The Hole Story

They may be full of holes, but metal–organic materials could lead to a revolution in clean energy.

Kia Wallwork prepares for another set of synchrotron powder diffraction experiments.
Photo: Sandra Morrow

Metal–organic frameworks (MOFs) are small clusters of metal atoms linked by rigid organic molecules. These exciting new materials can store huge quantities of gaseous fuels, such as hydrogen, methane and carbon dioxide. Their amazing storage capacity is due to a periodic, open structure that creates internal surface areas as high as 6000 m^2 per gram of material. That's about the size of a football field – or the internal floor area of the Australian Synchrotron.

The huge surface areas in MOFs can be used to store fuels and greenhouse gases, or for industrial catalysis or medical diagnosis.

However, although MOFs are the subject of intense research activity around the world, their synthesis is not well understood.

Danielle Kennedy and her CSIRO colleagues are developing high-throughput methods for preparing and screening lanthanide MOFs. They are using X-ray powder diffraction at the Australian Synchrotron to find out whether the materials produced are crystalline and have the large "unit cells" (the main repeating units of a crystal structure) that indicate the ordered porosity that are common to MOFs.

As part of the work, Danielle and co-workers Matthew Hill and David Hay designed and built a high-throughput sample stage that allowed them to analyse more than 600 samples on the powder diffraction beamline in less than 36 hours. Without a super-bright synchrotron source, the samples would have taken almost 2 months to analyse.

The synchrotron findings enabled the researchers to quickly work out the synthetic "hot spots" for MOFs, putting the materials on the fast-track for some exciting applications.

Pore Performance Is Promising

Meanwhile, Bridget Ingham in New Zealand is "poring" over another new kind of advanced material: nanoporous gold.

Removing one metal from a bimetallic alloy such as copper–platinum, nickel–silver or silver–gold can create a sponge-like material with pores just a few nanometres across. That's roughly ten times the size of an atom, or about 20,000 times thinner than a human hair.

Like metal–organic frameworks, nanoporous materials have high surface-to-volume ratios. Their many potential applications include gas sensors and industrial catalysts.

Bridget and her collaborators are using X-ray powder diffraction at the Australian Synchrotron to study nanoporous gold formed by electrochemically dealloying silver–gold alloys. The pores in nanoporous gold range in size from tens to hundreds of nanometres, depending on the length of the dealloying process, and coarsen with post-formation ageing or annealing.

The aim is to measure the strains that affect the atoms in nanoporous gold as a result of dealloying and various ageing processes. The powder diffraction beamline enables the researchers to analyse their samples during the actual dealloying and post-formation processes. The findings should help identify the best conditions for producing pores of particular sizes.

"We can learn much more about the process from watching the reactions happen in real-time than from using samples 'stopped' at intermediate stages of dealloying," Bridget says. "For example, how long it takes to form the pores, how pore formation induces strain, and how the nanopores coarsen to relieve the strain. We're keen to come back for more."

Powder Power

Kia Wallwork, who heads the Australian Synchrotron's powder diffraction team, says the technique is well-suited to studying how materials behave during chemical reactions and over a wide range of temperatures and pressures. Her beamline has been used to examine an extensive variety of materials and processes, including pigments from historic paintings and artefacts, wool dyed with silver nanoparticles, and the side reactions that reduce the efficiency of the Bayer process used to extract alumina from bauxite ore.

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