Poster

Understanding Carbon Dioxide Uptake in ZIFs Via In-Situ Single Crystal Diffraction

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Porous crystalline materials are now regularly designed and studied for use in capturing or storing harmful gases as a means to addressing some of the problems of the climate crisis. This work is using the family of Zeolitic Imidazolate Frameworks (ZIFs) to develop approaches to studying the structural properties of these materials whilst they perform these functions. The process of Carbon Dioxide absorption by ZIFs has been studied by neutron and X-ray powder diffraction [1, 2], but the ability to apply in-situ single crystal diffraction analysis is almost exclusively confined to specialised facilities, such as Beamline I19 at Diamond Light Source, UK [3]. It should be equally possible to perform equivalent experiments in-house and so this highlights the need for an adaptive gas cell mount that can be used with commercial small molecule X-ray diffraction instruments.

Our work has produced a single crystal X-ray diffraction gas cell in which crystals can be mounted on a conventional X-ray diffractometer and enables experiments with in-situ gas environment or the analysis of air-sensitive crystals protected within the cell. The cell is based on a previous design from The University of Southampton and Diamond Light Source [4], with most adaptations catering for the variation in diffractometer geometries between the beamline and conventional instruments.

Our initial applications of this cell have focused on the breathability and open-gate pore structures of ZIF-7 when interacting with Carbon Dioxide at various pressures. The comparatively small size of Carbon Dioxide within the pores of ZIF-7 means it can be situated in many possible disordered orientations and so it is difficult to locate their exact positions. However, even after only 1 hour at 1 bar of Carbon Dioxide, it is possible to tell from the diffraction patterns that Carbon Dioxide is present. Current experiments are exploring the time before measurements are taken and the gas pressure to optimise uptake and thereby determine the exact occupancy.

Establishing a replicable method for collecting gas cell data for porous crystals will expand the capabilities of single crystal diffraction to contribute atomic resolution structural information to increase the understanding of materials properties with respect to gas interaction. These capabilities will be more accessible to a wider range of researchers with the possibility to perform such experiments using the single crystal X-ray diffractometers already available in-house.

The next stage of this work is to develop methodologies to extend this approach to electron diffraction. The potential of this development is huge, as it would enable investigation of gas interaction with nanocrystals, which is often the size range of typical gas adsorption materials. We have access to a Rigaku Synergy-ED instrument and have recently begun development of a new holder system to provide a contained environment which a gas can be flowed through whilst conducting an electron diffraction experiment. ZIF-7 will be used as the benchmark comparison sample for this work and the poster will present early developments of this work.

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