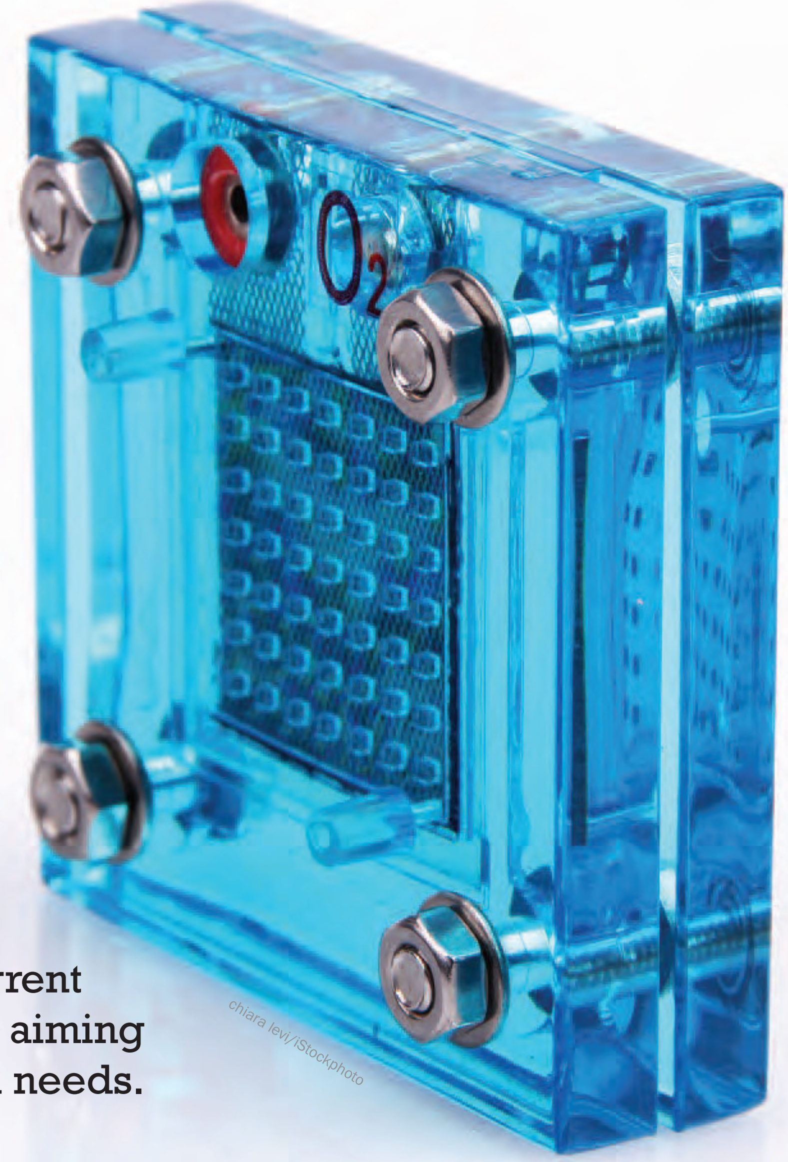
From thin air

Seeking the next source of transport energy



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Dave Sammut explores current and emerging technologies aiming to meet future transport fuel needs.

More than ever before, society is turning to the scientific community to offer the solutions by which people can have their cake and eat it too. We're being asked to bring forth viable alternatives to a fossil fuel economy, without compromising on standards of living or consumer culture.

Like my hero, Scotty of the Starship Enterprise, we might grumble that 'ya cannae change the laws of physics', but the fact is that every day science *is* making strides towards the better future demanded of us.

The current problem is the issue of energy for transport. Starting in the 1800s, but most particularly over the past century, cheap, readily available transport has transformed society across the globe. This has become a critical vulnerability because, even with a ten-year horizon, there is no transformative technology to step into the looming fossil fuel shortfall.

Transport, effectively, is an issue of chemical energy density. The internal combustion engine converts chemical energy to thermal energy, then in turn to mechanical energy. Ignoring the losses to extract the fossils fuels from the earth and transport them to the point of use, the efficiency of the conversion is only around 20%. So the energy contained per unit mass of fuel is critical to the performance.

There are really only two alternatives to fossil fuels for transport, again both relying on chemical energy density: batteries and fuel cells. In both cases, chemical energy is converted to electrical energy, and then in turn to mechanical energy. The efficiency of these engines is much higher (potentially >80%), but to date the issue has been in achieving practical energy density at practical prices.

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Unlike fossil fuels, the key difference with both batteries and fuel cells is that the chemical energy might – in theory at least – be restored in a cyclic process, albeit one that in turn requires further energy, most commonly from non-renewable sources.

Fundamentally, batteries and fuel cells are very similar. The difference is that in batteries the chemical mass is contained and static, while in fuel cells the reagent mass can flow through the cell, and may be partially sourced from atmospheric gases (just as in combustion engines).

And just like the myriad battery technologies, there are quite a few fuel cell technologies. I'm going to discuss just three, due to their comparatively advanced development.

First, there's the alkaline fuel cell. This is pretty much the original practical version, developed for the US space program in the 1950s. It uses hydrogen and oxygen, with a potassium hydroxide electrolyte. In simple terms, hydrogen gas is oxidised with hydroxide at the anode to form water, while oxygen is reduced at the cathode to re-form hydroxide.

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ (anode)
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (cathode)
$2H_2 + O_2 \rightarrow 2H_2O$ (net reaction)

The chemistry is virtually ideal in concept. It is based on readily available, abundant elements, with completely safe wastes. With the exception of the oxygen cylinder explosion on the famous Apollo 13 mission, it was particularly ideal for space missions because both the reagent gases and wastes had dual purposes in the vessel's environmental systems.

However, alkali fuel cells aren't practical for terrestrial use because carbon dioxide can't be effectively removed from either of the reagent gases. Neither hydrogen nor oxygen can be readily produced at sufficient purity.

This problem is avoided in the fuel cell being most commonly considered for transport purposes: the proton exchange membrane fuel cell (PEMFC). Here, the KOH electrolyte is replaced with a 'polymer electrolyte' that will only permit the passage of the protons.

Hydrogen is catalytically split into protons and electrons at the cathode. These protons can permeate the membrane to the cathode (to react with oxygen), while the electrons are forced to 'make the loop' through the electrical circuit.

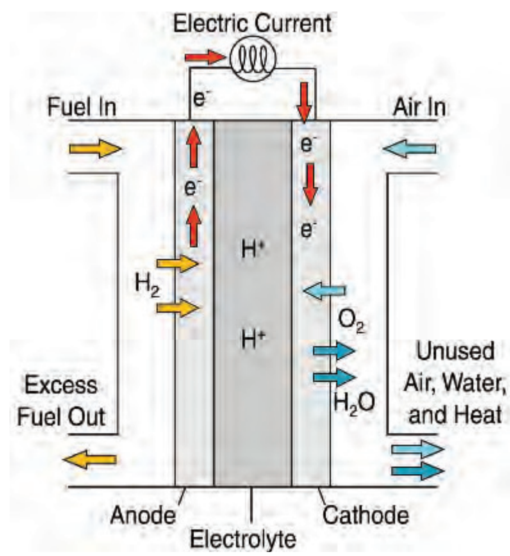
$2H_2 \rightarrow 4H^+ + 4e^-$ (cathode)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (anode)
$2H_2 + O_2 \rightarrow 2H_2O$ (net reaction)

Each couple generates approximately 0.7 V of potential, requiring stacked cells. These operate at comparatively low temperatures (typically 60–80°C), and can potentially be developed into engines that are compact and light enough to be used for transport purposes.

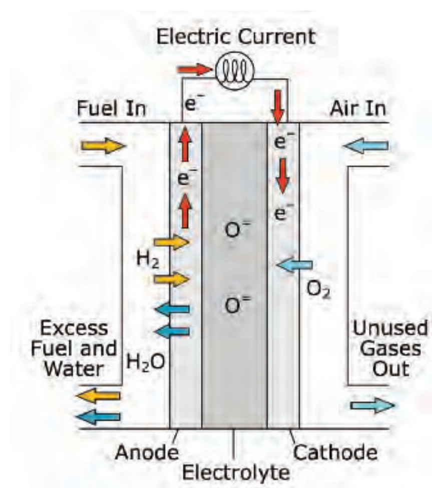
By contrast, solid oxide fuel cells (SOFCs) use a solid electrolyte, most commonly yttria-stabilised zirconia (YSZ). Oxygen is oxidised at the anode to anions, which are transported through the electrolyte to the cathode:

$O_2 + 4e^- \rightarrow 2O^{2-}$ (anode)
$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$ (cathode)
$2H_2 + O_2 \rightarrow 2H_2O$ (net reaction)

SOFCs require high operating temperatures (typically 800–1000°C) and can use a variety of fuels. They offer significant potential for large-scale continuous base-load operation, possibly as an adjunct to industrial wind and solar power generation.



A proton exchange membrane fuel cell.
Mattuci [CC0], via Wikimedia Commons



A solid oxide fuel cell.
Sakurambo, via Wikimedia Commons

Both PEMFCs and SOFCs face major technological challenges in materials and cost, but both appear to offer significant potential benefits as part of the solution to the looming energy crisis. So how close are these fuels cells to commercial application?

In his State of the Nation address in 2003, US President Bush announced a Hydrogen Fuel Initiative, inclusive of a planned US$1.7 billion investment over five years 'to develop hydrogen-powered fuel cells, hydrogen infrastructure and advanced automotive technologies'.

This announcement followed closely on the heels of a report by the US Department of Energy that analysed the state of hydrogen fuel cell technology, and identified six key areas for detailed investigation (including basic research):

- catalysis
- nanostructured materials
- membranes and separations
- characterisation and measurement techniques
- theory, modelling and simulation
- safety and environmental issues.

While considerable advances have been noted in all of these areas in the intervening decade, we have yet to see the fundamental breakthroughs that would bring fuel cell technology to widespread commercial use. And in that same time, considerable advances in battery technology have seen electric vehicles take the lead in the race to market.

At least part of the issue has been politics. Many observers interpreted Bush's Hydrogen Fuel Initiative announcement as a means of staying wedded to traditional fuel paradigms, and history showed that the majority of the money earmarked for fuel cell research was ultimately diverted into research into incremental improvements in conventional combustion engine technologies. *Issues in Science and Technology* notes that of US$1.6 billion spent under the related programs in the decade to 2012, only US$500 million was spent on fuel cell research, and often not on critically needed basic research (bit.ly/2eT9PvW).

For many observers, electric vehicle and fuel cell technologies do not seem at all incompatible. There is a range of hybrid vehicles on the market that use combustion engines to top up electrical storage, and a similar suggestion has been very sensibly made to use fuel cells in place of the combustion engine to do exactly the same.

While inventor Elon Musk has been famously dismissive of fuel cell technology – at one point referring to it as 'incredibly silly' – his primary objections appear to be hydrogen storage and infrastructure, which are widely accepted as two of the major drawbacks to commercial PEMFC take-up.

In this respect, recent news from RACI Fellow Professor Richard O'Hair might represent another incremental step. In a recent article in *Nature Communications* (doi: 10.1038/ncomms11746), O'Hair and colleagues used silver catalysts to produce hydrogen from formic acid at PEMFC operating temperatures (70°C), producing CO_2 as waste.

The ability to store hydrogen and the infrastructure for refuelling are both important commercial considerations for PEMFC technology. Transferring hydrogen under pressure requires dedicated infrastructure, and is potentially too slow for general transport purposes. O'Hair's approach would have the advantage of potentially being able to use existing technology and infrastructure to transport, store and deliver the formic acid. Vehicles could potentially continue to use existing fuel tank technology, and the fuel would be potentially both safer and more palatable to the public.

However, the large-scale production of formic acid would sacrifice many of the greenhouse gas advantages of hydrogen fuel cells. In the associated press release, O'Hair noted that

While the safety of hydrogen has been given significant consideration, as well as the need to change public perception of a gas that has been demonised since the *Hindenburg*, there appears to have been little subsequent research on environmental issues.

'… there are still many barriers to overcome, such as the production of carbon dioxide and how it could potentially be recycled to regenerate formic acid.'

Another issue that has been raised is the potential environmental issues of a hydrogen economy. While the safety of hydrogen has been given significant consideration, as well as the need to change public perception of a gas that has been demonised since the *Hindenburg*, there appears to have been little subsequent research on environmental issues. One obvious question would be what effect, if any, would the inevitable leakages of hydrogen gas have on the atmosphere, and particularly the ozone layer?

While PEMFC technology currently requires considerable platinum for the catalyst (which, in turn, contributes to the current high cost), progress is being made in both reduction (to date, from about 80 grams to about 30 grams) (*Nature*, doi: 10.1038/

4641262a) and substitution – such as with gold nanoparticles (bit.ly/2fASHyL) – another aspect of science that is advancing rapidly.

Faced with a seemingly insuperable challenge, scientists across the globe are incrementally advancing towards solutions. The large manufacturers are backing these efforts. Toyota and Honda both have significant vested interests in hybrid and electric vehicle technologies, yet both also have fuel cell concept vehicles and significant R&D programs in the field.

I don't know how the technologies will shape up over the decade and more to come, but I predict that we won't see just one become reality. Material science, electrochemistry, nanotechnology and much more will combine and diverge, and multiple solutions will emerge to address the problems that we see.

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SOFC multifuel automotive system under development

Nissan's SOFC system test bench. The system generates electricity from ethanol and air to charge the battery.

Nissan Motor Co. Ltd. is researching and developing an SOFC-powered system that runs on bio-ethanol electric power. The new system – a world first for automotive use – features an e-Bio Fuel-Cell with an SOFC power generator. The SOFC fuel cell uses the reaction of multiple fuels, including ethanol and natural gas, with oxygen to produce electricity with high efficiency.

The e-Bio Fuel Cell generates electricity through the SOFC (power generator) from bio-ethanol stored in the vehicle. The fuel cell uses hydrogen transformed from fuel via a reformer and atmospheric oxygen, with the subsequent electrochemical reaction producing electricity to power the vehicle.

The fuel cell affords greater power efficiency to give the vehicle cruising ranges similar to petrol-powered cars (more than 600 kilometres). The car has distinct electric-drive features, including silent drive, linear start-up and brisk acceleration.

Nissan Motor Corporation