The Oil Drum
DISCUSSIONS ABOUT ENERGY AND OUR FUTURE

Local Scientist Splits Water, Saves World, Gets On TV

Posted by JoulesBurn on August 7, 2008 - 10:00am
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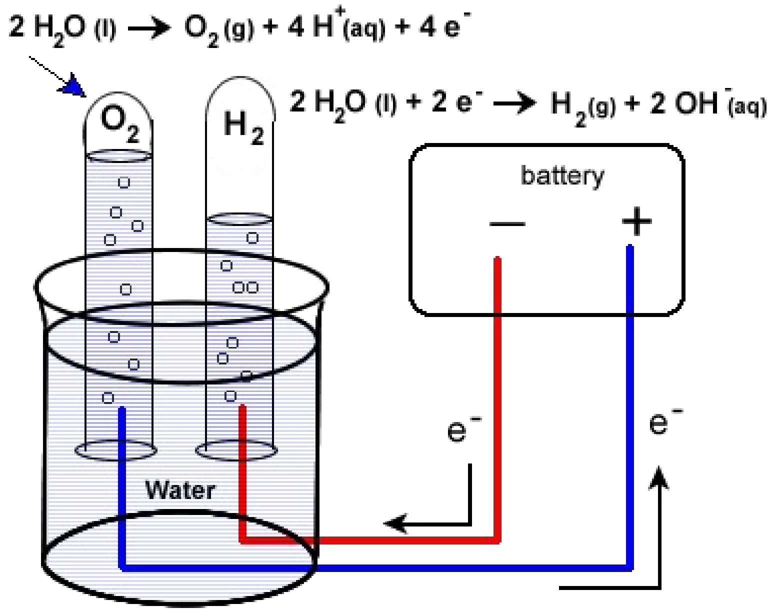
This might have been a story of how a couple of MIT scientists happened upon a breakthrough discovery in the electrolysis of water; but they didn't (and so it isn't). This might also have been a story about an informed media which correctly and skeptically reports on such scientific discoveries -- in the midst of a public relations barrage from a leading university -- but nobody really expects such journalistic vigilance anymore. Instead, this story will try to examine what (if anything) was discovered, and how this news affects the landscape of the looming energy crisis. In addition, given that a number of encouraging research reports have surfaced suggesting a seamless transition to a hydrogen economy, I will revisit the fundamental challenge posed by moving to alternate liquid fuels: getting used to the idea of diffuse energy. (Some names have been omitted to protect the less guilty).

What the Report Reportedly Reports

Massachussets Institute of Technology chemistry professor Daniel Nocera and a postdoctoral fellow (who will remain blameless here) have published a report in **Sciencepress**, a rapid online publication channel for the journal Science, entitled *In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and* Co^{2+} (link). The report itself does not make outrageous claims, but when supercharged by misleading statements and exaggerated claims from Nocera to the media as well as by an apparent MIT public relations blitz, these modest research findings have been transformed into a calming salve for the public's current angst over high energy prices. A sampling:

- Why Oil Really Fell Today—and Could Keep Falling, US News and World Report
- MIT Scientists Unlock 'Nirvana' of Solar Power Storage PC Magazine
- 'Major discovery' from MIT primed to unleash solar revolution From MIT (of course)
- Hydrogen Power on the Cheap--Or at Least, Cheaper Scientific American
- Sunny Forecast For Fuel Cells
  Chemical and Engineering News
- MIT develops way to bank solar energy at home Reuters
- Solar-Power Breakthrough ABC News

So what is really in the report? Nocera et. al. are working to improve the economics of hydrogen production via electrolysis by reducing the cost and improving the efficiency of electrolyzers used to split water into the component gases. Shown below is a simplified diagram showing the basics of water electrolysis.



The red and blue wires protruding into solution are the cathode and anode respectively. (Note that the configurations of real electrodes are more complicated). When sufficient voltage is applied across the electrodes, current will flow and oxygen gas (O_2) will form at the anode and hydrogen gas (H_2) at the cathode. The needed voltage, from thermodynamics, is termed the Standard Potential for the overall reaction and is equal to 1.23 volts at 25C. In reality, more voltage than the Standard Potential must be applied to get appreciable water splitting and gas production, for reasons discussed below. This means that the electrolyzer is less than 100% efficient in converting electric power to power theoretically available by recombining the gases in a fuel cell. Remember that power is current times volts. For example, if double the Standard Potential (i.e. 2.46) volts is applied, only half of the power goes into splitting water and the rest is wasted -- giving an efficiency of 50%.

Making A Better Electrode

Why is this extra voltage needed? Part is needed to overcome the resistance of the solution. For this reason, electrolytes are added to make the liquid more conductive. The more vexing problem has to do with the nature of the electrodes upon which the reactions take place. The rate of a reaction at an electrode, known as the kinetics, limits how fast hydrogen can be generated and turns out to be very dependent on what the electrode is made of. Precious metals such as platinum and palladium generally make good electrodes, but they are of course expensive. The reaction can be "overdriven" by applying a larger voltage than the minimum required, but this reduces the efficiency. For water splitting, the oxygen-evolving anode is the larger contributor to the problem, requiring a larger "overpotential". The goal of the Nocera et. al. research is to build a better (smaller overpotential) and cheaper anode.

They fabricated their anode by electrodepositing a thin film containing cobalt, phosphorous, potassium, and oxygen onto an inert (but conductive) surface. They fully analyzed the film to determine its composition and to verify that it was indeed producing oxygen when a voltage was placed between it and a cathode. They then measured how much current flowed (i.e. how much hydrogen could be produced) vs. how much voltage had to be applied.

The Early Returns

Cheaper? Perhaps. but it depends on what you compare it to. It's eye-opening to contrast the price of cobalt with that of platinum, but commercial anodes aren't made of platinum. It is difficult to get information on commercial electrolysis anodes, but most today are probably made of a nickel alloy. Nocera makes much of the fact of having his cell at neutral pH and open to air (where the nickel wouldn't function as well), but the cell has to be enclosed anyway to collect the hydrogen.

More Efficient? Not based on the data they presented. For example, they reported a current density of 1 milliampere per square centimeter (mA/cm^2) with an overpotential of 410 millivolts. In comparison, this patent from 1979 reports better performance (e.g. 1mA/cm^2 at < 200 mV overpotential) for nickel anodes. Remember, the goal is to minimize the overpotential for a given current density. There have also been many recent reports of better performance for a variety of anode compositions, including alloys or oxides containing cobalt.

Anything? Hello?

If the Nocera electrode material isn't more efficient, then we are back to cheaper. This remains to be seen in the context of a working electrolyzer, but there might be some advantages to a neutral pH and the simplicity of fabrication. Thus, this is research worth doing. But what has been communicated to the outside world is that hydrogen will soon be flowing from our pores because of this research. Let's look at some of the more amazing claims.

Deconstructing the Media

I will chastise MIT first, since (although they are not a disinterested party) they should know better. Here is one bold claim:

> Until now, solar power has been a daytime-only energy source, because storing extra solar energy for later use is prohibitively expensive and grossly inefficient. With today's announcement, MIT researchers have hit upon a simple, inexpensive, highly efficient process for storing solar energy.

No, they've made an anode which may or may not be cheaper and is not more efficient. And according to this report, capital costs (of which the anode cost is only a part) account for less than half of the overall cost of producing hydrogen -- the largest being the cost of the electricity. And for smaller systems, since the amount of electrode material scales directly with capacity, more of the capital cost is incurred by other equipment such as control electronics and gas handling and compression hardware.

> Inspired by the photosynthesis performed by plants, Nocera and [the other guy], a postdoctoral fellow in Nocera's lab, have developed an unprecedented process that will allow the sun's energy to be used to split water into hydrogen and oxygen gases.

Inspiration from leaves aside, there are decades of precedence for the electrolysis of water. Nocera doesn't reference any of it, but you can easily find it with Google.

From EETimes we have this thermodynamically challenged claim:

> A liquid catalyst was added to water before electrolysis to achieve what the researchers

> claim is almost 100-percent efficiency.

The MIT catalyst components are solids (salts) dissolved in water, but where would the 100% claim come from? Perhaps from quoting Nocera:

> "The hard part of getting water to split is not the hydrogen -- platinum as a catalyst works fine for the hydrogen. But platinum works very poorly for oxygen, making you use much more energy," said MIT chemistry professor Daniel Nocera. "What we have done is made a catalyst work for the oxygen part without any extra energy. In fact, with our catalyst almost 100 percent of the current used for electrolysis goes into making oxygen and hydrogen."

First, platinum isn't presently used for the anode anyway. But the last sentence should be rewritten as "exactly 100%", since where else is the current going to go? An electrochemical cell is a closed circuit. But that has nothing to do with efficiency, which is instead the amount of power effecting the chemical change relative to the total power input (see earlier discussion). Clearly, their anode is nowhere near 100% efficient.

From Reuters, we have:

> Nocera's catalyst is made from cobalt, phosphate and an electrode that produces oxygen from water by using 90 percent less electricity than current methods, which use the costly metal platinum. ... "It's cheap, it's efficient, it's highly manufacturable, it's incredibly tolerant of impurity and it's from earth-abundant stuff," Nocera explained. ... "For the last six months, driving home, I've been looking at leaves, and saying, 'I own you guys now,'" Nocera said.

It's not clear where the 90% figure comes from, since commercial anodes (which don't use platinum) do at least as well as Nocera's -- his claims are not supported by his report. As for as the abundance of cobalt, it is a first-row transition metal. But according to the Encyclopedia of Earth, the abundance in earth's crust of cobalt(25 mg/kg) is less than that of nickel (84 mg/kg). According to the U.S. Geological Survey, Mineral Commodity Summaries:

> Periods of high prices and concern about availability have resulted in various efforts to conserve, reduce, or substitute for cobalt. In many applications, further substitution of cobalt would result in a loss in product performance. Potential substitutes include barium or strontium ferrites, neodymium-iron-boron, or nickel-iron alloys in magnets; nickel, cermets, or ceramics in cutting and wear-resistant materials; nickel base alloys or ceramics in jet engines; nickel in petroleum catalysts; rhodium in hydroformylation catalysts; nickel or manganese in batteries; and manganese, iron, cerium, or zirconium in paints.

As for price, remember that soy oil was rather cheap before a new market (biodiesel) appeared for it.

Scientific American plays the platinum card as well:

> Chemist Daniel Nocera, head of the M.I.T.'s Solar Revolution Project, focused on one

> side of the equation: splitting water into its constituent hydrogen and oxygen molecules. This can be done well, but it remains difficult to actually separate the molecules. But Nocera and postdoctoral fellow [the other guy] discovered it could be accomplished by simply adding the metals cobalt and phosphate to water and running a current through it. In contrast to platinum, cobalt and phosphate cost roughly $2.25 an ounce and $.05 an ounce, respectively.
>
> "We [have] figured out a way just using a glass of water at room temperature, under atmospheric pressure," Nocera says. "This thing [a thin film of cobalt and phosphate on an electrode] just churns away making [oxygen] from water."

No, they haven't invented water electrolysis, doing it in a glass of water at RT and 1 atmosphere isn't important, "separating the molecules" isn't the problem, and phosphate isn't a metal (or even an element). Churning is for butter.

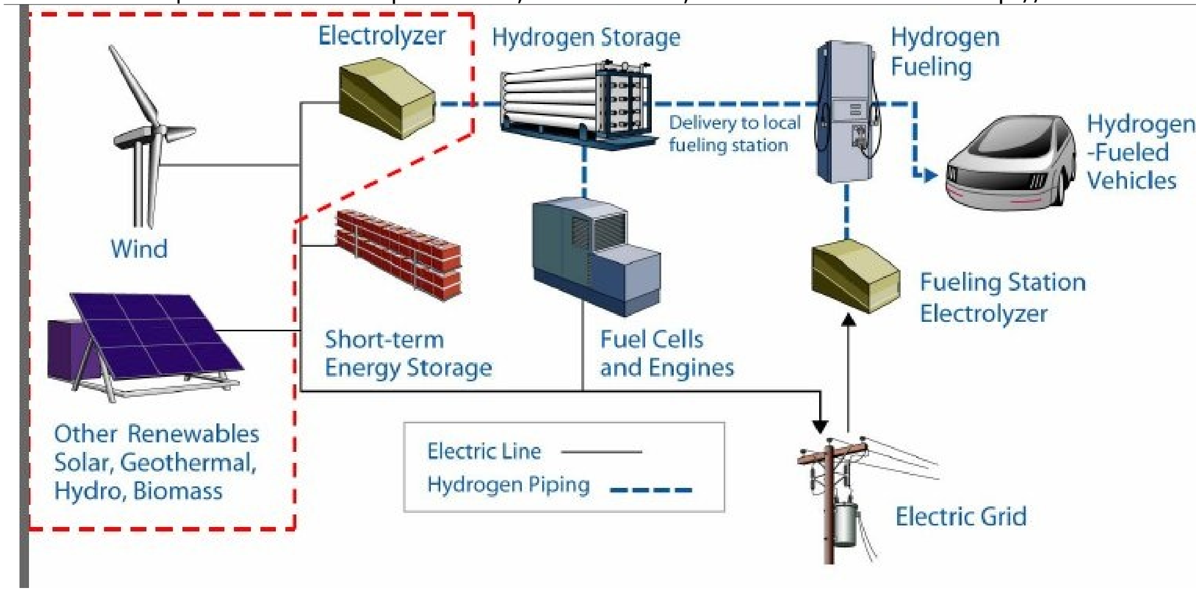
The journalistic arms of scientific journals aren't much better. From the print edition of Science (1 AUGUST 2008 VOL 321):

> The catalyst isn’t perfect. It still requires excess electricity to start the water-splitting reaction, energy that isn’t recovered and stored in the fuel. And for now, the catalyst can accept only low levels of electrical current. Nocera says he’s hopeful that both problems can be solved, and because the catalysts are so easy to make, he expects progress will be swift. Further work is also needed to reduce the cost of cathodes and to link the electrodes to solar cells to provide clean electricity. A final big push will be to see if the catalyst or others like it can operate in seawater. If so, future societies could use sunlight to generate hydrogen from seawater and then pipe it to large banks of fuel cells on shore that could convert it into electricity and fresh water, thereby using the sun and oceans to fill two of the world’s greatest needs.

That's one (il)logical leap into the future.

Electrolysis in Context

Given that last vision, it's best to put the electrolysis of water to make hydrogen into the broader context of the prospects for alternative energy. Consider the following diagram:



Moving to hydrogen as an end-use fuel presents many challenges, and the cost and efficiency of electrolysis are rather minor in the larger scope. Shifting from concentrated and easily transportable fuel sources (oil converted to gasoline/diesel) to diffuse sources (solar/wind/biomass) converted to a somewhat less concentrated and much less transportable fuel (hydrogen) will result in energy inefficiencies that cannot be overcome (entropy problem). In addition, substantial changes in infrastructure are needed, and in the context of higher energy costs in the near term, making these changes will be difficult. (See the Hirsch Report for a sobering assessment.) Both an articulation and an assessment of the real challenges are somehow absent in the excitement generated by the Nocera et. al. report. Hydrogen will have uses, particularly in energy storage, but solving a few problems (when they are actually solved) will not painlessly transition us to a new energy future.

Summary

1. Despite the hype, it doesn't appear that Nocera et. al. have made any significant advances in water electrolysis.
2. Even if the researchers drove the cost of the oxygen-evolving anode to zero and its efficiency close to 100%, we are still only marginally closer to being able to produce significant quantities of hydrogen from solar energy.
3. Want to invest in cobalt futures? Too late.