black, and that those pores with widths less than 2 nm hosted sites where N atoms could bind the Fe ion (see figure 1). They also noted that the etching reaction by ammonia occurred 10 times as fast in disordered C as in structured C crystallites, so the micropores formed primarily in the region of disordered C.

If micropores were so important, the team reasoned, why not simply use commercially available, highly microporous carbon black as the C support? Doing so, however, did not improve the activity of the resulting catalyst. Then the experimenters realized that microporous carbon black as delivered was mostly devoid of the disordered C. Hence, the nitrogen essential for ligating Fe ions to the C support could not enter the pores by ammonia etching of disordered carbon.

The experimenters decided to introduce into the microporous carbon black some material that would function as the disordered C. They used a ball-milling technique to force that pore filler, along with Fe acetate, into the micropores. They then heated the resulting material first in argon and then in ammonia.

Resulting performance

Dodelet and his colleagues estimate that the best hydrogen fuel cells produced with their new method extrapolate to a current density of 99 A/cm^3 at a fuel-cell voltage of 0.8 V. That is close to the 2010 target of 130 A/cm^3 that the US Department of Energy has adopted for oxygen reduction on non-precious-metal catalysts and beats the best previous result by more than a factor of about 30.

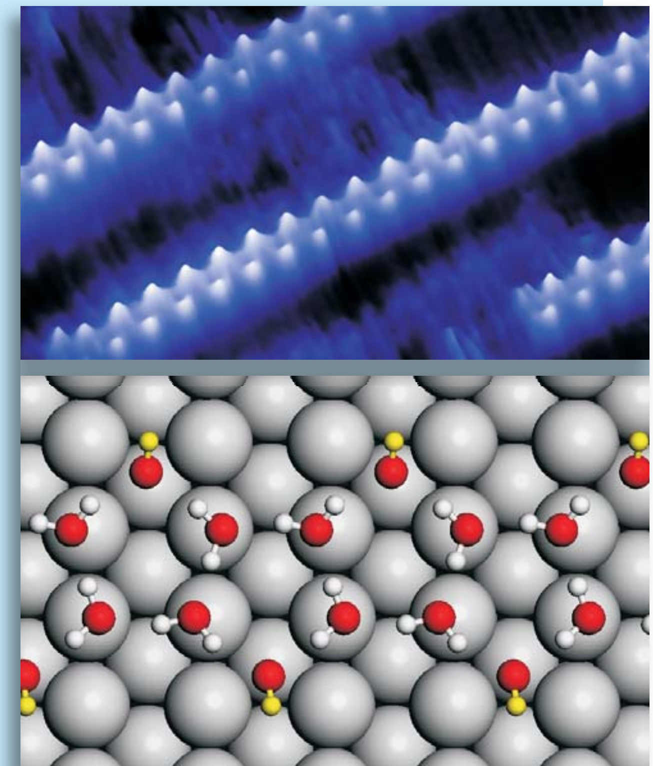
Figure 2 compares the performance of a commercially available Pt fuel-cell cathode with that of cathodes made using the best new Fe-based catalysts. The two types perform similarly at low current densities, where performance is governed only by the kinetic activity of the catalyst. However, the voltage for the Fe-based fuel cells falls sharply just above 0.1 A/cm^2. Automotive fuel cells would have to operate at around 0.1–1.0 A/cm^2, says Jiujun Zhang of the Institute for Fuel Cell Innovation of Canada's National Research Council.

The falloff in voltage is caused by the mass transport problem: To boost the current density for a given voltage, one needs to improve diffusion of oxygen and protons to the active sites within the catalyst. That's the next hurdle facing scientists and engineers.

Another hurdle is the instability of the Fe-based catalysts, whose cause is

Ice chains on copper are built from pentagons

Before they form snowflakes and other familiar hexagonal crystals, water molecules nucleate in smaller configurations. Determining the structure of those precursors—even in the outwardly simple case of water on a clean metal surface—is an area of ongoing interest and controversy. Water forms different structures on different surfaces. For example, Andrew Hodgson and Sam Haq of the University of Liverpool in the UK noticed several years ago that when less than a single monolayer of water was adsorbed onto a copper (110) surface, vibrational spectra showed features characteristic of highly ordered, reduced-dimensional structures. They suspected that the water molecules were forming 1D chains, rather than 2D islands. Their hypothesis was confirmed by Hiroshi Okuyama and colleagues at Kyoto University in Japan, who obtained scanning tunneling microscopy images showing adsorbed water chains up to tens of nanometers in length but just 1 nm wide.[1] But the STM images could not resolve the positions of individual water molecules, and the exact structure of the chains remained a mystery. Says Hodgson, "We—or at least I—assumed that they would probably be made up of hexamer rings, with just one molecule per hexamer buckled out of the plane and the rest bonding to the metal." But no arrangement of water molecules into hexagonal units was found that could entirely explain the experimental data.



Now, Hodgson and colleagues have collected STM images of the chains with much higher resolution, as shown in the top panel of the figure. And they've teamed up with computational chemist Angelos Michaelides of University College London to find the structure.[2] Michaelides and his postdoc Javier Carrasco decided against making the usual assumption that the adsorbed structures, like bulk ice, are made up of hexagons. Instead, they considered some 50 arrangements of water hexamers, pentamers, and tetramers in unit cells of various sizes.

The most energetically stable structure, as revealed by density-functional theory, was also the one that gave the best fit to the STM images and vibrational spectra. That structure, pictured in the bottom panel, is an arrangement not of hexagons, but of edge-sharing pentagons. The water molecules shown in red and yellow are perpendicular to the plane of the surface—their hydrogen atoms pointing up are responsible for the bright spots in the STM image, while the hydrogen atoms pointing down (not visible in the figure) interact with the copper atoms. "The pentamer chain is the most stable," Hodgson explains, "because it optimizes the water–metal bonding, allowing the maximum amount of water to bond flat directly above a copper atom while still making a reasonably strong hydrogen bonding network." The researchers suggest that arrangements of nonhexagonal units might be involved at other water–metal interfaces where the structure of water is unknown.

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References

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