Using electricity to give chemistry a boost

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UD researchers have developed a new method for making iron-based metal organic framework (MOF) materials. Pictured: Graduate student Amanda Weaver (left) sets the UD-developed electrochemical process in motion, while chemistry professors Eric Bloch (center) and Joel Rosenthal (right) observe. Credit: Kathy F. Atkinson

Metal organic frameworks (MOFs) are a promising class of materials that have many applications as catalysts, sensors and for gas storage. Widely studied over the past two decades, MOFs are typically produced using chemical processes that require high heat and high pressure.

Now, University of Delaware chemists Joel Rosenthal and Eric Bloch report that it is possible to produce iron-based MOF materials directly using renewable electricity at room temperature.

The UD-developed method is 96% efficient in using electricity to form the MOF materials quickly, reliably and inexpensively. The UD researchers reported the advance in a new paper published in *ACS Central Science*.

According to Rosenthal, professor of chemistry and biochemistry in UD's College of Arts and Sciences, an easy way to think about MOFs is to imagine tinker toys, where clusters of metal atoms represent the toy's wooden wheels and small organic molecules represent the spindly sticks that connect the clusters together.

In between are voids with tremendous potential for chemical storage and separations. For example, a pile of MOF material the size of a pea has an internal surface area the size of two football fields that can be used to store gases like methane or hydrogen, separate gases and catalyze reactions. They can even be used as sensors.

"The quality of the materials we can produce is as good as what you could expect from the best thermal methods, but far more scalable and sustainable," said Rosenthal, an expert in electrochemistry. "Our discovery is a major step forward in making MOFs a more practical option for many different applications."

Electricity drives the chemistry

One challenge that has constrained MOFs to academic labs is that making them on a large scale is difficult and not particularly environmentally friendly. So, Rosenthal had the idea to start using electricity to trigger the synthesis of MOFs. Using electricity allows the amount of energy introduced to a synthetic process to be easily adjusted at room temperature, creating a safer way to make MOFs without the high temperatures, high pressures and sometimes toxic reagents that are normally used.

Drive to the foot of the Delaware Memorial Bridge and on both the Delaware and New Jersey sides you will see chemistry plants that are each the size of a small arena or stadium. These plants house a few reactors that do a handful of different chemical reactions to make chemicals useful to society.

"To efficiently carry out many thermal chemical processes on commercial or commodity scales generally requires these large footprints and very expensive infrastructure, but electrochemistry provides a way to break these rules," said Rosenthal. "You don't need to build a giant electrochemical plant to efficiently scale up an electrochemical method. Electrosynthesis is often much more versatile in terms of translation from an academic lab to the commercial marketplace."

The chemistry isn't as simple as a child sitting in the living room connecting wheels and sticks, though. Advances in MOF synthesis to date have been limited by the combinations of metals that can be used and the kinds of synthetic and organic materials that can be combined using thermal approaches.

The paper specifically focuses on preparing MOF materials using clusters of iron atoms. Rosenthal and Bloch aren't the first to make iron MOFs. Traditionally, Rosenthal explained, researchers make these materials by taking an iron (3+) salt, an organic molecule and a relatively expensive solvent that decomposes under certain reaction conditions and heating it all up in a sealed container at high pressures for at least a day, sometimes multiple days, then opening it up and see what they get.

By contrast, he and Bloch begin with a solution containing solvent, organic molecules and iron (2+) ions, which have an extra electron that changes the way the iron behaves. The researchers use an electrode made from either carbon or a type of conducting glass to pass electricity through the solution and toggle the charge of the metal particles in the solution from iron (2+) to iron (3+). It's like a switch, making the iron more highly charged so it can produce the MOF in a way that is direct and efficient, without side reactions or effects typical of traditional thermal chemistry methods.

"As the electrode is taking electrons from iron, that iron goes and finds an organic linker and makes some MOF. It's almost 100% efficient, in that every electron we move results in MOF synthesis. There aren't any side reactions or undesired products," said Bloch, an assistant professor of chemistry and biochemistry who specializes in metal organic frameworks and adsorptive materials.

Further, if the right kind of electrode is used, it is possible to do more than create and collect the MOF product. The research team can grow the material directly on the electrically conductive substrate, an advantage that could enable MOFs to be used in various devices and patterned supports, bringing advanced MOF sensors within reach.

Rosenthal explained that to make an MOF into a sensor you need a way to interconnect it with an electrically conductive support to get a readout. This isn't something the research community had figured out how to do well, until now, he said. Electrochemically synthesizing and growing the MOF on the UD team's electrode support provides a way to hardwire the

MOF for better communication between materials.

One way this technology might be used is in miniature sensors, maybe in cell phones to measure air quality or to selectively detect particles in the air as part of security measures at airports.

"Sensing gases and molecules now can be pretty straight forward, similar to the way your smoke detector works to sense one type of gas over another based on its reactivity," said Bloch.

The electrosynthetic reaction is fast, too, causing MOF powder to form in the solution within minutes. And while materials that sit too long in solution often degrade with time or go on to become a different material entirely due to side reactions, MOF materials created via electrosynthesis are stable and simply settle onto the bottom of the vial. Since the electrosynthetic process is carried out at room temperature, material decomposition is much less of a concern.

The longer the electrolysis runs, the greater the amount of MOF material that can be siphoned off as a product. The method's simplicity makes it versatile in terms of translating it from an academic lab bench to the commercial marketplace, too, the researchers said.

Graduate student Anna Weaver, a co-author on the paper, only arrived at UD this summer but Rosenthal said she played a key role in demonstrating the effectiveness of the team's method. Weaver ran several late-stage experiments that provided additional data for the paper.

"Anna's ability to make contributions so quickly speaks both to her talents and the ease with which this chemistry can be carried out. It doesn't take learning a dark art to get this to work," he said.

Electrically driven chemistry also opens the door to exploring materials that have been predicted to have excellent properties for MOFs, such as those based upon cobalt, but remain unknown because they are incompatible with traditional chemistries that rely on heat to set the reaction in motion.

"As catalysts, we know certain metals would be phenomenal as MOFs, but the normal methods don't work. We think this is a path for making new MOFs that are stable and very reactive with totally different properties than we have been able to access before," said Bloch.

Other co-authors on the paper include current or former UD graduate students in Rosenthal's and Bloch's labs, including Wenbo Wu, Gerald E. Decker and Amanda Arnoff.

More information: Wenbo Wu et al, Facile and Rapid Room-Temperature Electrosynthesis and Controlled Surface Growth of Fe-MIL-101 and Fe-MIL-101-NH2, *ACS Central Science* (2021). DOI: 10.1021/acscentsci.1c00686

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