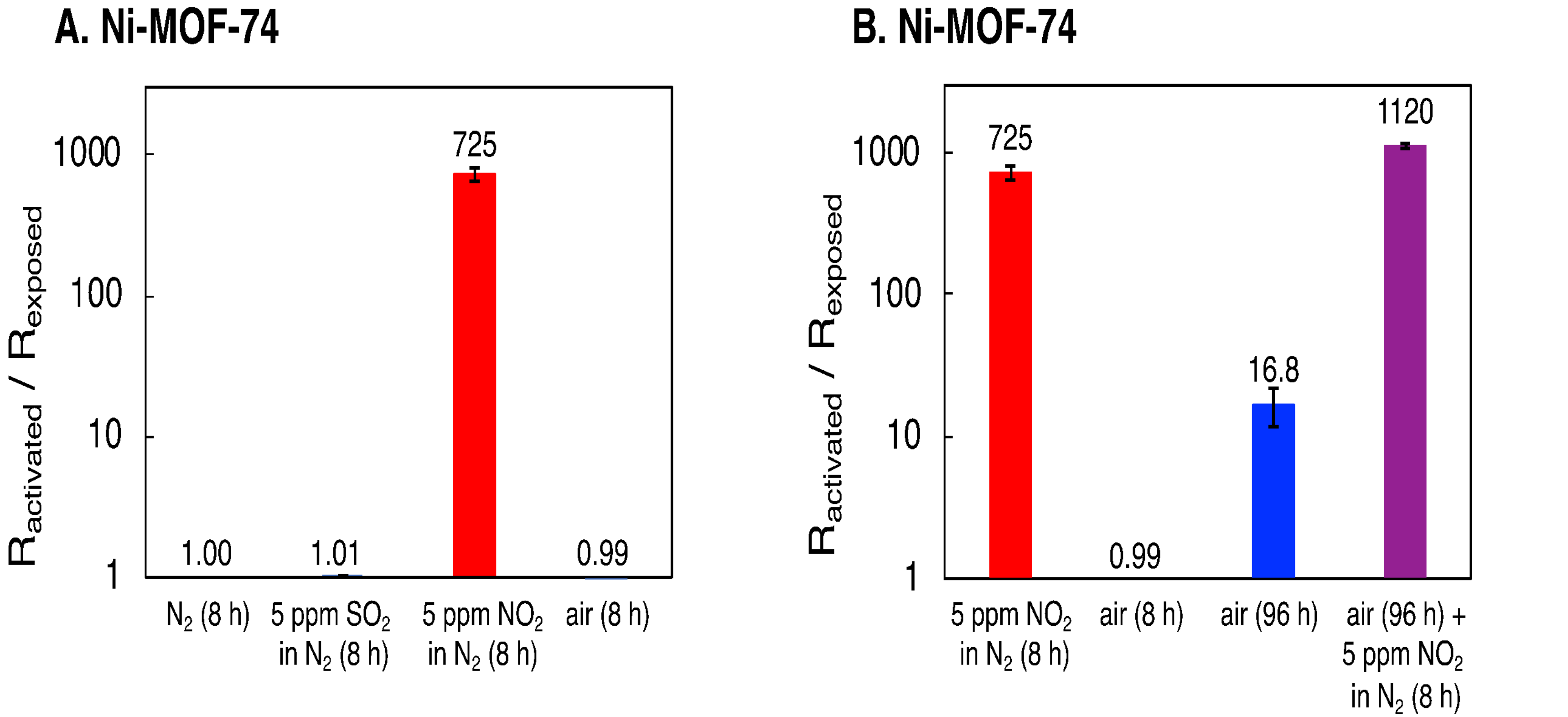
Impedance Responses as a Function of NO_2 Concentration

- 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



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

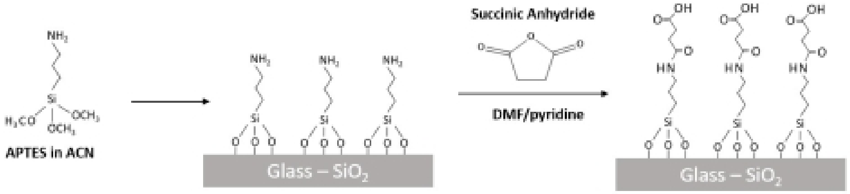
- A Ni-MOF-74-based sensor was activated and exposed to 5 ppm SO_2 in N_2, and ambient air (25 °C, 50% RH, 400 pm CO_2) heated to 50 °C, and its response compared to previous exposures to 5 ppm NO_2 in N_2
- An extended air exposure (96 hours) followed by subsequent NO_2 exposure was also performed
-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



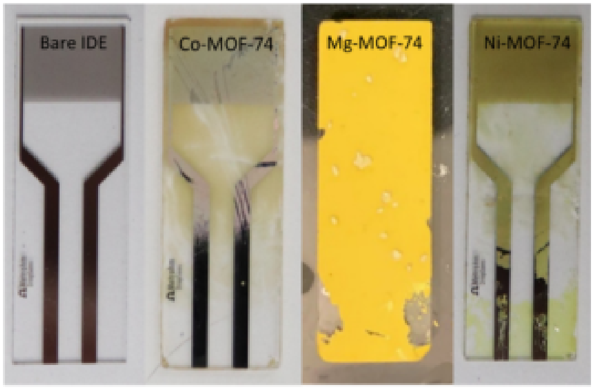
Enhanced Sensitivity of Nanoporous-Based Sensors Using MOF Thin Film Membranes

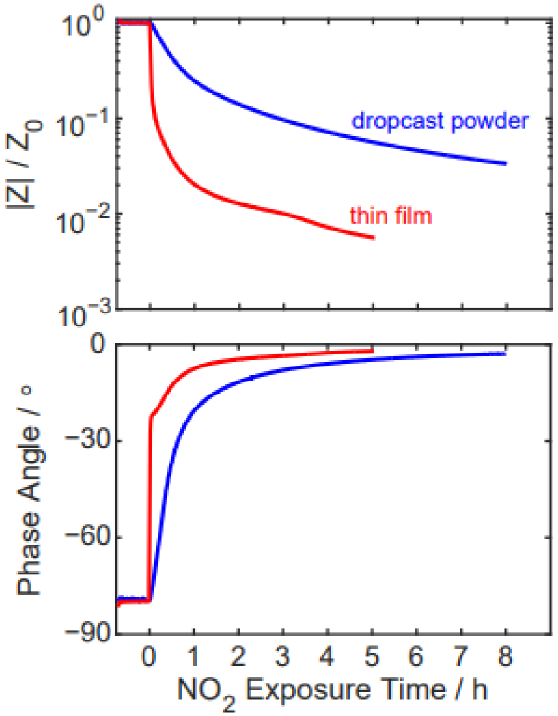
- M-MOF-74 (M=Co, Mg, Ni) MOFs synthesized as crystalline thin films on functionalized IDEs

  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
- Increased response rate and larger total change in impedance





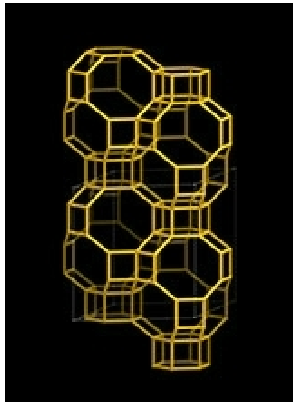
Henkelis, et al., "Continuous MOF Membrane-Based Sensors via Functionalization of Interdigitated Electrodes", INVITED: *Membranes* **2021**, *11*, 176

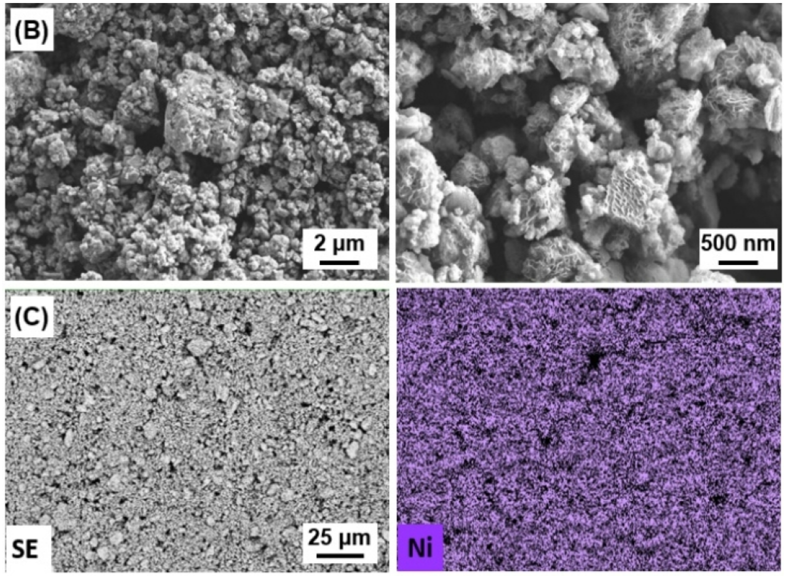
Ni-SSZ-13 based NO_2 Detection After Humidity Exposure

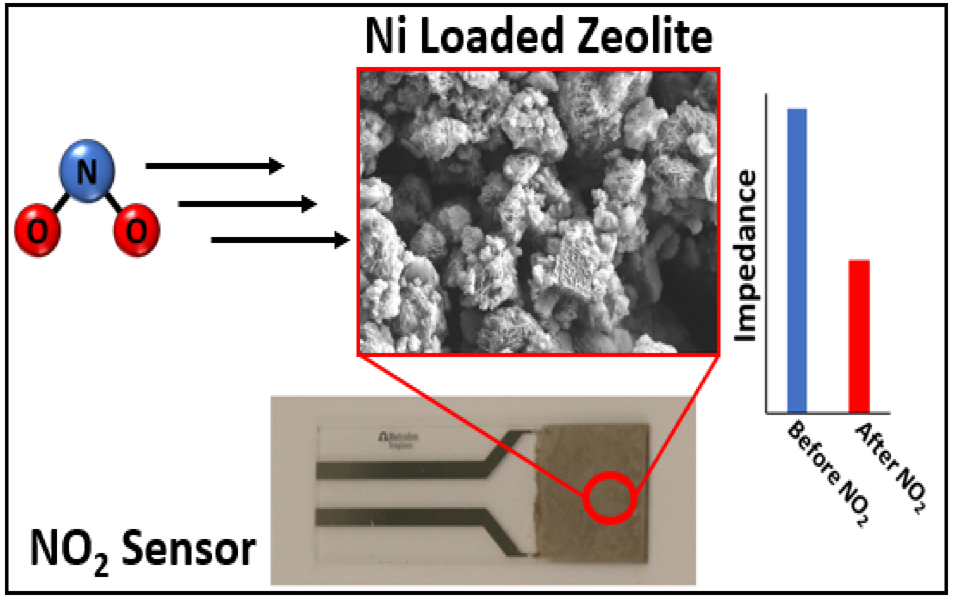
Zeolites have lower capacity but higher mechanical & chemical durability

Ni-SSZ-13 was synthesized via a liquid-phase ion exchange procedure

Ni-SSZ-13 sensor was activated at 50°C, exposed to lab air for 150 hours, and then exposed to 5 ppm NO_2

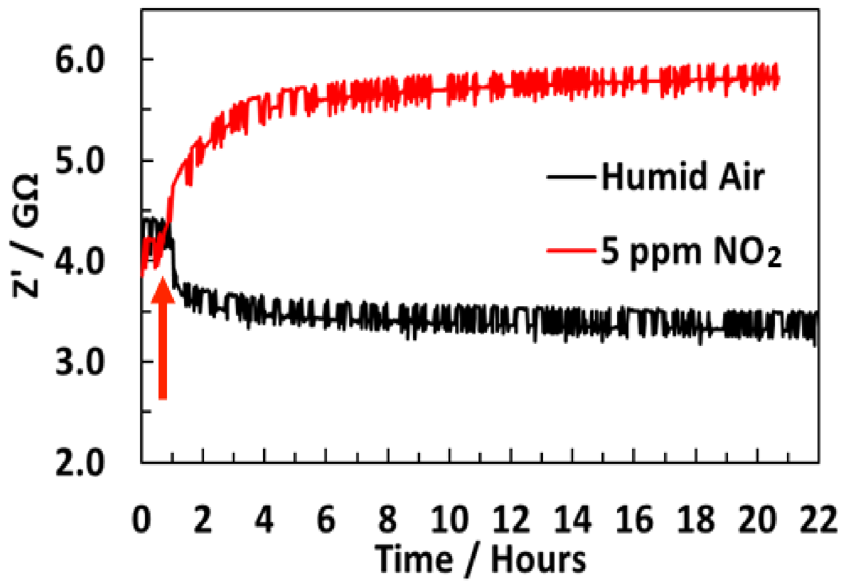




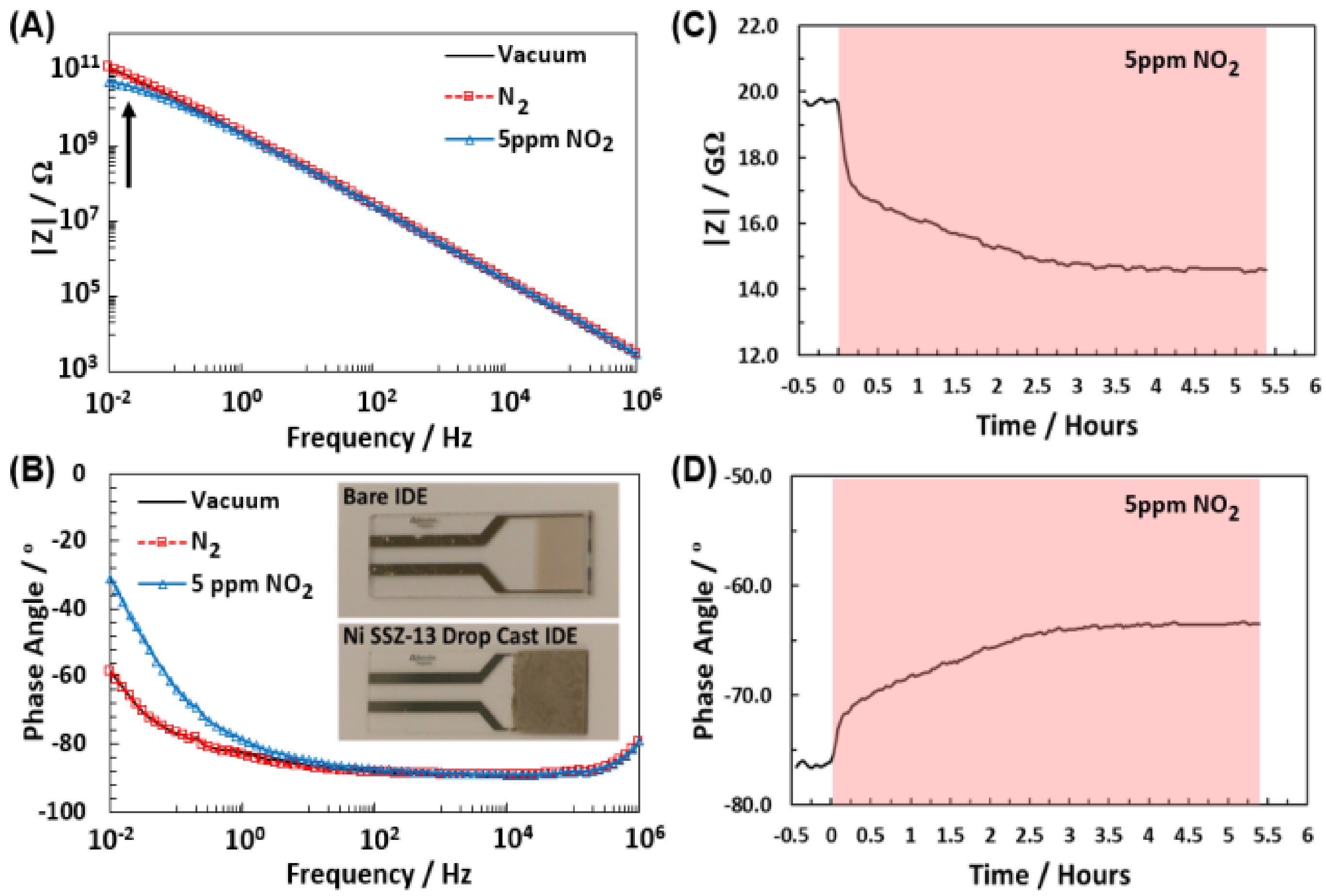


Percival, S.J., et al., "Ni-SSZ-13 Zeolite Sensors for the detection of NO_2" *I&ECR,* **2021**, *60*, 14371.

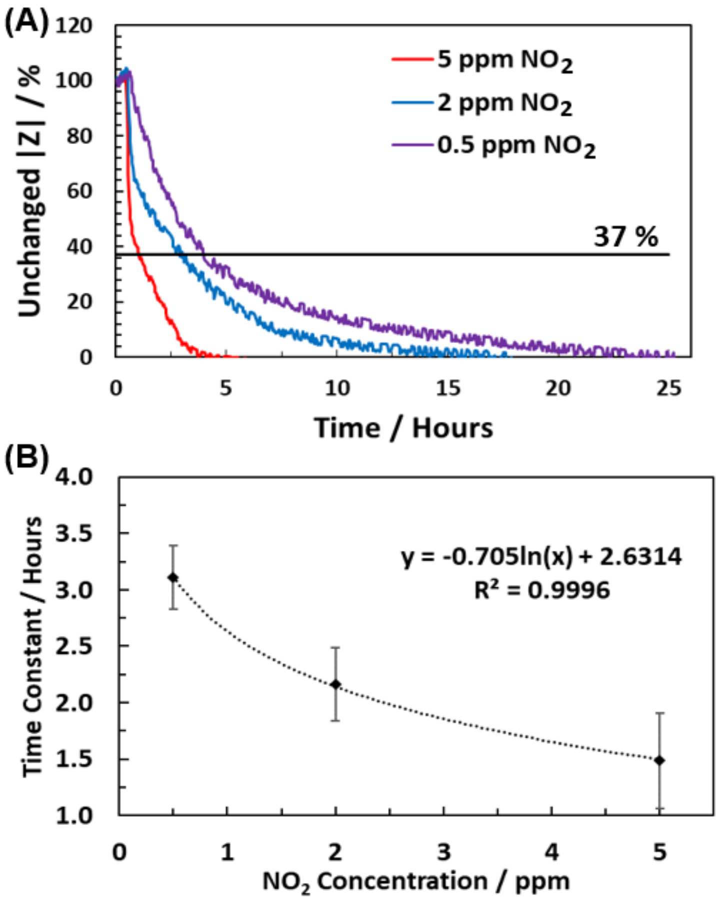
Ni-SSZ-13 based NO_2 Detection After Humidity Exposure



Even with exposure to humid air the Ni-SSZ-13 zeolite still showed impedance response when exposed to NO_2

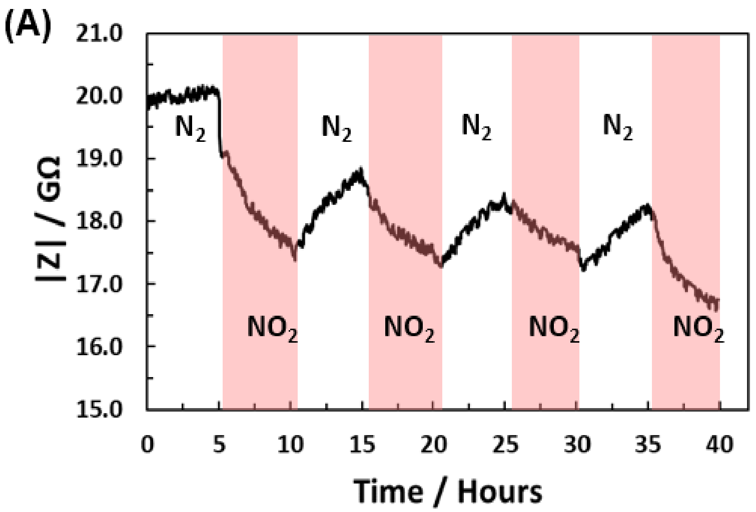


Ni-SSZ-13 based NO_2 Detection After Humidity Exposure



(A) Variations of concentration, observed intersection of experimental data curve with 37% line for the time constant.

(B) Plot of time constant data shows logarithmic dependence of NO_2 concentration



Reversibility of NO_2 detection with on/off gas flow

Conclusions

Judicious selection of nanoporous adsorbants enables the fabrication of highly selective direct electrical readout sensors

Durability for sensing environment need can be dictated by
the choice of zeolite or MOF,
the film: dropcast or thin crystalline film growth (mechanical durability)

Ni-SSZ-13 based sensors for NO_2 gas, have
- reversibility to NO_2 gas streams,
- durability in humid NO_2 streams,
- consistency in response to variations in NO_2 concentration

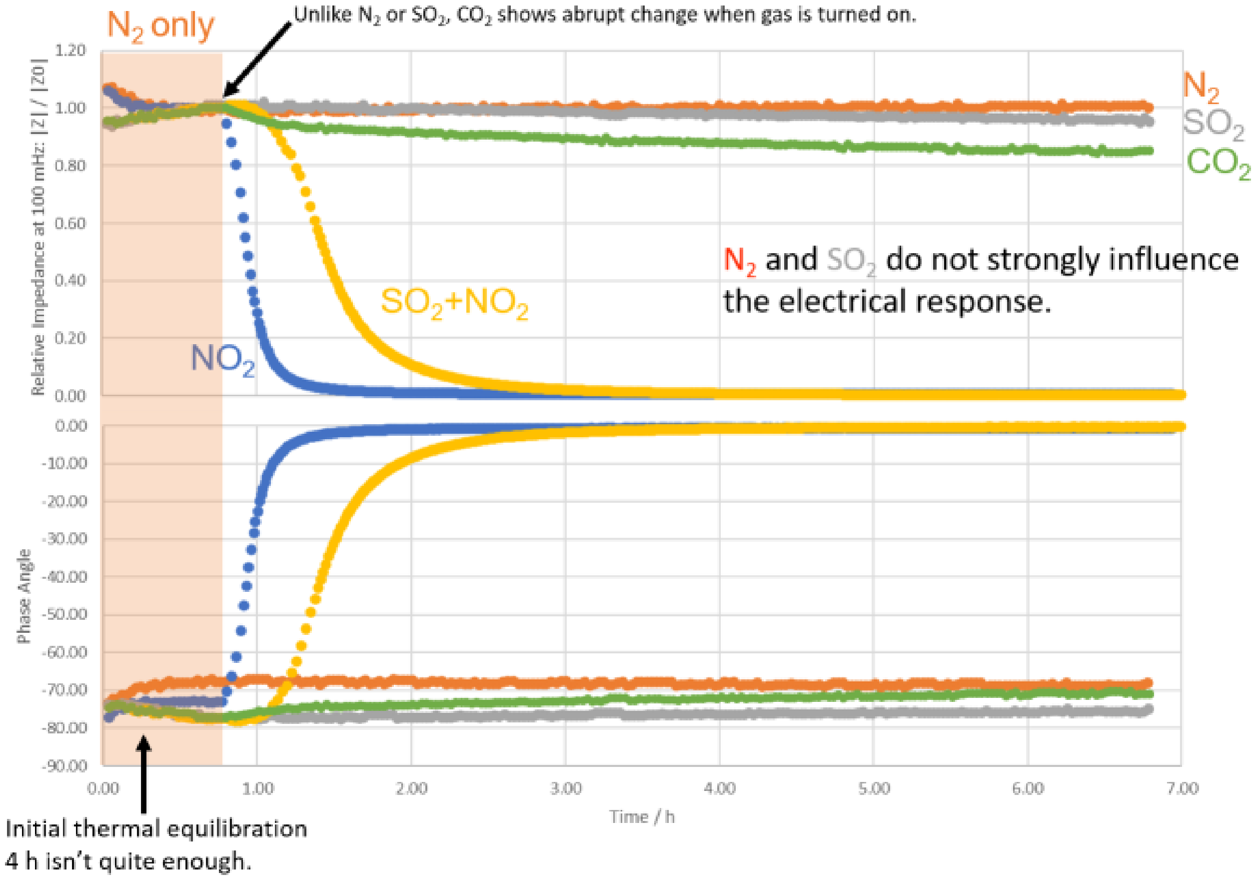
Ni-MOF-74 based sensors for NO_2 gas, have
- incredibly low power requirements (eg., <15 pW for Ni-MOF-74)
- exceptional sensitivity to target gas with a 725× decrease in resistance at 5 ppm NO_2 and a NO_2 detection limit <0.5 ppm,

On-going research in sensors:
- long term detection, cycling, and temperature extremes
- environmental/catalytic gases of interest
- added durability by film application and protective capping components

Questions?

June 2022, Sandia Park, NM, USA

Effect of Secondary Off-Gases on Material/Sensor Response

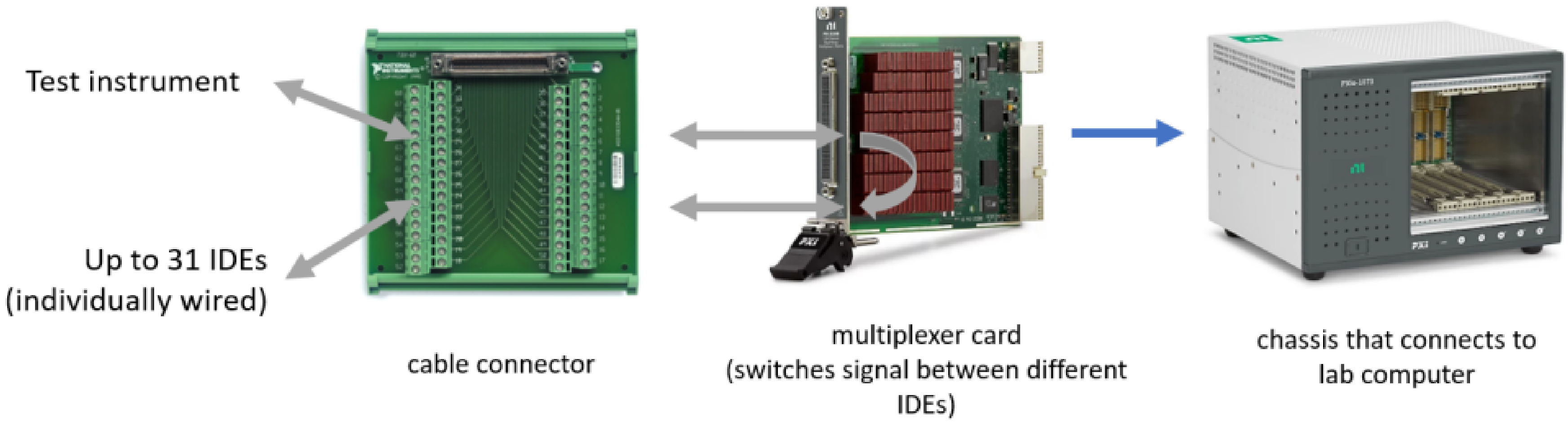


Test Gas
N_2 only
5 ppm NO_2 in N_2
5 ppm SO_2 in N_2
9.4% CO_2 in N_2
2.5ppm NO_2 + 2.5ppm SO_2 in N_2

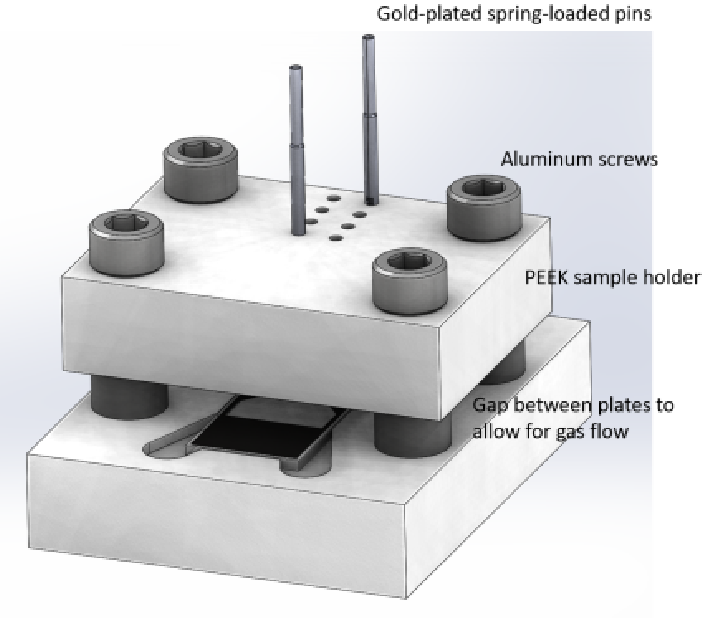
- After testing, material scraped off IDE into a vial and sent for synchrotron X-ray scattering analysis at the Advanced Photon Source / Argonne National Lab

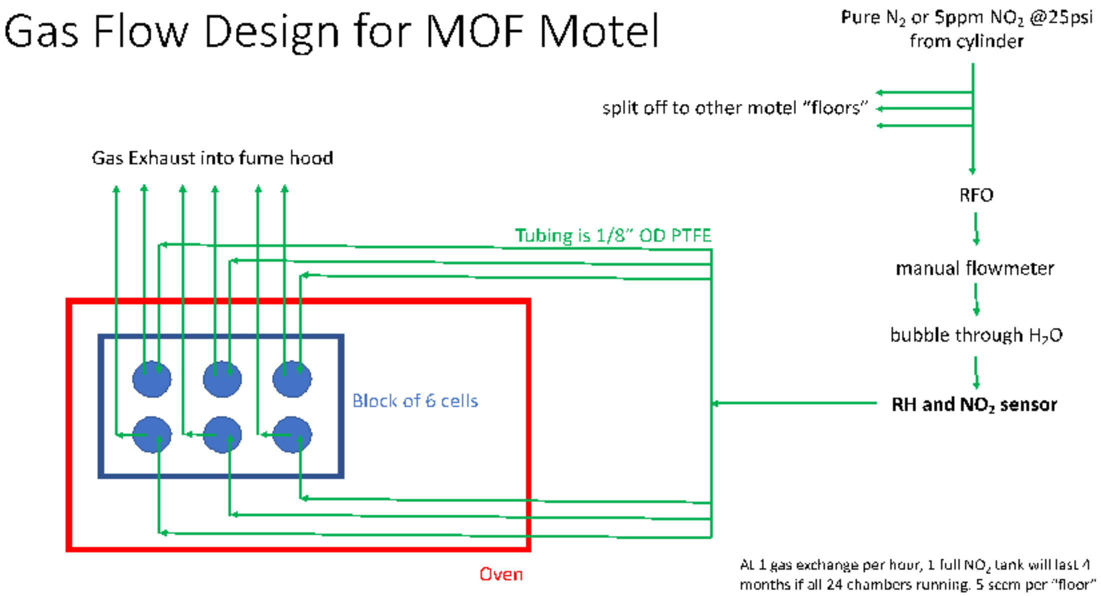
Perform long-term study of NO_x sensors

- Approach:
  - Down-select from material stability experiments and 24 hour sensor tests
  - Environments: 1) RT, dry; 2) 74°C, dry; 3) RT, 40% RH, 4) 74°C, 40% RH
  - 3 materials, 6 sensors per environment
  - Simulate slow leak of NO_2
  - Time 0, 24 hour exposure to NO_2; 2 weeks later, 24 hour exposure to NO_2; repeat monthly
  - After 6 months, switch to a constant low-level of NO_2



Custom Test Fixtures for Multiple & Simultaneous Long-Term Exposures and Electrical Testing





Custom designed test fixtures ('MOF Motel') for long-term exposures and in-situ electrical testing of sensors

24 test cells, each cell 70 mL

Humidity/NO_x levels controlled in each chamber with constant temperature across entire test fixture