Hard X-rays probe model fuel-cell catalyst

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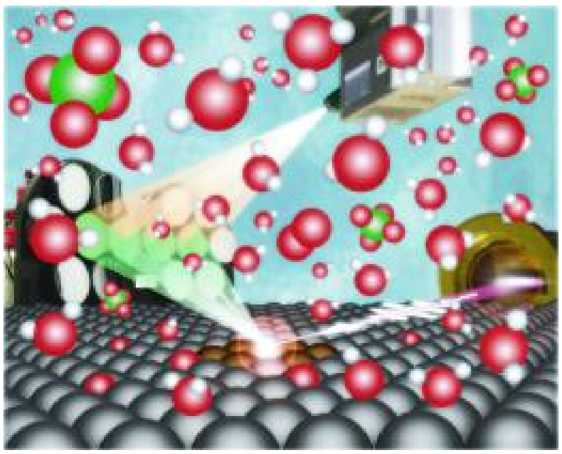

A beam of specially-tuned X-rays scatters off a platinum atom and into a detector, unaffected by the surrounding perchloric acid solution. (Image by Daniel Friebel.)

(PhysOrg.com) -- Researchers at the Stanford Synchrotron Radiation Lightsource have developed a new, more powerful way to probe the behavior of a key component in hydrogen fuel cells. The group shone SSRL's high-energy X-rays on a single-atom layer of platinum to illuminate how the metal helps the generation of electrical power inside a fuel cell. SSRL Research Associate Daniel Friebel led the work, together with Anders Nilsson of both SSRL and the Stanford Institute for Materials and Energy Sciences, a joint SLAC-Stanford institute. The new experimental approach appeared online recently in *Physical Chemistry Chemical Physics*, a publication of the Royal Chemical Society.

"People have tried to use synchrotron radiation and X-ray spectroscopic techniques over many years—decades—to measure what's happening to the platinum," Nilsson said. But insufficient resolution and sensitivity made those measurements hard to interpret. "And so nobody had been able to understand exactly what they see. I think what this particular study has done is improve the understanding of what we see."

Fuel cells show potential for generating electricity in a clean, renewable fashion. Like batteries, fuel cells provide energy using a chemical process divided into two" half-reactions" that take place at separate positive and negative electrodes. Unlike batteries, a fuel cell can run continuously so long as the negative electrode—or cathode—is supplied with oxygen and the positive electrode—or anode—is supplied with a fuel. One promising type of fuel cell is the polymer electrolyte membrane fuel cell, which uses hydrogen as fuel and creates water as its only by-product.

However, one major obstacle stands in the way of widespread use of fuel cells: cost. Large quantities of platinum are needed to speed up the conversion of oxygen to water on the cathode side. What's more, over time a process Nilsson terms "the second biggest issue" for fuel cells takes place; the platinum catalyst degrades, requiring even more of the precious metal to keep a fuel cell working. Researchers do not fully understand how this degradation happens, and observing the microscopic details of the various processes taking place at the cathode has proven to be difficult, Friebel said.

"Monitoring only the surface of a fuel-cell catalyst under realistic conditions is a challenge," Friebel said. "We needed a probe that could penetrate a relatively dense liquid environment that surrounded the catalyst, so that's why we use hard X-rays." At the same time, Friebel's group wanted to examine an Ångström-thin slice at the catalyst surface where the fuel-cell reaction takes place. Here, the same penetrating ability that let the X-rays cut through the liquid surrounding their sample worked against them. "Their ability to pierce through the liquid let them also enter the bulk of the catalyst," Friebel said.

Previous experiments generally looked at platinum nanoparticles—tiny bits of pure platinum with dimensions measured in nanometers, or billionths of a meter. However, even a particle that small still has the majority of its atoms sitting on the inside, and their response to the X-rays diluted the data from surface catalytic activity.

To get around this problem, the researchers coated a single crystal of rhodium with one layer of platinum atoms, in essence creating a platinum catalyst that was "all surface." The unique sample design allowed Friebel and Stanford graduate student Daniel Miller to observe how the catalyst surface interacted with the type of acid–water environment typical of fuel cells.

"A major part of the study was conducted using a relatively new type of spectroscopy" called high-energy resolution fluorescence detection, said SLAC senior scientist Uwe Bergmann, a collaborator on the project, who had built the spectrometer located at SSRL's Beamline 6-2 where Friebel's group ran their experiment. The instrument enabled the researchers to identify how oxygen is bound to the platinum surface under different conditions. These oxygen-platinum interactions ranged from merely placing oxygen atoms onto an intact metallic surface to forming a surface oxide, which was very difficult to remove. According to Miller, this surface oxide could play an important role in degrading the performance of fuel cells.

"[Platinum oxide] could be involved in many things," Miller said. "It could be one reason why the reaction on the oxygen side of the fuel cell is inefficient, but it could also be involved in the degradation of the catalyst."

These findings were made possible because the group was able to put together "three key ingredients," Nilsson explained: "a well-defined model catalyst, a high-resolution spectrometer that is unique in the United States, and theoretical calculations using a sophisticated structure model that reflects the quality of the sample in the experiment."

In previous studies, Nilsson and his group have proposed methods to reduce the cost of fuel cells by reducing the amount of platinum needed. The new findings could nicely complement their previous efforts toward both improving the efficiency and extending the lifetime of the platinum catalyst.

More information: Paper online: pubs.rsc.org/en/Content/Articl … g/2011/CP/C0CP01434F

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