

Seeking disorder as a catalyst for change

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Dr Rosalie Hocking is shining a light on disordered minerals to find catalysts that can make water into clean fuels. Credit: Swinburne University of Technology

Green chemists dream of replicating the reactions of photosynthesis. Of the possible outcomes, one of the most talked about is the ability to make affordable hydrogen fuels from water. In theory, the only by-product of burning hydrogen is water. But right now most hydrogen is either extracted from fossil fuels or made using energy intensive

processes powered by fossil fuels.

However, if scientists such as Swinburne's Dr. Rosalie Hocking could find a way to make hydrogen in a similar way to the steps plants take during photosynthesis, many of our issues with fossil fuel emissions could evaporate.

To create sugars for their own use, plants absorb carbon dioxide from the atmosphere and suck up water through their roots. In the chloroplasts of the leaves, pairs of water molecules split into two hydrogen molecules and one oxygen molecule (see page 32). The molecules only do this with an input of energy. In plants, chlorophylls with manganese clusters and various enzymes serve as photocatalysts to speed up the reaction, all within a protein complex known as photosystem II. Plants are then provided with their basic energy unit when hydrogen reacts with CO_2 to form glucose in another set of reactions. Even with sunlight, however, these reactions are slow.

It's the first and most difficult part of the equation—the reaction that splits water into hydrogen and oxygen—that fascinates Hocking, a senior lecturer at Swinburne, and the recipient of a Vice-Chancellor's Women in STEM Fellowship. She's searching for a substance to act as a chlorophyll-like catalyst to speed up water-splitting reactions. But as her team looks at the crystal structures of possible catalysts, a couple of odd, misfit minerals have come into focus.

Manganese-like misfit

In 2011, Hocking's data from an X-ray spectroscopy beamline at the Australian Synchrotron in Melbourne, showed something striking about a mineral called Birnessite (manganese oxide). The mineral, it turned out, has distinct similarities in catalytic reactivity to the manganese in photosystem II. Robust, inexpensive and abundant, Hocking and her

collaborators concluded that this Birnessite could potentially help in water-splitting if stimulated by electricity.

"Actually, people knew for a long time that Birnessite was similar to parts of photosystem II," says Hocking. "But, early on, they tested a stable version of this material, found that it was 'dead' in terms of catalytic activity and then moved on."

She thinks a lot of useful catalysts have been hiding in this way. "When you make a manganese oxide in a chemistry lab, you might use a fairly pure system in distilled water," she explains. "But when these phases are made in nature, there's calcium around, potassium, sodium, a bit of iron. It's messy and it's the messiness that changes the reactivity."

"A lot of our research has shown that if you stabilise a system, you reduce the reactivity and make it less able to do the business of catalysis—it's thermodynamically happy and doesn't want to accept or release electrons."

Birnessite is among a handful of other metal oxides found to be capable of splitting water, including ruthenium oxide, iridium oxide and cobalt oxide.

A 2015 study by researchers at Florida State University and The University of California, Berkeley, showed a way of layering Birnessite to efficiently capture solar energy to split water.

One of the researchers involved in this study suggested that future roofs might be covered in this mineral, and that it could turn rain water into energy with the help of the sun.

But realising this prediction is a long way off. Catalysts useful to artificial photosynthesis are still little understood and often require very

high temperatures to work. Hocking says, for example, that if the classical catalysts were going to work in the way photosynthesis does, she thinks we would have seen it already. "If you look at a lot of industrial catalysts, they tend to catalyse reactions that don't involve nearly as much energy," she explains. "The mechanisms in these types of catalysts must be fundamentally different."

Wielding beams of light

Catalysts are among Hocking's specialities. Trained as an X-ray spectroscopist at Stanford University in the United States, she uses a form of light known as synchrotron radiation to understand materials.

The light of synchrotron beamlines, generated by accelerating electrons to almost the speed of light in facilities the size of football fields, reveals X-ray structural data impossible to observe in any other way. "People often call me to say they have a great new catalyst, but they need help to study its structure, because they don't know how to use the beamline," says Hocking.

"Being an X-ray spectroscopist gives me the advantage of seeing lots of other researchers' materials. And I would always take notice of the commonalities and differences between them."

Hocking thinks science may have overlooked catalysts like Birnessite because their structure is too messy for most chemists' tastes. She says that chemists are trained from early on to seek out order in molecules to better understand them, and so they have an inbuilt bias towards ordered crystalline versions of minerals.

"Think about a first-year chemistry textbook," says Hocking. "We are teaching students about the radii of ions and atoms, and that comes directly from X-ray crystallography, an analytical technique that can only

be applied to materials that are completely ordered. These concepts underlie some of our very first assumptions as chemists." According to Hocking, chemists are really good at characterising solids that are crystalline and are pretty good with molecular systems in solution, "but we are terrible at everything in between! And in doing so we've ignored a lot of things."

Another potentially very messy mineral is iron sulphide, which is found in sulphur emanating from low-oxygen environments, such as swamp water. Iron sulphides' prevalence in extra-terrestrial objects has led to suggestions that it may also be linked to the very first blossoming of life on Earth, and thus the early evolution of photosynthesis. Iron sulphides also help regulate metabolic processes in living systems by accepting or releasing electrons.

Despite their simple composition of iron and sulphur atoms, iron sulphides can take on a surprising number of different structures, but may have also fallen into a chemistry blind spot. "Iron sulfide phases have been overlooked because scientists looked at their very stable forms instead of their natural states, which are extremely disordered with many impurities. With iron sulphides being rediscovered as functional electro-catalyst materials, it's reasonable to ask 'What did we miss decades ago?'"

Hocking's recent work has focussed on 'metastable' forms of manganese and iron sulphides. These materials transform into another state over time. Her Swinburne lab is trying to tweak metastable iron sulphides to be more disordered using tricks like rapid precipitation, or by adding soapy surfactants that interfere with crystal formation. "It's easy to make things non-crystalline," Hocking jokes. "You just have to try to reverse what you've been trained to do as a chemist your entire life".

Big machinery and beyond

Understanding these new compounds using the huge machinery at the synchrotron can be slow. "They take a long time to set up, and it's difficult to get your electrochemistry and spectroscopy right at the same time," says Hocking. The team may only get three or four days a year to run crucial tests. "My record for staying up is more than I should admit, 48 hours or so."

Adding to the difficulty is the fact the characterising 'disordered' compounds is a lot of extra work. For a crystalline order, researchers can look for a group of atoms, known as a unit cell, which can reproduce the entire crystal structure when repeated in three dimensions. For more disordered materials these experiments just don't work. Often the materials are described as amorphous, meaning they have no unit cell, so they can't be analysed in conventional ways.

"This is where synchrotron based X-ray absorption spectroscopy can be quite useful," explains Hocking. "We can use the high-energy light to home in on the metal parts of a sample and understand the nanostructure in that region. In our group, we combine X-ray spectroscopy with electron microscopy to understand disorder."

Hocking and her collaborator, Dr. Alexandr Simonov at Monash University, have also spent the last five years developing a device, called an in situ electrochemical cell, to measure a potential catalyst's structure and response to electrical potential simultaneously. The team can use it to link a material's atomic framework with the number of times a [catalyst](#) performs a reaction before becoming inactivated.

It has already produced results. "There are some surprising differences in materials that we hadn't noticed," says Hocking. "We are also able to see whole material responses, changes in its structure, or oxidation state, rather than just the active sites that people usually focus on in catalysis."

She hopes that using this new technology on overlooked disordered minerals will speed up the process of identifying many game-changing results. "I'm not a terribly tidy woman," she adds, "and my group joke about me being interested in disordered materials when I'm a little disordered myself." But if she finds the key to splitting water, Hocking's finding will be far from a joke.

Provided by Swinburne University of Technology

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