CSEM's
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Building better fuel cells

As our world chokes on its own carbon emissions, the hunt is on for alternative energy sources that are reliable, cost-effective and carbon free. Fuel cells have long been held up as one potential energy solution but to date they are simply too expensive to compete. However, that might be about to change as researchers at ANU apply plasma processing to improve the performance and cost of the key components that drive fuel cells.

Imagine a black box in which hydrogen gas is fed in at one end and electricity comes out the other. There's no noise, no dirty exhaust fumes, just clean electricity and a little water vapour at the flick of a switch. Sounds like magic but this black box has a name – it's called a fuel cell. It's not a new invention but, thanks to recent advances in the plasma processing of materials at ANU, the age of the fuel cell may soon be opening. In the not too distant future you may be plugging into a fuel cell to power your car, motor bike and even your home.

Most people associate fuel cells with space exploration as they first gained prominence in the 1960s and 70s when they were used to provide electricity to astronauts in space. However, fuel cells actually originated a couple of centuries earlier. In the 1800s William Grove reasoned that if you could use electricity to split water into hydrogen and oxygen (a process called electrolysis) then the opposite would also be true. That is, by combining hydrogen and oxygen you should be able to produce electricity. After a bit of experimentation he built a device called a gas battery that did just that. It was later renamed the fuel cell, but the invention remained an academic curiosity because it was much more convenient (and cheaper) to generate energy by burning fossil fuels.

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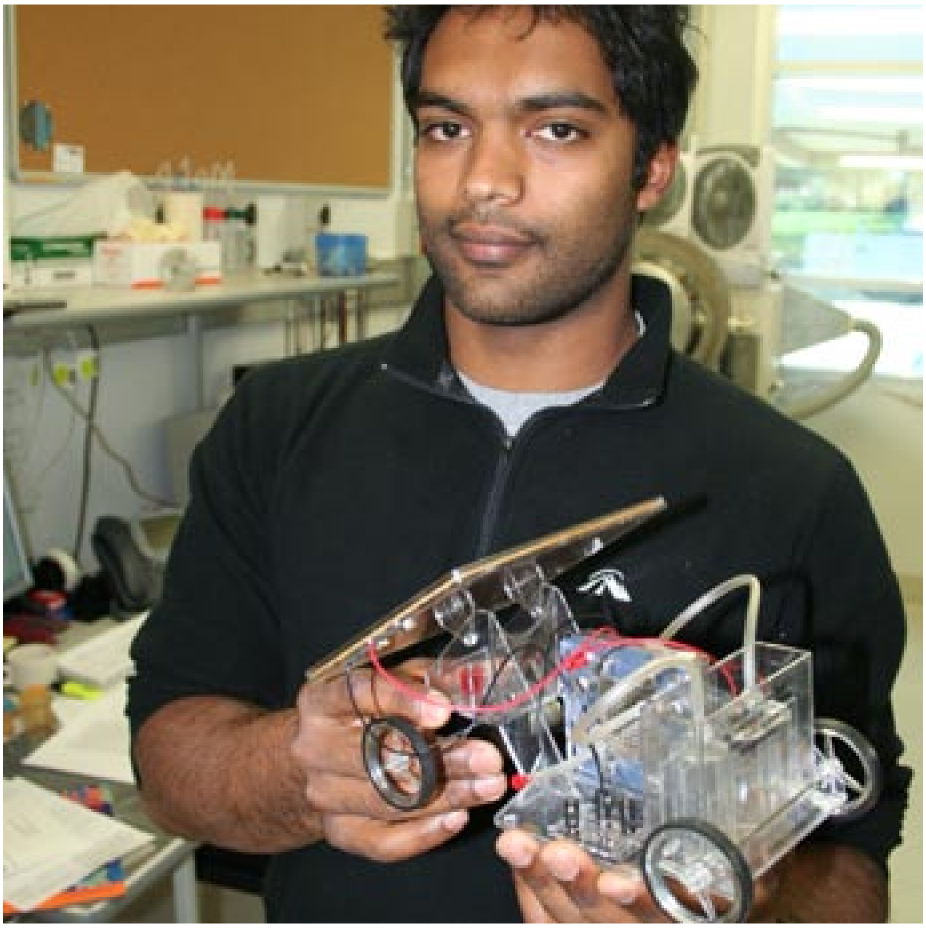

Devin Ramdutt from SP3 holds a model car powered by a fuel cell. The front panel (tilted away from us) is a solar cell that produces electricity. The electricity is used to split water into hydrogen and oxygen gas which is stored in the clear compartments at the back of the vehicle. At the flick of a switch, these gases can be fed into the fuel cell in the centre of the vehicle, which again produces electricity that drives the vehicle forward. The solar cell only generates energy when the sun shines. By storing that energy as hydrogen you can use energy whenever you like - and no carbon is released in the process.

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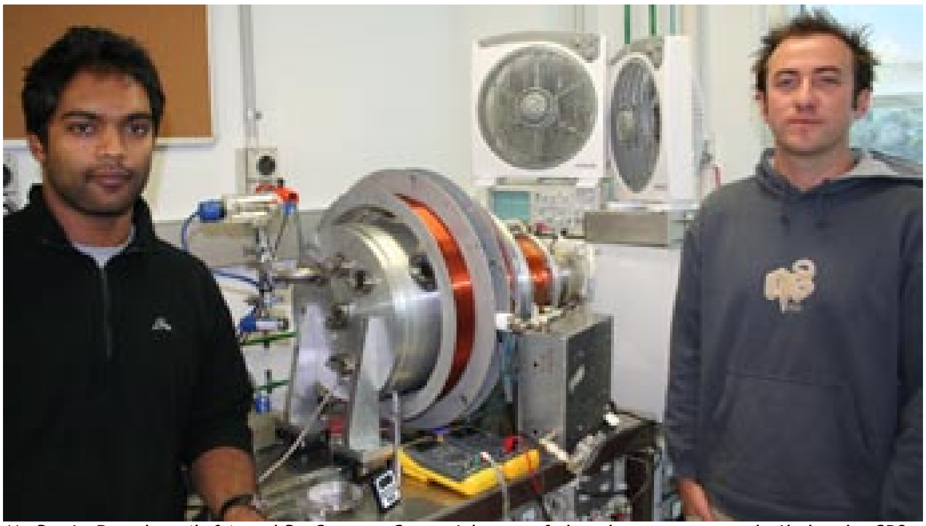


Mr Devin Ramdutt (left) and Dr Cormac Corr with one of the plasma reactors built by the SP3 group. The reactor produces a plasma that is used to coat electrodes used in fuel cells with platinum. Mr Ramdutt is a PhD student at SP3 working on improving the plasma processing of fuel cell electrodes.

The rise of the modern fuel cell

Then, in the 1960s, NASA needed a method for providing electricity in space craft. Combusting fuel was impractical (as well as too dangerous), batteries were too heavy and photovoltaics were too bulky at that time. So, they developed fuel cells that could use liquid hydrogen and oxygen to produce electricity (and, of course, liquid hydrogen and oxygen are the rocket fuel that propel the space craft). Besides providing a reliable source of electricity, the byproduct of the process was water which the astronauts could drink.

"Modern fuel cells were developed for the space race by NASA but then they were forgotten for 20-30 years because they weren't cost effective against other forms of energy," says Dr Cormac Corr, a plasma physicist based at the Australian National University. "Now there's a big drive for clean energy from environmental friendly sources and the fuel cell is seen as an ideal way of producing it. The challenge, however, is to cost effectively produce superior materials to build fuel cells. Our research is on how plasma processing can be used for this and our results so far are very promising."

Dr Cormac Corr is an ARC Postdoctoral Fellow working with the Space Plasma, Power and Propulsion (SP3) group (RSPSE) headed by Professor Rod Boswell. The Fuel Cell group is headed by Dr Christine Charles and includes Mr Amael Caillard and Mr Devin Ramdutt.

"The SP3 group has been at the forefront of plasma physics and materials processing for more than two decades," says Professor Boswell. "We've played a significant role in the semiconductor industry in developing new high-density plasma sources and their application to innovative thin film deposition. In our work on fuel cells SP3 is bringing the 1970s microelectronic revolution to the hydrogen economy."

Fuel cell basics

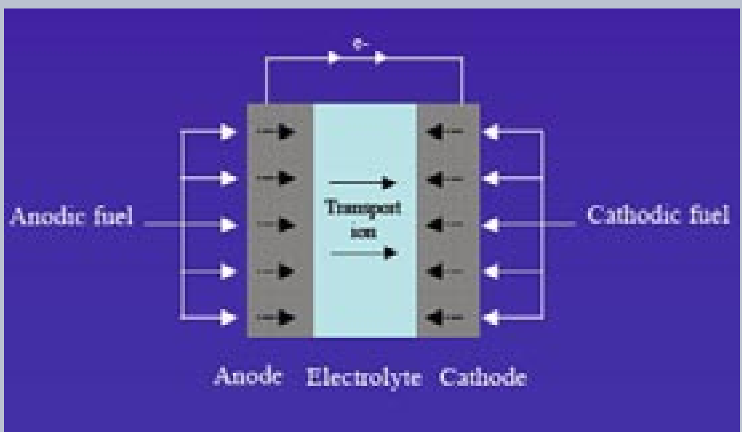
To understand the connection between plasma processing, fuel cells and the hydrogen economy, and why this is potentially a very big business, we need to go back to fuel cell basics.

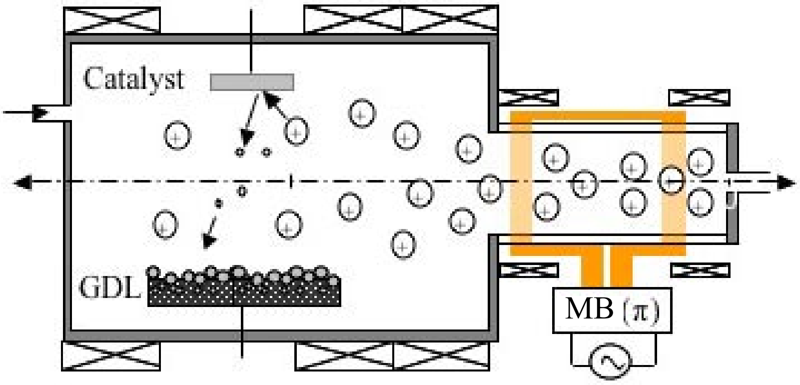
Hydrogen fuel cells consist of a two electrodes, an anode and a cathode, connected by a proton conductor in the form of a polymer membrane. Hydrogen gas is fed to the anode which most commonly is a piece of carbon cloth covered in a layer of platinum. The platinum acts as a catalyst causing the hydrogen gas to break down into protons and electrons. The protons transfer over to the cathode via a connecting polymer membrane. At the cathode, which is also a piece of carbon covered in platinum, the protons combine with oxygen gas to form water and heat. The electrons back at the anode also want to cross over but they can't pass through the polymer membrane. They travel via an external circuit which provides the electricity.

An operational fuel cell unit consists of many stacks of these cells and their use is no longer restricted to space craft. Indeed, you can buy them off-the-shelf from many companies. For example, one commercially available unit takes up the space of a half metre cube, costs around 10 thousand (Australian) dollars and produces 1 kilo Watt of power. All you have to do is connect up a bottle of hydrogen. The oxygen is extracted from the surrounding air and water produced at the cathode is absorbed into the surrounding air as water vapour. You can take it with you anywhere you like and it'll silently

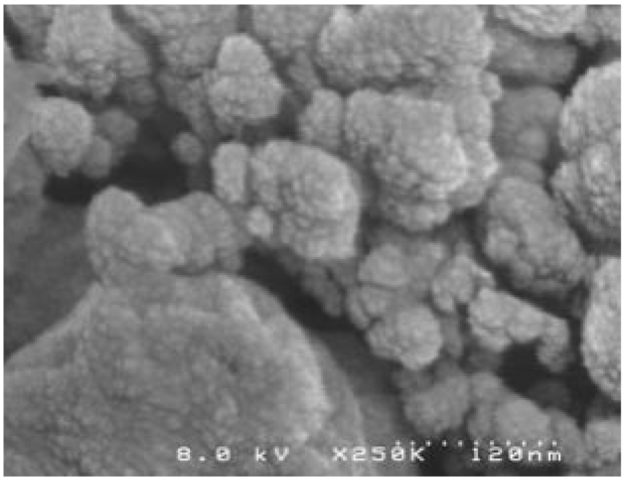
What is a fuel cell

A fuel cell is an electrochemical engine (no moving parts) that converts the chemical energy of a fuel, such as hydrogen, and an oxidant, such as oxygen, directly to electricity with water vapour and heat being the only by-products released. The principal components of a fuel cell are the catalytically activated electrodes for the fuel (anode) and the oxidant (cathode) and an electrolyte to conduct ions between the two electrodes.





A diagram of the plasma reactor known as 'piglet' (pictured between Mr Ramdutt and Dr Corr). A plasma of charge argon atoms is generated (on the right). This bombards a target of the platinum catalyst. Dislodged platinum atoms form a tailor-made deposition layer on the carbon electrode.



A scanning electron micrograph of the deposited layer of platinum. With plasma technology it's possible to reduce the thickness of the catalytic layer (hence keeping the platinum use to a minimum) while increasing the effective surface area for maximising catalytic activity.

produce electricity to run a dozen standard (incandescent) light globes or a few computers. What's more, the generation of this energy has released no carbon emissions into the atmosphere.

Of course, 10 thousand dollars is a fairly expensive outlay compared to simply connecting up to the power grid (or cranking up a diesel generator) however the fuel cell doesn't require the combustion of fossil fuels as does most of our standard forms of power generation. Imagine the benefit if the cost of the fuel cell could be dramatically reduced?

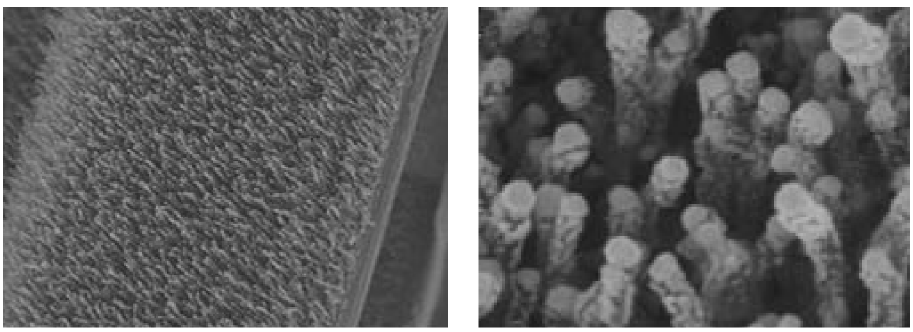
Better electrodes

"Platinum plays a crucial role in fuel cells," says Dr Cormac Corr. "Platinum is also what makes fuel cells very expensive. The standard technique for creating layers of platinum on the anode and cathode involves wet chemistry. Unfortunately, while this works it doesn't offer much in the way of control.

"Instead of wet chemistry we use a dry process involving plasma-sputter deposition. A plasma is an ionised gas, a gas of charged atoms. We bombard a platinum target with this plasma, usually a gas of charged argon ions. This dislodges platinum atoms which are then redeposited onto the electrode surface, usually a clothe of carbon fibres.

"Plasma processing offers incredible control over the layer being deposited. By varying over time the amount of plasma we use and the energy of that plasma use we can control the deposition rate and the thickness of the deposited layer. Compared with standard wet techniques we can produce layers that use significantly less platinum but which possess a greater surface area and so are more effective at breaking down hydrogen gas at the anode. The cumulative effect is a much cheaper and more efficient fuel cell.

"And now we're also looking at incorporating carbon nanofibres onto the surface of the electrode as one way of improving even further the surface area and efficiency of the carbon cathode. The platinum is then deposited onto this weave of carbon nanofibres."



SP3 is now examining if carbon nanofibres deposited using plasma processing onto the carbon electrodes (pictured on the left) with platinum nanoparticles mixed in (pictured on the right) will increase the surface area and efficiency of fuel cells.

Better membranes

"In addition to improving the efficiency and cost effectiveness of the electrodes we're also investigating ways of applying plasma processing to improve the polymer membranes that connect the electrodes," says Dr Corr. "The polymer membrane is used to transfer protons from the anode to the cathode.

"Currently, most fuel cell membranes operate with commercially available polymer electrolytes. The most common is product called Nafion and it was developed by DuPont over 50 years ago. Although Nafion is a good proton-exchange membrane with fairly high chemical and thermal stabilities, it has some weaknesses such as a high membrane thickness, weak mechanical properties and high methanol cross-over which causes a reduction of efficiency.

"Currently we're setting up a processing system to synthesize the polymer membranes using plasma enhanced chemical vapour deposition. Previously, these plasma polymers have been shown to be thin, dense and highly cross-linked; exactly what you're looking for. They have a very good chemical and thermal stability and have a low permeability to organic liquids such as methanol. However, a disadvantage of these polymer membranes is that the proton conductivity is lower than that of Nafion and this is something we're looking to improve. We're confident we can overcome this."

The researchers at SP3 are working

Continued on page 6

Nanotubes in space

Building multifunctional walls for spacecraft

If humans are ever to travel through deep space they'll need protection against the hazards of space radiation associated with solar flares and cosmic rays. To protect their precious human cargo, spacecraft will need special shields incorporating materials consisting of the lighter elements such as hydrogen, boron, and lithium. However, additional shielding comes at a significant price in the form of extra weight, more fuel and increased flight costs.

In order to maintain low weight while increasing safety, reliability, and functionality, many scientists are suggesting that the body of future spacecraft will need to simultaneously serve multiple functions. In other words, the body will need to provide structural integrity, effective shielding, energy storage and carry an array of sensors.

What material or mix of materials could serve so many different functions? A blend of carbon nanotubes is one future material under consideration because of it's light weight, excellent mechanical properties and it's capacity to store energy. Now researchers from the Department of Electronic Materials Engineering are proposing a variation on this theme – isotopically enriched boron nitride nanotubes.

"Isotopically enriched boron nitride nanotubes have many similar properties to carbon nanotubes," says Dr Ying Chen. "However, they also offer some important advantages as they have better radiation-shielding properties and stronger resistance to oxidation.

"By isotopically enriched we mean the boron nitride has a higher

Image NASA

concentration of the isotope boron 10. Normally boron nitride is 80% or more composed of boron 11.

"The isotope boron 10 is an efficient neutron absorber with a very high neutron-capture cross section. Consequently it's widely used as the inner shielding layer inside nuclear reactors.

"We have now demonstrated for the first time that it's possible to produce large quantities of high quality isotopically enriched boron nitride nanotubes using a ball-milling/annealing process."

Dr Chen and colleagues Mrs Jun Yu, Professor Rob Elliman and Dr Mladen Petravic has been refining the ball milling process for preparing boron nitride (BN) nanotubes for many years. It involves grinding down a powder of boron into nanoparticles in a ball mill in which steel balls tumble against each other for hundreds of hours. The fine boron material is then heated in an atmosphere of nitrogen (in the form of ammonia, NH_3).

"To produce isotopically enhanced BN nanotubes (referred to as ^{10}BN nanotubes) you begin by grinding down a powder of the isotope boron 10 (often noted as ^{10}B). Our analysis of the final product shows we can produce BN nanotubes with up to 96% boron 10.

"We found we could produce ^{10}BN nanotubes with different diameters (up to 100 nm) and lengths (up to 100 lm) by varying the growth conditions and atmosphere. For example, nanotubes with a larger diameter (greater than 50 nm) can be produced by annealing at a higher temperature of 1200 °C for a longer period of time.

"The control over the nitriding reaction between the ^{10}B and the NH3 gas is crucial for the formation of thin, cylindrical ^{10}BN nanotubes that contain fewer defects and exhibit stronger mechanical properties than other nanostructures. To avoid the formation of large crystals or thick, bamboo-type nanostructures through fast 3D crystalline growth, the nitriding reactions are carried out at lower temperatures. This can be achieved because of the ball-milling of the boron 10 powders."

"The ^{10}BN nanotubes are lightweight, with a density of 1.85 g cm–3 and have an excellent resistance to oxidation. They exhibit a high neutron-absorption cross section because of the high content of ^{10}B, as recently determined at ANSTO. The successful production of high yield ^{10}BN nanotubes using a ball-milling/annealing process makes ^{10}BN nanotube samples available in large quantities for space-radiation tests."

And there are many other potential applications for ^{10}BN nanotubes back here on Earth. For example, there is a lot of talk about developing fusion energy to feed an energy-hungry world. One of the major challenges in developing fusion energy on a commercial basis is coming up with materials that can provide shielding from the high neutron fluxes produced by the fusion process. What will be needed is a strong, light weight, cost effective radiation shielding. 10BN nanotubes may just fit the bill. The results have been published in Advanced Materials (18, 2006, 2157).

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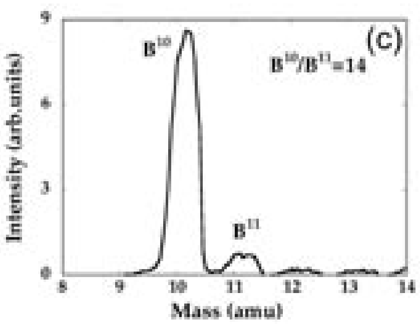
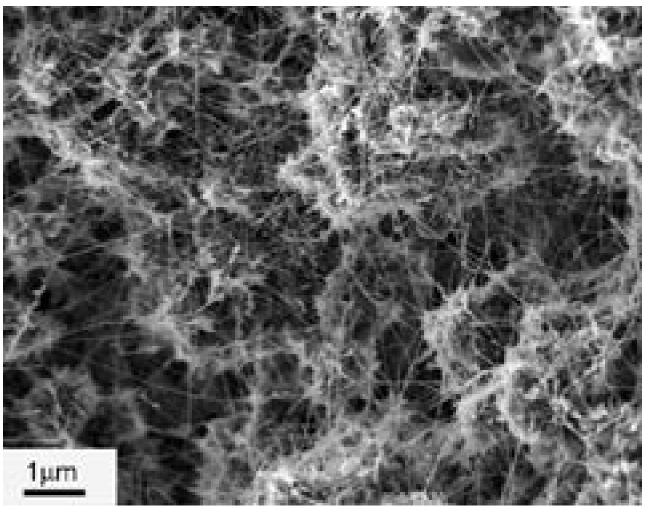


Secondary ion mass spectrometry of a sample of ^{10}BN nanotube sample, showing the dominant presence of ^{10}B over ^{11}B.



A scanning electron microscope image of the boron nitride nanotube (enriched with boron 10). They were produced by grinding a powder of the isotope boron 10 in a ball mill for many hours and then heating the crushed powder to around 1100 °C for 6 hours in an atmosphere of ammonia.

Complexity, materials & snakes in the grass

Every Aussie knows how much fun it is watching a visitor receive a safety briefing on the dangers of the Australian bush. You know the blurb – "be careful of leeches and ticks, and be warned that most Australian snakes are deadly, as are a couple of our common spider species". As the list grows, so does the visitors' discomfort. Of course, most of us never see any of these creatures but it's a completely sensible thing to warn visitors that they're around.

And so it was at the opening of *Materials and Complexity IV* down at the ANU Kioloa field station. Dr Christoph Arns, coordinator of this year's event, warmly welcomed everyone and then warned about the standard cast of dangers lurking out in the bush. And, because Kioloa is right on the beach, he also had to warn people about the unpatrolled beaches, dangerous surf, stinging blue bottles and potentially deadly rips.

Networking on the soccer field

Having got the formalities out of the way, Professor Jean-Marc Di Meglio from Paris University opened up proceedings with an eloquent discussion on non-Euclidean foams. He began with the observation that a foam of ordinary bubbles when confined between two panes of glass forms an array of hexagonal cells, a pattern that is very common in nature. To illustrate this point he showed an image of snake scales with the repeating pattern of hexagonal cells.

Professor Jean-Marc Di Meglio then observed that Dr Arn's friendly warning on dangerous animals was worth listening to, and revealed that the snake he'd used in the example was actually a two metre red belly black that he'd photographed the day before at the entrance of the very lecture theatre in which everyone was seated. While most of the people gathered found this enormously amusing, a few of the assembled scientists began looking outside a bit nervously.

"If we know there are deadly snakes around these buildings shouldn't we do something and remove them?" remarked one researcher of Italian origins. Dr Tim Senden responded by pointing out there are no records of anyone dying from the bite of a red belly black, and that you're most likely to get bitten when attempting to handle them, so they're best left alone. He also pointed out that everyone should also be careful about funnel webs known to be outside the other side of the building.

Dr Ray Roberts opens up the first session on the second day of the workshop.

And so began three days of formal presentations, informal chats, networking and fun involving a truly mind-boggling diversity of topics revolving around the broad themes of complexity and materials. To give you a flavour of the variety, presentations included: topological optimisation, wave attenuation in partially saturated rock, Devonian fish, measurement of photon pressure, resilience, leaf genesis, imaging oil-bearing rock, the wettability of tree capillaries, and the degradation of profitability of firms.

Materials and Complexity is a workshop held at the Kioloa campus towards the end of each year. It's organised by the Department of Applied Maths (RSPSE) and serves as a means of discussing topics of mutual interest in a relaxed setting far removed from the hustle and bustle of ANU. Guests from other departments, institutions and countries are always invited to come along and play a large part in enlivening the event.

Materials and Complexity IV was staged with the support of three ARC research networks (the Australian Research Network for Advanced Materials, the Nanotechnology Network and the Complex Open Systems Research Network) and the Cooperative Research Centre for Functional Communication Surfaces.

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(Above) Dr Rosemary White reads up on deadly spiders at Materials & Complexity IV. (Below) The red belly black in question.

Building better fuel cells

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with scientists at the University of Montpellier on improving the polymer membrane and with Dr Pascal Brault at the University of Orleans on improving the catalyst utilisation on the electrode via plasma sputter deposition. They are also involved with researchers at the University of Queensland and CSIRO working on aspects of hydrogen storage and generation. Fuel cells use hydrogen as their primary sources of energy and the widespread uptake of fuel cell technology will require the continued development of the hydrogen economy. However, given the current focus on alternative energy generation and growing concerns about climate change it appears certain that the hydrogen economy is destined to boom.

Devin Ramdutt holds a carbon electrode of a fuel cell that he has coated with platinum using plasma deposition. Besides running several plasma processing reactors, SP3 also maintains a fuel cell test station (behind Mr Ramdutt) to characterise the results of different treatments.

A prototype car powered by fuel cells.

Towards a hydrogen economy

As discussed at the beginning of this story, it's possible to produce hydrogen by passing electricity through water. In a sense you're storing the energy in the form of hydrogen. Fuel cells offer one of the safest and most reliable way of unlocking that energy. Therefore, many people believe that fuel cells are the key to making the hydrogen economy work. And it could be that the plasma processing techniques being developed at ANU are the key to developing user-friendly, cost-effective fuel cells.

Consider the car model pictured on page 1. It's a toy that demonstrates a few basic scientific principles. Solar energy can be converted to electrical energy which can be used to split water into hydrogen and oxygen. With a flick of a switch, these gases can be fed into the fuel cell to again generate electrical energy.

However, this toy is also a potential signpost to the future. With so much effort going into improving solar, wind and tidal energy the challenge is not so much how to harvest the energy but how to store, transport and use that energy when it's needed. In the past it's been the expense of the fuel cell that has limited the process but it could be that these limitations are about to be lifted.

So, when Professor Boswell says SP3 is "bringing the 1970s microelectronic revolution to the hydrogen economy", it might be that he's suggesting that this technology has the potential to transform the world (just as the microelectronic revolution has).

And if you wanted one small example of how fuel cells will achieve this, consider the example of motor scooters. Companies in China are currently discussing with SP3 the possibility of developing a fuel cell to power Chinese motor scooters. Imagine the impact on China's bustling cities if its citizens were able to get around on silent, cheap, emission-free electric scooters. Then imagine the size of the potential market. With examples like this you begin to see a glimmer of what the future might hold in a world dominated by a hydrogen economy driven by fuel cells.

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http://prl.anu.edu.au/SP3/research/fuelcell

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