Platinum in Fuel Cells Gets a Helping Hand

The behavior of nanoscopic bits of platinum may determine whether a hydrogenpowered car is in your future. The precious metal is the key ingredient in fuel cells that power electric cars with hydrogen, producing water as the only byproduct. Unfortu-

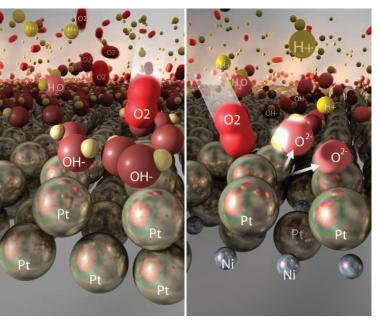
nately, current models are expensive because they use so much platinum, and their performance degrades too quickly for practical use. But advances by two U.S.-led groups offer new hope for tackling these problems.

The researchers targeted what is widely considered to be the biggest concern in fuel cells: improving the performance of the platinum on the positively charged electrode, or cathode—the part of the cell where chemicals react to split oxygen molecules in half. One group, led by materials scientists Vojislav Stamenkovic and Nenad Markovic at Argonne National Laboratory in Illinois, reports in a paper published online by Science this week (www.sciencemag. org/cgi/content/abstract/ 1135941) that it increased the

catalytic activity of a platinum surface 90-fold over conventional cathode catalysts used today. Meanwhile, the other group, led by chemist Radoslav Adzic of Brookhaven National Laboratory in Upton, New York, reports on page 220 that adding tiny gold clusters to the outside of their cathode materials dramatically reduced the tendency of platinum to dissolve from the cathode over extended use. "Both of these results could be quite important if the concepts can be brought to fruition in a practical manner," says Fred Wagner, a platinum catalyst expert at General Motors' fuel cell research center in Honeoye Falls, New York.

Platinum is the key to fuel cells because of its unusually high catalytic properties. This ability comes into play first at the negative electrode, or anode, to split hydrogen molecules (H₂) into two protons (2 H⁺) and two electrons (2e⁻). The electrons then pass through a wire and power the car. At the end of their journey, they wind up at the cathode and pass to oxygen molecules, breaking them into negatively charged oxygen atoms

 (O_2^{2-}) . These oxygens then pair up with protons from the anode to create water molecules. Typically, catalyzing the reactions at each electrode are platinum nanoparticles that lightly coat a highsurface-area carbon skeleton.



Loose grip. All-platinum electrodes (left) grab hydroxides (OH) tightly, preventing oxygen (O₂) from getting access to the catalyst. Adding nickel (right) softens this grip, speeding the desired oxygen-splitting reaction.

In practice, however, unwanted side reactions also occur around the cathode. Some charged oxygen atoms react with protons to create hydroxide molecules (OH) and likely other oxides as well. These oxides have an affinity for platinum atoms. They bind to the cathode surface, where they typically block access to as many as 45% of the platinum atoms, Markovic says. Even worse, the oxides tug on the platinum atoms and eventually pull many of them off the surface, drastically reducing the cathode's catalytic ability.

Researchers have made some progress on both problems by alloying platinum with other metals. In previous work, Stamenkovic and colleagues studied polycrystalline platinum electrodes alloyed with other metals and found that some of the crystalline portions seemed to perform better than others. They suspected that the disparity reflected different ways platinum atoms can pack on a surface—such as a squarelike arrangement versus a hexagonal arrangement.

To find out, for their current study Stamenkovic, Markovic, and colleagues created pure single crystals of platinumnickel alloys with different atomic arrangements of their crystalline lattices. They compared the samples with single crystals of pure platinum as well as with conventional platinum-carbon fuel cell catalysts.

They found that the most tightly packed arrangement of atoms, known in the materials lingo as a 111 surface, far outperformed all the others. The material wound up with a uniform layer of platinum atoms on top of a layer with 50% nickel atoms. All the layers under that had essentially a steady composition of three parts platinum to one part nickel (see diagram).

Stamenkovic says the group's theoretical work shows that the 111 arrangement lowers the electronic interaction between platinum atoms on the surface and oxides seeking to bind to them. The upshot is that far fewer oxides bind to the platinum surface, leaving those sites open to carry out O₂-splitting reactions. That setup boosts the PtNi alloy's

activity 10-fold over a single-crystal platinum surface and 90-fold over the standard platinum-carbon combo. The reduced interaction also tugs less on the surface Pt atoms and therefore yanks fewer atoms off the surface.

That increase in stability was echoed by the result from Adzic's team. Adzic and colleagues deposited tiny gold nanoclusters on the top of a conventional carbon-platinum fuel cell cathode. They found that the clusters produced a similar change in the electronic behavior of the surface of the cathode that prevented platinum atoms from dissolving into the electrolyte, while leaving the overall oxygen-splitting activity of the platinum unchanged.

The key now, Wagner and others say, will be to create highly active, stable real-world catalysts. Markovic says his group is already catalysts. Markovic says his group is already working on creating octahedron-shaped platinum-nickel nanoparticles that theory shows should have all the desired 111 surfaces. If they work, hydrogen fuel cell–powered cars -ROBERT F. SERVICE will take a major step toward widespread use.