

Energy technology: Hydrogen quick and clean

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Systems for producing pure hydrogen for fuel cells from methanol run into problems with energy efficiency and short lifetimes. Unless, that is, you combine the right catalyst and the right purification membrane.

While the power demands of portable electronic gadgets – laptops, mobile telephones, iPods and the like – have exploded in the past few years, the storage capacity of the batteries used to power them has not kept pace. In a worldwide push to find alternative power sources, systems based on fuel-cell technologies, with their potentially much higher energy-storage densities, have been receiving considerable attention.

So far, however, that attention has not translated into practical systems. Writing in *Advanced Materials*, Benjamin Wilhite and colleagues¹ report a substantial advance towards that goal. They have developed a catalytic system that allows them to produce pure hydrogen, the basic power source of proton-exchange membrane fuel cells, from methanol at a much higher rate per unit volume than has been achieved before.

In the way they work, fuel cells are much like batteries: they use electrochemical reactions to produce electricity. First, a reaction on an anode coated with a catalyst such as platinum produces electrons. These electrons pass through a circuit, delivering power to a device. They then return to the fuel cell, where they are collected by a second reaction on a catalytic cathode, generally producing water as a waste product. For example, in proton-exchange membrane fuel cells, the

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reactions are $2\text{H}_2 + 4\text{H}^+ + 4\text{e}^-$ (anode) and $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (cathode).

Because of its lightness and the large amounts of heat energy it releases on combustion, hydrogen can supply much more energy per unit weight than can the lithium batteries conventionally used in laptops and similar electronic devices. Thus hydrogen fuel cells are an attractive proposition to supplement, or even replace, such batteries.

The catch is that it is difficult to find a way to store or produce enough pure hydrogen in the laptop. One could imagine putting a tank of very pure hydrogen in the laptop and refilling it at filling stations, rather like those proposed for cars. But in practice, the explosive nature of hydrogen rules that possibility out. One could not, for example, countenance taking a laptop with a hydrogen cylinder on to an aeroplane. In fact, of possible fuels, so far only formic acid and methanol have been approved by the dangerous-goods committee of the International Civil Aviation Organization for use in aeroplanes and storage in luggage². Small butane cylinders are allowed in the passenger compartment, but not in the hold. Hydrogen cylinders, metal hydrides and borohydrides are currently banned. A hydrogen-powered laptop, therefore, would need to generate its hydrogen internally from methanol or formic acid.

There have been many suggestions^{3,4,5} for how to generate hydrogen from methanol, which has the chemical formula CH_3OH . A common approach is to perform 'steam reforming' via the reaction $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$. The catch here is that a side-reaction yields carbon monoxide: $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$. Carbon monoxide is highly poisonous for the catalysts used in fuel cells: if as much as one part per million of carbon monoxide is mixed in with the hydrogen that reaches the anode, this will, over a few weeks of continuous operation, poison all the active sites on the catalyst and effectively kill the fuel cell. A trace presence of carbon dioxide can also be fatal, as this produces carbon monoxide through the reverse water-gas shift reaction: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$.

In the past, differentially permeable membranes have been used to purify hydrogen of such trace gases, with limited success. Membranes made from the lattice-structured mineral zeolite or mesoporous silica allow too much carbon monoxide through for practical use. Palladium and palladium-silver membranes produce pure hydrogen, but so far have been found to degrade quickly in the presence of carbon monoxide and methanol. A further problem is that it takes considerable energy to push hydrogen through a membrane that is of the thickness required for mechanical stability. Thus, no one has yet been able to produce hydrogen of sufficient purity at a high enough rate to power a laptop for an extended period.

Fig. 1

Figure 1 | All in one.

Wilhite et al.¹ found that, by building a composite structure that combined a hydrogen-permeable palladium-silver membrane with a catalyst for the hydrogen-producing methanol-oxidation reaction $2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2$ (Fig. 1), they could prevent the membrane from degrading. Protective layers are often used⁶ in commercial applications to protect sensitive materials from corrosive gases by forming an impenetrable barrier in front of them. But such an impermeable system is of no use in a fuel-cell system, where hydrogen must pass through both the protective layer and the membrane to reach the anode of the fuel cell.

But Wilhite and colleagues use a permeable catalytic layer that assists in the oxidation of most carbon monoxide and methanol, rendering them harmless before they reach the membrane, while letting hydrogen past. Any traces of the corrosive gases that reach the membrane are small enough to be oxidized there before they can do any damage, leaving the hydrogen to filter through. Thus, hydrogen can be both produced and purified in one stage. That is important for portable devices, but this all-in-one approach to corrosion protection could also be useful in many other chemically reacting systems.

As with most scientific endeavour, progress comes in small steps. Wilhite et al. have demonstrated¹ that their membrane is stable for days, as opposed to a few hours with an unprotected membrane. But a laptop's power supply needs to be stable for years. More thermal management is needed, too: the temperature in the authors' system is about 400 °C, higher than you would be comfortable with in your lap or pocket. Nevertheless, this step represents a significant advance towards practical portable fuel-cell power systems.

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