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

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The detection and capture of toxic nitrogen oxides (NO_x) is important for emissions control of exhausted gases and general public health. The ability to directly electrically detect trace (0.5-5ppm) NO_2 by a nanoporous material based sensor at relatively low temperatures (50°C) is demonstrated via changes in electrical properties of the nanoporous phase.[1] Herein, we have successfully fabricated and tested both zeolite and metal-organic framework (MOF) materials as the gas selective phase in these sensors.

For the zeolite sensors, Ni-SSZ-13 phases were utilized by dropcasting a film onto a Pt based interdigitated electrode (IDE).[2] The SSZ-12 zeolite was loaded with nickel(II) through a liquid-phase ion exchange procedure. The exposure of the zeolite-based sensor to trace NO_2 gas elicits an electrical impedance response measure at a single frequency. The sensor shows the same final change in impedance magnitude upon equilibration to different concentrations of trace NO_2 in N_2, suggesting that the occupation and eventual saturation of adsorption sites lead to the impedance change. The sensors response is partially reversible in an inert gas environment, indicating the reversible adsorption of NO_2 at the nickel surface sites. Upon exposure to NO_2, the real impedance of the sensor increased by a factor of 1.42x, whereas upon exposure to humid air, a decrease of 0.77x of the sensor real impedance was observed. These results indicate that control of metal-ion loading into SSZ-13 will allow these NO_2 selective catalytic reduction catalysts to be leveraged as low-temperature NO_2 sensors.

For the MOF based sensors, M-MOF-74, M = Co, Mg, Ni have been tested both as dropcast films [3] and as crystallographically grown thin-films on to the IDE support.[4] See figure 1. In the dropcast films, the magnitude of the change is ordered Ni > Co > Mg and explained by each variant's NO_2 adsorption capacity and specific chemical interaction. Ni-MOF-74 provides the highest sensitivity to NO_2; a 725x decrease in resistance at 5ppm NO_2 and detection limit <0.5 ppm, levels relevant for industry and public health. Furthermore, the Ni-MOF-74 based sensor is selective to NO_2 over N_2, SO_2 and air.

Crystallographically grown thin films show very promising results. To demonstrate their use as NO_2 gas sensors, Ni-MOF-74 was chosen as it was consistently fabricated as the best thing and homogenous membrane, as confirmed by SEM. The membrane was exposed to 5ppm NO_2 and the impedance magnitude was observed to decrease 123x in 4 hours, with a large change in impedance and a faster response than the bulk material. Importantly, the use of these membranes as a sensor for NO_2 does not require them to be defect-free, but solely continuous and overlapping growth.

Linking this fundamental research with future technologies, the high impedance of MOF-74 enables applications requiring a near-zero power sensor or dosimeter, with the active material drawing <15 pW for a macroscale device 35mm^2 with 0.8 mg of dropcast MOF-74. This represents a 10^4-10^6x decrease in power consumption compared to other MOF sensors and demonstrates the potential for MOFs as active components for long-lived, near-zero power chemical sensors in smart industrial systems and the 'internet of things'.

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Figure 1: M-MOF-74 (M -Co, Mg, Ni) based NO_2 sensors and impedance responses.

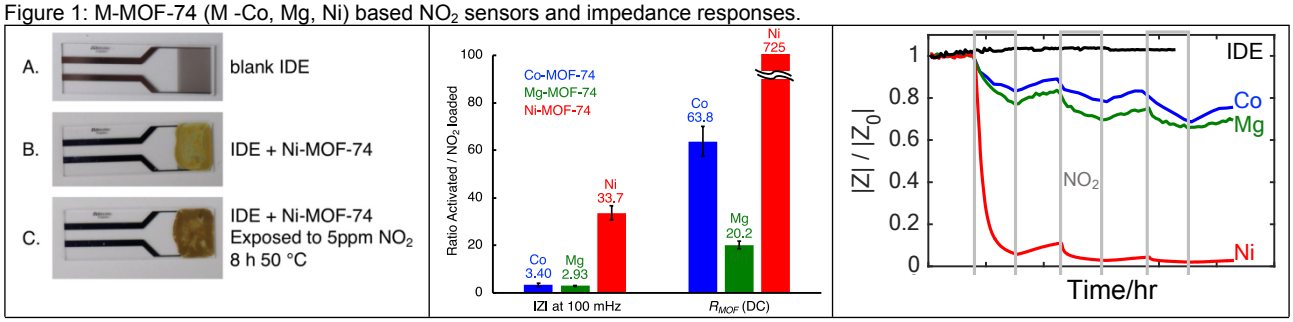

Figure 1: (left) M-MOF-74 based sensor, (center) impedance response to NO_2 per MOF metal center, (right) impedance response as a function of NO_2 concentration

References

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