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Core-shell metal-organic-frameworks for direct air capture

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Abstract

Metal-organic-frameworks (MOFs) are a promising solid sorbent technology for direct air capture due to their high CO\textsubscript{2} binding strength and CO\textsubscript{2} capacity per unit volume. However, one of the main challenges associated with MOFs for direct air capture (DAC) is that moisture in the air can interfere with CO\textsubscript{2} adsorption. The main goal of this project is to identify and characterize a core-shell MOF that strongly binds CO\textsubscript{2} and has a high selectivity for CO\textsubscript{2} over N\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O. More specifically, we propose to develop a core-shell MOF where the core MOF has a strong affinity for CO\textsubscript{2} and the shell MOF is hydrophobic to protect the core from H\textsubscript{2}O, as shown in Figure 1. These MOFs can either be formed into pellets, or they can be 3D-printed into monolith structures. A packed bed of these MOFs would then undergo CO\textsubscript{2} adsorption from air followed by thermal- or pressure-swing desorption of CO\textsubscript{2}, as shown in Figure 2.

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Figure 1: Graphic representation of a core-shell MOF where the shell protects the core from H\textsubscript{2}O and the core strongly binds CO\textsubscript{2}.
The first task for this project was to computationally screen a catalogue of potential MOFs to find the best candidates for core and shell materials. This task was led by Prof. Wilmer’s team in the Chemical Engineering department at the University of Pittsburgh. This task was accomplished using a custom find/replace software called MOFUN developed by Paul Boone on that team. Two MOF bases were selected (UiO-66 and UiO-67), and 15 different functional groups were considered in this screening. Adsorption and selectivity values were simulated for each functionalized MOF for CO₂, N₂, and H₂O. The results of this screening helped us identify the best MOF candidates for the core and shell, as shown in Figure 3.
The second task for this project (led by Prof. Rosi, Chemistry at Pitt) was to synthesize the best candidate core-shell MOFs and characterize their adsorption performance for CO$_2$, N$_2$ and H$_2$O. UiO-66 and UiO-67 were selected as the base MOFs for synthesis because they are structurally robust and easily tunable with various ligands and functional groups. Several candidate MOFs that were identified during computational screening were synthesized and compared based on adsorption selectivity of CO$_2$ over N$_2$, as shown in Table 1. The experimental and simulated values don’t match exactly because the simulation doesn’t capture all adsorption mechanisms. However, the trends the experimental and simulated results do match, providing some validation of the best MOF candidates. Adsorption tests for CO$_2$, N$_2$ and H$_2$O were performed at 298K over a range of pressures to generated isotherm data for each MOF, as shown in Figure 4.

<table>
<thead>
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<th></th>
<th>Experimental Results</th>
<th>Simulation Results</th>
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<tr>
<td>UiO-67</td>
<td>9.33</td>
<td>7.11</td>
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<tr>
<td>NH$_2$-UiO-67</td>
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<td>7.45</td>
</tr>
<tr>
<td>2NH$_2$-UiO-67</td>
<td>38.4</td>
<td>8.33</td>
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<td>Me-UiO-67</td>
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<td>13.5</td>
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<tr>
<td>Me$_2$-UiO-67</td>
<td>9.42</td>
<td>10.0</td>
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</tbody>
</table>

Figure 4: Adsorption isotherm data for CO$_2$ (left), N$_2$ (middle) and H$_2$O (right) at 298 K for best candidate MOFs.

Based on these results, (CyNH)$_2$-UiO-67 was selected as the core MOF due to its high CO$_2$ capacity and CO$_2$/N$_2$ selectivity, and NH$_2$-UiO-67 was selected as the shell MOF due to its high CO$_2$ diffusivity and high CO$_2$/H$_2$O selectivity. These properties should enable the shell to block H$_2$O while shuttling CO$_2$ to the core, where it can adsorb at a high capacity.

The final task of this project is to perform mutliphysics modelling of the optimal core-shell MOFs to optimize parameters such as shell thickness, core-shell diameter, and bed packing design (led by Prof. Hornbostel, Mechanical Engineering at Pitt). So far, a model of a single MOF spherical pellet has been developed in COMSOL Multiphysics, and we are currently modifying this model to incorporate separate core and shell domains. Sample CO$_2$ concentration results are shown in Figure 5, where air flows in from the bottom and the sphere in the middle of the domain is the MOF pellet. The model is 2D-axiymmetric and transient with the simulation running until steady-state CO$_2$ loading in the MOF pellet is achieved. Isotherms for CO$_2$, N$_2$ and H$_2$O have been input to this model by performing Langmuir curve fits to the experimental data provided by Prof. Rosi’s team. CO$_2$ isotherms at 298K are shown for various candidate MOFs in Figure 6, and a good agreement can be observed between the experimental and theoretical isotherms. Future work on this task will involve parametric studies to determine the optimal core-shell MOF pellet design.
Figure 5: CO$_2$ concentrations (mol/m$^3$) for air flowing over a spherical MOF pellet. Model was developed in COMSOL Multiphysics and represents fluid flow, transport, and adsorption vs. time.

Figure 6: Experimental (Exp) vs. theoretical (th) isotherms for CO$_2$ at 298 K for plain UiO-67 MOF and UiO-67 with various functional groups.

In conclusion, core-shell MOFs are a promising technology for direct air capture because a hydrophobic MOF shell can theoretically protect the core MOF from water and improve CO$_2$ adsorption in the core. Our team used computational screening to determine a handful of optimal MOFs for the core and shell, then synthesized and measured adsorption for these candidate MOFs. Our team is now performing multiphysics simulations to determine...
the optimal core-shell MOF geometric parameters. Overall, this work will result in an optimal core-shell MOF design for direct air capture that can then be scaled up and integrated into a DAC adsorber.

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Keywords: direct air capture; negative emissions; metal-organic-frameworks

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1. https://github.com/paulboone/mofun/