Chemistry with sunlight: Combining electrochemistry and photovoltaics to clean up oxidation reactions

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Kevin Moeller, PhD, professor of chemistry in Arts & Sciences at Washington University in St. Louis, holds an electrochemical cell and Alison Redden, a graduate student in chemistry holds a photovoltaic cell. Connecting the two provides a way of running the oxidation reactions that play a key role in organic-molecule synthesis without producing toxic byproducts or relying on a dirty source of energy. Credit: David Kilper/WUSTL

The idea is simple, says Kevin Moeller, PhD, and yet it has huge implications. All we are recommending is using photovoltaic cells (clean energy) to power electrochemical reactions (clean chemistry). Moeller is the first to admit this isn't new science.

"But we hope to change the way people do this kind of chemistry by making a connection for them between two existing technologies," he says.

To underscore the simplicity of the idea, Moeller and his co-authors used a $6 solar cell sold on the Internet and intended to power toy cars to run reactions described in an article published in Green Chemistry.

If their suggestion were widely adopted by the chemical industry, it would eliminate the toxic byproducts currently produced by a class of reactions commonly used in chemical synthesis — and with them the environmental and economic damage they cause.

The trouble with oxidation reactions

Moeller, a professor of chemistry in Arts & Sciences at Washington University in St. Louis, is an organic chemist, who makes and manipulates molecules made mainly of carbon, hydrogen, oxygen and nitrogen.
One important tool for synthesizing organic molecules — an enormous category that includes everything from anesthetics to yarn — is the oxidation reaction.

"They are the one tool we have that allows us to increase the functionality of a molecule, to add more "handles" to it by which it can be manipulated," says Moeller.

"Molecules interact with each other through combinations of atoms known as functional groups," he explains. "Ketones, alcohols or amines are all functional groups. The more functional groups you have on a molecule, the more you can control how the molecule interacts with others."

"Oxidation reactions attach functional groups to a molecule," he continues. "If I have a hydrocarbon that consists of nothing but carbon and hydrogen atoms bonded together, and I want to convert it to an alcohol, a ketone or an amine, I have to oxidize it."

In an oxidation reaction, an electron is removed from a molecule. But that electron has to go somewhere, so every oxidation reaction is paired with a reduction reaction, where an electron is added to a second molecule.

The problem, says Moeller, is that "that second molecule is a waste product; it's not something you want."

One example, he says, is an industrial alcohol oxidation that uses the oxidant chromium to convert an alcohol into a ketone. In the process the chromium, originally chromium VI, picks up electrons and becomes chromium IV. Chromium IV is the waste product of the oxidation reaction.

In this case, there is a partial solution. Sodium periodate is used to recycle the highly toxic chromium IV. A salt, the sodium periodate dissociates in solution and the periodate ion (an iodine atom with attached oxygens) interacts with the chromium, restoring it to its original oxidation state.

The catch is that restoring the chromium destroys the periodate. In addition, the process is inefficient; three equivalents of periodate is consumed for every equivalent of desired product produced.

Seeking cleaner byproducts

"All chemical oxidations have a byproduct, says Moeller, so the question is not whether there will be a byproduct but what that byproduct will be.

People have starting thinking about how they might run oxidations where the reduced byproduct is something benign."

"If you use oxygen to do the oxidation, the byproduct is water, and that is a gentle process," he says.

But there is a catch. Like all other molecules, oxygen has a set oxidation potential, or willingness to accept electrons. "So whatever I want to oxidize in solution has to have an oxidation potential that matches oxygen's. If it doesn't, I might have to change my whole reaction around to make sure I can use oxygen. And when I change the whole reaction around, maybe it doesn't run as well as it used to. So I'm limited in what I can do," Moeller says.

“Electrochemistry can oxidize molecules with any oxidation potential, because the electrode voltage can be tuned or adjusted, or I can run the reaction in such a way that it adjusts itself. So I have tremendous versatility for doing things,” says Kevin Moeller, professor of chemistry at Washington University in St. Louis. Moreover, the byproduct of electrochemical oxidation is hydrogen gas, so this too is a clean process.Bit electrochemistry can be only as green as the source of the electricity. The answer is to use the cleanest possible energy, solar energy captured by photovoltaic cells, to run electrochemical reactions. Credit: David Kilper/WUSTL

There's another way to do it. "Electrochemistry can oxidize molecules with any oxidation potential, because the electrode voltage can be tuned or adjusted, or I can run the reaction in such a way that it adjusts itself. So I have tremendous versatility for doing things," says Moeller.

Moreover, the byproduct of electrochemical oxidation is hydrogen gas, so this too is a clean process.

But again there is a catch. Electrochemistry can be only as green as the source of the electricity. If the oxidation reaction is running clean, but the electricity comes from a coal-fired plant, the problem has not been avoided, just displaced.

The answer is to use the cleanest possible energy, solar energy captured by photovoltaic cells, to run electrochemical reactions.

"That's what the *Green Chemistry* article is about," says Moeller. "It's a proof-of-principle paper that says it's easy to make this work, and it works just like reactions that don't use photovoltaics, so the chemical reaction doesn't have to be changed around."

The next step

The *Green Chemistry* article demonstrated the method by directly oxidizing molecules at the electrode. No chemical reagent was used. Since writing the article, Moeller's group has been studying how solar-powered electrochemistry might be used to recycle chemical oxidants in a clean way.

Why would manufacturers choose to use a chemical oxidant, if the voltage of the electrode can be matched to the oxidation potential of the molecule that must be oxidized?

"An electrode selects purely on oxidation potential," Moeller explains. "A chemical reagent does not. The binding properties of the chemical reagent might differ from one part of the molecule to another. And there's also something called steric hindrance, which means that one part of the molecule might physically block access to an oxidation site, forcing substrates to other sites on the reagent."

"The chemistry community has learned how to use chemical reagents to make reactions selective," he says. "The reagents are usually expensive and toxic, so they are recycled," he says. "We are working on cleaning up reagent recycling."

In the chromium oxidation described above, for example, chromium IV could be recycled electrochemically instead of through a reaction with periodate. Instead of periodate waste[consistent with description above where periodate consumed?], the reaction would produce hydrogen gas as the byproduct.

"Another example is an industrial process for carrying out alcohol oxidations that convert the alcohol group to a carbonyl group," says Moeller. This process uses TEMPO, a complex chemical reagent discovered in 1960. TEMPO is expensive so it is recycled by the addition of bleach. This regenerates the TEMPO but produces sodium chloride as a byproduct."

In small quantities sodium chloride is table salt, but in industrial quantities it is a waste product whose disposal is costly. Once again, the TEMPO can be recycled using electrochemistry, a process that produces hydrogen as the only byproduct.

"We can't make all of chemical synthesis cleaner by hitching solar power to electrochemistry," Moeller says, "but we can fix the oxidation reactions that people use. And maybe that will inspire someone else to come up with simple and innovative solutions to other types of reactions they're interested in."

Provided by Washington University in St. Louis

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