



Power-to-gas plants use renewable energy to make sustainable fuel

By **Melissae Fellet**
 Feature Editor
Christian Bach

Renewable energy provides electricity with significantly less greenhouse gas emissions than fossil-fuel-based power plants. But some sources of renewable energy, such as wind and solar power, produce electricity intermittently. Power produced when electricity demand is low could go unused.

Power-to-gas (PtG) plants use excess renewable electricity to electrochemically split water into hydrogen and oxygen. The hydrogen is then used to chemically reduce carbon dioxide into methane that can be stored or used immediately in the existing natural gas infrastructure.

In 2013, Audi opened one of the world's largest industrial scale PtG plants to produce methane as a renewable fuel for some of their natural-gas-powered cars. According to the company's calculations, methane produced by a PtG plant reduces the lifetime carbon footprint of an Audi compact passenger car enough to be comparable to that of an electric car charged only with renewable electricity.

There are three approaches to water electrolysis for PtG applications: alkaline, polymer electrolyte membrane, and solid-oxide electrolyzers. The challenge for all of these approaches is managing the fluctuating power supply from renewable sources.

Most commercial alkaline electrolyzers contain a liquid sodium or potassium hydroxide electrolyte. Common electrode materials include Raney nickel cathodes and nickel-iron-cobalt alloy anodes. Affordable, long-lasting, and durable alkaline electrolyzers have been available commercially for decades. Because this technology is well developed, many pilot PtG projects utilize alkaline electrolysis.

However, alkaline cells are slow to respond to power fluctuations, taking up to an hour to start up after shutdown. The relatively slow kinetics of the electrochemical reactions on either side of the cell can reduce the cell's current density or overall efficiency. The combined thickness of the liquid electrolyte and the diaphragm that separates the two sides of the cell also contribute to low-current density. This distance causes charge carriers to move farther across the cell, essentially increasing the ionic resistivity of the cell. Finally, corrosion from the caustic electrolyte can limit the lifetime of these reactors.

Electrolyzers that contain a polymer electrolyte membrane (PEM) can respond within minutes to fluctuating loads. Typically, the membrane is a perfluoro-sulfonic acid polymer, approximately 100–200 μm thick. Protons travel easily through this membrane to carry charge between the electrodes on either side.

The cell design of PEM electrolyzers facilitates high-pressure operation, which generates pressurized hydrogen that can be used directly for methane production. This eliminates energy that would otherwise be needed for gas compression prior to methanation. Hydrogen collected for future use in fuel-cell vehicles would need to be pressurized to 700 bar. To reduce the amount of compression needed for this application, Thomas Justus Schmidt, at the Paul Scherrer Institute in Switzerland,

and his colleagues are working on a PEM electrolyzer technology that operates up to 300 bar.

Increasing the operating pressure of a PEM cell also increases the amounts of hydrogen and oxygen that cross over to opposite sides of the cell and create a potentially explosive mixture. Thicker membranes reduce the crossover, but they also increase the electrochemical resistance and reduce efficiency. Researchers are working to build new membranes that maintain conductivity without increasing gas crossover. One strategy is reinforcing current membranes with silicon, tungsten, or titanium oxide.

The cathode for PEM cells is commonly a carbon black electrode coated with platinum nanoparticles at a loading of 0.5–1 mg cm^{-2} . The anode, however, contains higher loadings of iridium, a noble metal in low abundance. Concerns that increased demand for iridium would increase costs for the metal and its applications have led researchers to reduce the amount of iridium in PEM anodes to less than 2 mg cm^{-2} . They also have been reducing iridium by adding ruthenium, its oxide, or other transition metals to the catalyst, as well as developing catalysts that do not require noble metals.

Some components of PEM cells, such as the noble metals for the anode, titanium current collector, and titanium separator plates, are more expensive than those in alkaline cells. But other components help PEM cells to be more efficient than alkaline ones. The thin membranes and electrodes in PEM cells reduce resistive losses, enabling current densities in the best commercial cells to reach more than 2 A cm^{-2} , five to ten times greater than alkaline electrolyzers.

The high-current density of PEM cells means that these cells will be smaller than an alkaline one that consumes the same amount of electricity. Smaller units contain less materials that might offset the increased installation costs of PEM cells compared to alkaline, Schmidt said. The lifetime of PEM cells, however, is still significantly shorter than alkaline cells.

Christian Bach, Empa, Switzerland
 Melissae Fellet, melissae.fellet@gmail.com

The third type of electrolyzer for PtG uses an oxygen-conducting solid-oxide ceramic electrolyte, such as yttria-stabilized zirconia. It can operate at temperatures of 700–900°C that enable the electrolysis of steam instead of liquid water. This decreases the electrolysis equilibrium voltage and increases the cell efficiency. However, the high-temperature operation increases start-up and break-in time. While this technology is mostly in the research phases, the high efficiency could make it useful in the future for PtG plants, said Tom Smolinka, at Fraunhofer Institute for Solar Energy Systems ISE. The Helmeth EU project, a collaboration of companies, universities, and institutions throughout Europe, is developing the first demonstration plant to connect a solid-oxide electrolyzer with a methanation reactor.

Some PtG plants only produce hydrogen from water electrolysis. Others combine the hydrogen with carbon dioxide to produce methane. Often, these plants utilize carbon dioxide collected as a byproduct from biogas plants that burn or ferment biomass to generate methane. Directing this carbon dioxide to a PtG plant for methanation doubles the amount of methane produced from biomass.

The best state-of-the-art methanation catalyst is typically supported nickel nanoparticles, and commercial catalysts can reach carbon dioxide conversions of more than 90% when operated above 250°C. Still, researchers are working on better and cheaper catalysts.

Andreas Borgschulte, at Empa—Swiss Federal Laboratories for Materials Science and Technology, and his colleagues have altered the methanation catalyst to increase the carbon dioxide conversion. The researchers attached nickel nanoparticles to a porous zeolite. The zeolite absorbs water produced during methanation, shifting the reaction equilibrium toward generating more methane. This catalyst achieves 100% conversion at 300°C.

The zeolite's function as a local water absorber enables the nickel density of the catalyst to be 10 times lower than traditional supported catalysts. Borgschulte said the reduced amount of nickel also helps reduce hot spots that plague the



Audi's power-to-gas plant in Werlte, Germany. Credit: Audi.

methanation process. Typically, reactor designs manage the heat from the exothermic reaction, which if allowed to build up, reduces the conversion. Though the heat-density of Borgschulte's catalyst is lower than traditional ones, the reactor is also larger.

Since the zeolite absorbs water produced during the methanation reaction, the material needs to be dehydrated before it can be used again. A PtG plant using this catalyst needs two methanation reactors: one performing the conversion, and one drying and regenerating the catalyst. The frequent regeneration seems to reduce carbon deposits on the surface, though the catalyst can still be poisoned by sulfur contaminants, Borgschulte said.

Most of the newest pilot and demonstration PtG plants are located in Germany, due to the growing demand for renewable energy. In 2014, about 25% of Germany's electrical energy came from renewable sources, and a governmental initiative pledges to increase that proportion to 60% by 2035.

PtG plants also help ease the country's transition to renewable energy. Audi's PtG plant, located in northwestern Germany, can consume 6 MW of power within five minutes of starting. This fast response time enables the PtG plant to stabilize the electric grid by preventing spikes of renewable energy from flooding the system.

Audi's plant uses wind power to drive hydrogen production through alkaline electrolysis. A methanation reactor produces 1000 metric tons of synthetic natural gas each year using carbon dioxide from a nearby biogas plant, with an overall conversion efficiency from electric power to synthetic methane of 50%. The plant injects methane directly into the existing natural-gas infrastructure, so that synthetic natural gas from the plant goes directly to vehicle filling stations.

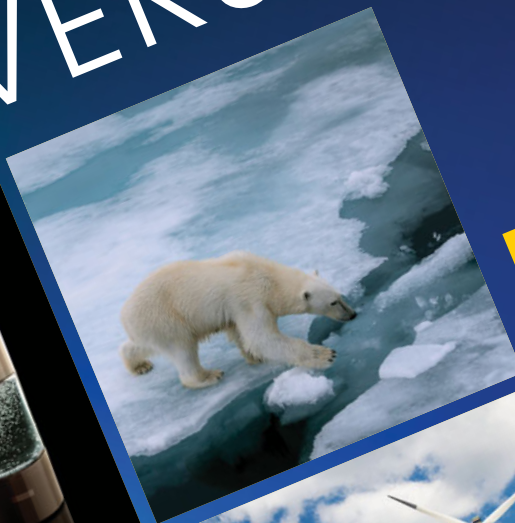
Hermann Pengg, director of renewable fuels at Audi, said that methane from their plant can power 1500 compact passenger cars for 15,000 kilometers. Because the amount of carbon dioxide emitted while using this fuel equals the amount used to make it, methane produced from the PtG plant is considered carbon neutral. This reduces the lifetime carbon footprint of a natural-gas-powered compact car by 70% compared to a gasoline car, according to company calculations.

Currently, there are 14 PtG projects in Germany, with another 17 under construction. Many consume only kilowatts of electricity, but they are all working to advance the next generation of sustainable electricity and transportation powered by methane and hydrogen. Lessons learned as PtG plants support the growth of renewable energy and advance renewable fuels can be applied to forwarding the development of future sustainable technologies. □

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