Which Way to the Hydrogen Highway?

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It may be the fuel of the future, but it’s a challenge to store and costly to generate.

Imagine most cars in the nation running on an energy source that’s carbon-free, produced entirely in the U.S. and as abundant as water. You wouldn’t be the first to have this vision. The dream of a hydrogen-based economy has been around as long as concerns about oil imports and global warming. And at least one technology that’s crucial to this dream, the hydrogen fuel cell, is already in use. So why isn’t America on
the hydrogen highway now?

The answer, as with so many other energy issues, is a matter of technology, economics and consumer preferences. Hydrogen is abundant, but it is costly to extract in environmentally sustainable ways (most of it now is produced from fossil fuels). It can be used?and is being used?to power vehicles ranging from spacecraft to buses. But the current method of storing it, in bulky tanks, rules it out for the typical passenger car.

Chris Van de Walle, a materials professor at UCSB, breaks down the hydrogen engineering task into three issues. One of these, the conversion of hydrogen into useful energy, has been in engineers? sights the longest. The technology of fuel cells, which produce electricity from the combining of hydrogen and oxygen to form water, is more than a century old and is ?very well developed.? Van de Walle says the other two issues, generation and storage, ?are still very much in the research stage.? It?s not that producing and storing hydrogen is difficult. The challenge is to do so in ways that make environmental and economic sense for large-scale consumer markets, such as the car-owning public.

Storage and generation are both targets of research at UCSB. Van de Walle?s group focuses on storage, particularly on finding lightweight materials that can hold and dispense hydrogen efficiently. Another group of researchers, including Professor Umesh Mishra in Electrical and Computer Engineering and professors Steven DenBaars and Shuji Nakamura in Materials, are experimenting with a new method to extract hydrogen directly from solar cells in water.

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The extraction experiments use semiconductor technology similar to that of blue or white light-emitting diodes (LEDs). Researchers have found that gallium nitride, which produces the light in the LEDs, can be used in combination with the element indium to separate hydrogen and oxygen in water when exposed to sunlight. The process essentially combines photovoltaics (the production of electricity from light) and electrolysis (the separation of hydrogen and oxygen using an electric current in water). The difference is that a separate power source, such as an external solar cell, is not needed. Everything happens in the gallium indium nitride semiconductor.

The gallium nitride technique was first discovered by a Japanese scientist, Kazuhiro Ohkawa, who works with Nakamura. Mishra says UCSB researchers are now working to develop electrode designs and grow materials that can produce hydrogen more efficiently than the existing technology of electrolysis powered by separate solar cells. Mishra says they are ?just starting work and the results so far are much worse than
electrolysis at the moment. But the new technology, if honed to high efficiency, is potentially a big leap forward for the hydrogen economy. Van de Walle says, ?Everyone here is excited about this and wants to push the research further.? "At the current state of knowledge, storing lots of hydrogen and storing it in a way you can easily get it out is really difficult,? Van de Walle says.

Van de Walle has found that magnesium is able to bind to not one, but to two hydrogen atoms.

Mishra says gallium nitride hydrogen extraction has the advantage of simplicity in structure and manufacturing. ?You don?t need any metals to collect the electrons,? he says. ?You don?t have to fabricate anything. Basically what you do is just grow the material and you?re done.? He also notes that success here would also move photovoltaic technology forward: ?If we make this work, we can also make a good gallium nitride solar cell.? On the storage side, the engineering problem is basically that of packing sufficient energy into a small enough space without adding too much weight. Most hydrogen-powered vehicles today use compressed hydrogen stored in large tanks. This works for buses ? it?s widely used in Germany, for instance ? but Van de Walle says ?it takes up a heck of a lot of space.? There?s also a problem of leakage. Loading hydrogen is a more complicated operation than filling a gas tank. Van de Walle thinks auto manufacturers feeling pressure to get hydrogen cars on the road are likely to use tanks in the early models, but he and other engineers have a different and more efficient storage technology in mind for the longer run.

Their focus is on substances that hold hydrogen like a sponge, with the hydrogen atoms bonded weakly to the crystal structure of the host material so that they can be released
with a small amount of heat. Plenty of metals are known to do this. Palladium, for instance, can absorb 900 times its volume in hydrogen at room temperature. For every atom, the metal holds one hydrogen atom when the two come together as palladium hydride. But each palladium atom is 100 times heavier than a hydrogen atom, so the weight-percent storage efficiency of palladium hydride is no more than 1%. Even if this metal were more abundant and less costly, it would not work as a substitute for today’s gas tank. The amount of it needed to store hydrogen for a 300-mile driving range would be far too heavy. Researchers are aiming to produce materials that can hold at least 6% of their weight in hydrogen.

Getting the H2 out of H2O

Scientists have long known that water can be split into molecular hydrogen (H2) and oxygen (O2) by passing a current through the water between two plates (electrodes). Hydrogen collects at the cathode, the negatively-charged electrode (where electrons enter the water), and oxygen collects at the positively charged anode. The method being investigated at UCSB by Umesh Mishra and others also uses electric current to extract hydrogen, but without the need for an external electrical source.

In the UCSB experiments, a semiconductor made from gallium nitride (GaN) with indium (In) added is immersed in water and exposed to sunlight. Like a solar cell, the semiconductor reacts to the light by creating a flow of negatively charged electrons with positively-charged spaces (called “electron holes”) that the electrons leave behind. Without water around them, the electrons would flow toward the holes, generating electrical current. Immersed in water, they bind to positively-charged hydrogen atoms, forming H2 molecules that bubble to the surface and can be collected there. The holes bind to negatively-charged oxygen atoms, forming O2 molecules.

At first glance, 6% doesn’t seem such a hard target to reach. Many materials with hydrogen-holding ability are much lighter than palladium. Magnesium is four times
lighter, and each of its atoms binds not just to one but to two hydrogen atoms. So by weight, it’s eight times more efficient than palladium. That sounds very exciting, but there are lots of other criteria to be satisfied, says Van de Walle. A crucial requirement is easy extraction of hydrogen at low temperature. Magnesium hydride needs to be heated to 300°C (572°F) to release its hydrogen, burning up a lot of energy in the process. At the current state of knowledge, he concludes, storing lots of hydrogen and storing it in a way you can easily get it out is really difficult.

Van de Walle and his collaborators tackle this problem with computational experiments. Instead of producing and testing actual materials, they perform quantum-mechanical calculations to find which materials might hold the most hydrogen per weight with just the right amount of bonding strength. A key quantity is the formation enthalpy, the difference between the energy of a material in combination with hydrogen (the hydride compound) and the energy of the same material and the hydrogen when the hydrogen is removed. Palladium hydride is lower in energy than hydrogen and palladium separately, but not much lower. So its formation enthalpy is small, and its hydrogen atoms are not too tightly bound.

Van de Walle’s group has now taken the calculations to a higher level of complexity, investigating how bonding strength changes as hydrogen is gradually drawn out of a hydride compound as it would be in a real-world hydrogen car. Calculations for sodium alanate, a promising storage material, show that when hydrogen atoms diffuse through the material they carry an electrical charge. No one had seen this before, Van de Walle says. Everybody was implicitly assuming that these hydrogen atoms were neutral.

The upshot of this discovery is that these charges make a big difference in how storage materials release hydrogen, and a big difference in how the materials respond to the presence of impurities. Van de Walle has calculated, for instance, that a small amount of titanium added to sodium alanate has a huge impact on the release of hydrogen, lowering the needed temperature from over 200°C to 100°C, the boiling point of water. We have an explanation for why adding titanium is a good thing, he says. Now that we know what the mechanism is, we can look for other impurities that might be able to do a better job than titanium.

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