The thermodynamics of the hydrogen economy

At some point very soon, we are going to need to move to a method of powering our world that does not involve burning the reduced carbon under the ground and simply releasing it into the atmosphere. We need to generate some kind of cycle. Now that cycle can be a carbon cycle (e.g., photosynthesis) or something else, but almost certainly it will be a redox cycle, with renewable energy (e.g., solar, wind) or at least carbon neutral energy (nuclear) powering the process. Energetically and kinetically, what is involved in making this work?

This is a redox process. That means we need an electron source and an electron sink that can be cycled back and forth. We are going to have to use power to reduce something and then that something (fuel) will be oxidized to power our cars and such. There really is no choice, I suspect, about one end (one half reaction) of the process. We will have to cycle between water and oxygen:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23V$

This is because oxygen and water are everywhere so we don't have to carry them around with us. That is very handy and cheap. This reaction also generates A LOT of energy.

There are many more options for the other half reaction. We need to reduce something using the electrons from water to make a fuel that can then be burned with oxygen, regenerating water again. We could use reduced carbon for this (methanol for example) or sugar (that is what biology uses) and reduced carbon may well be the best way to go. It is not yet clear. Back to that later, but another very simple choice is hydrogen:

$4H^+ + 4e^- \rightarrow 2H_2 \qquad E^0 = 0V$ (by definition)

Add these two reactions together (reverse the bottom one) and you get

$O_2 + 2H_2 \rightarrow 2H_2O \qquad E^0 = 1.23V$

That corresponds to a free energy of about 475 kJ/mole (calculated for a 4 electron process-try this and see if you get the same answer). There is enough energy in 2 moles (that's 4 grams) of hydrogen to send a 80 kg person almost half a mile straight up into the atmosphere (try this as well, such problems might appear on the test). Sounds pretty good.

Of course it takes just as much energy to make it as it you can get from it, but in principle that is fine. You hook your solar panel or wind turbine or nuclear power plant up to an electrolysis chamber, make the hydrogen, pump it into your car and off you go.

You may have noticed, however that this is not what we do. We pump fossil fuel out of the ground, burn it and release the CO_2 into the atmosphere. Why? Because there are some very serious problems with this scheme that impact its economic feasibility and its safety/practicality.

First, electrolysis is not very efficient. The big problem is on the oxygen electrode. As you can see from reversing the first reaction above, splitting water and stealing its electrons is a four electron process. This is going to generate some very unstable intermediates. That means that the activation energy for this reaction is very high. In practice, this means that we have to run the reaction at an elevated temperature and it uses a much higher potential than the thermodynamically required 1.23V. At 1.23V it works, but it goes really slowly, even at high temperature. We normally run it at almost twice this voltage to get the desired reaction rate (we have to be practical – we need a lot of hydrogen to run our economy and we need to produce it rapidly). Since the power used in a reaction is just the current times the voltage, if you have to increase the voltage by a factor of two, you have wasted half the power as heat. You can get some of this back by powering a heat engine with it, but that is not very efficient either.

Is there a solution? Yes, just look to Nature. Plants run this half reaction (that is where the oxygen we breathe comes from). They do it without much of any activation energy at all. They have a marvelous catalyst which is called, in typical scientific fashion, the oxygen evolving complex. So, we know such a catalyst can be made, but so far we have not pulled it off (at least in a stable, practical form), though many people have tried and continue to do so.

The other half reaction also has an activation energy. Here again, Nature has an enzymatic solution, but again we lag behind in building practical, robust versions of such catalysts for our own commercial use.

Hydrogen is not very dense. One of the wonderful things about gasoline is its energy density. The energy density of isooctane (one component of gasoline) is about 33000 kJ per liter (I just looked that up in a book). One liter is about 6 moles of isooctane. Of course under normal pressures and temperatures, hydrogen is a gas and only contains about 13 kJ per liter of energy. One mole of hydrogen gives nearly 238 kJ/mole according to the calculation we did above, while isooctane is provides around 5500 kJ/mole from the numbers given above (do you understand where these numbers are coming from? Could you generate them on an exam given the numbers above?). Of course, a mole of hydrogen only weighs two grams while a mole of isooctane weighs about 111 grams, so in fact on a per gram basis, hydrogen is much better (about 50 kJ/gram for isooctane and 120 kJ/gram for hydrogen). But a gram of hydrogen takes up a lot of room, unless you cool it and condense it.

So what would it take to compress hydrogen all the way to the point where it had the same energy density as isooctane? From the numbers above, I calculate that we need to have about 140 moles of hydrogen compressed into a liter in order to have the same energy density as (33000kJ/liter /238 kJ/mol). This is a problem, since liquid hydrogen has a density of only about 70 moles per liter, so in principle, we will never get hydrogen up to better than about half the energy density of gasoline. There is an even worse problem here.   We need to contain it. The pressures and temperatures involved are huge. The worse case scenario would be to treat it as an ideal gas and compress it 70 moles to 1 liter. If I did this reversibly, starting with 70 moles of hydrogen at room temperature and pressure (about 1700 liters – you should be able to calculate that from PV=nRT) and ending at 1 liter (1700 atms) it would take about 1280 kJ or about 18 kJ/mole used in the compression ($w = -nRT \ln(V_f/V_i)$). It is presumably not that bad as we will get some interaction between hydrogen molecules at high pressure making them easier to compress. The big problem is that the tank we need to contain this in is probably a lot heavier than the hydrogen. Remember, we have to be able to contain this stuff in the tank during a high speed collision (if we want to use it for automobile travel, that is).

People are working on materials that bind up hydrogen so that it forms a liquid or solid at more reasonable pressures (and thus is not as hard to contain), but progress in this area is slow. Right now we waste about half the energy making the hydrogen (if you make it from renewable resources, that is) and we have to make very expensive and heavy tanks to transport it in. Particularly if hydrogen is going to take the place of gasoline in cars, these problems are going to have to get solved.