The Ceramic Fuel Cells Limited research facility at Churchill, Victoria.

Clean powerplay

Graeme O'Neill traces the evolution of solid-oxide fuel cells, a technology destined to generate more for Australia than clean electricity and heat.

Australia has precious few export industries in the billion-dollar league, and most trace their roots to the agricultural and mining sectors: wool, wheat, coal, gold, iron and natural gas. New billion-dollar industries have proved elusive this century, and none have come from the manufacturing sector.

But a CSIRO research project that began three decades ago in a modest attempt to extend the life of a most prosaic object – a slurry pump nozzle – has spawned an infant technology with genuine prospects of maturing into a billion-dollar manufacturing industry early next century.

In August this year, Melbourne company Ceramic Fuel Cells Limited announced it had successfully tested a prototype five-kilowatt (kW) solid-oxide fuel cell stack module. These devices can generate electricity directly from fuels such as hydrogen and natural gas, and combine unprecedented efficiency with low emissions of carbon dioxide and other greenhouse gases.

Scaled up, a one-cubic-metre solid-oxide fuel cell stack could generate a megawatt of electrical energy, enough to power a medium-sized city office tower, with the heat from its exhaust providing the building's hot water and space heating needs.

At the heart of the prototype fuel cell is a remarkable ceramic 'alloy', similar to transformation-toughened, partially stabilised zirconia (PSZ). The alloy made scientific history in 1975 when researchers at CSIRO's former Division of Tribophysics developed a super-tough, non-brittle ceramic that could substitute for metals in hot, corrosive or abrasive environments. The world's premier science journal, *Nature*, hailed the advance with the headline: 'A ceramic steel?!'.

As well as being the world's toughest ceramic, the alloy had another important characteristic. Some PSZ alloys, when heated could become superior solid-state electrolyte, able to transmit charged oxygen atoms (oxygen ions) rapidly. When a thin membrane of the material is sandwiched between air and fuel electrodes, a voltage difference between the faces of the membrane causes an electrical current to flow.

The electrolytic and physical properties of PSZs make them ideal components of solid electrolyte (or solid-oxide) fuel cells (see story below). Their advent in the 1970s sparked international interest in fuel cells, and in engineering ceramics. A race to develop the first commercial solid-oxide fuel cells began between America's Westinghouse Corporation and the multinationals Siemens of Germany and Mitsubishi in Japan.

Australia joins the race

Observing these developments in 1989, Division of Materials, Science and Technology chief, Dr Mike Murray, and two senior ceramics researchers, Dr Sukhvinder Badwal and Dr Karl Foger, developed a bold idea. Why not compete with the giants by developing Australia's own solid-oxide fuel cell around PSZ and a number of other CSIRO technologies, and capture a slice of what promised to become a multi-billion dollar international industry?

Ceramic Fuel Cells Limited was incorporated in 1992, and with the backing of some of Australia's biggest companies and major energy utilities, has remained at the forefront of solid-oxide fuel cell research. CSIRO is the major shareholder and has contributed to the company's success by providing essential infrastructure and through the secondment of key research and development staff.

An early obstacle for the company was to fabricate the ceramic alloy in flawless, flat, ultra-thin sheets. Warping during firing would impair electrical contact with the interconnects that sandwich the ceramic sheet.

Evidence of this challenge lies in the components displayed in the office of research director, Sukhvinder Badwal. Visitors are handed a flexible, glossy cream square of a material with the look and feel of white polyethylene plastic. It is actually 'green', unfired PSZ, mixed with organic binding agents and plasticisers so it can be rolled into sheets and cut into squares before firing. The organic materials evaporate during firing at high temperatures, leaving a thin, impermeable crystalline PSZ membrane of exceptional purity.

Hot ions lead the charge

EVEN though the PSZ membrane of a fuel cell is airtight, at high temperatures (800-1000°C) charged oxygen atoms (ions) can be induced to flow across it. In other words, it becomes a solid-state electrolyte. Dr Sukhvinder Badwal says the secret lies in PSZ's formulation, and an unusual crystal structure that develops during firing.

At an atomic level, pure zirconium oxide forms a regular crystalline array in which oxygen atoms bond with metallic zirconium atoms at a 2:1 ratio, in a configuration resulting in alternating layers of oxygen and zirconium. The zirconium oxide is doped with small amounts of several rare-earth elements, notably yttrium, which substitute for some of the zirconium atoms in the lattice.

Yttrium's lower valency is satisfied by just 1.5 atoms, which leaves gaps in the crystal lattice. At high temperature, charged oxygen ions from an adjacent site will 'jump' into a gap, which in turn leaves a vacancy at the site it has just left. Another oxygen ion can jump into this vacancy, and the resulting chain-reaction moves oxygen ions from one side of the membrane to the other.

Badwal says the process of ionic conduction is somewhat analagous to a car changing lanes on a multi-lane freeway. The car slots into a vacancy in an adjacent lane, then waits for another gap before changing lanes again, until eventually it ends up on the opposite side of the freeway.

In a ceramic electrolyte, the driving force behind the movement of oxygen ions is a gradient in oxygen concentration across the membrane, created as methane and oxygen combine in a combustion reaction on the fuel side. Air flowing over the opposite face provides a pool of molecular oxygen (O_2). Oxygen molecules contact the surface of the membrane and dissociate into two charged atoms of oxygen (O_2) As these ions move through the membrane, their charge causes an electrical current to flow.

The layers of ceramic electrolytes alternate with interconnects: sheets of stainless steel about 3 mm thick. Each interconnect makes broad contact with an anode on the fuel face of one PSZ membrane, and with a cathode on the air face of another, collecting the current produced as oxygen ions flowing through the electrolyte.

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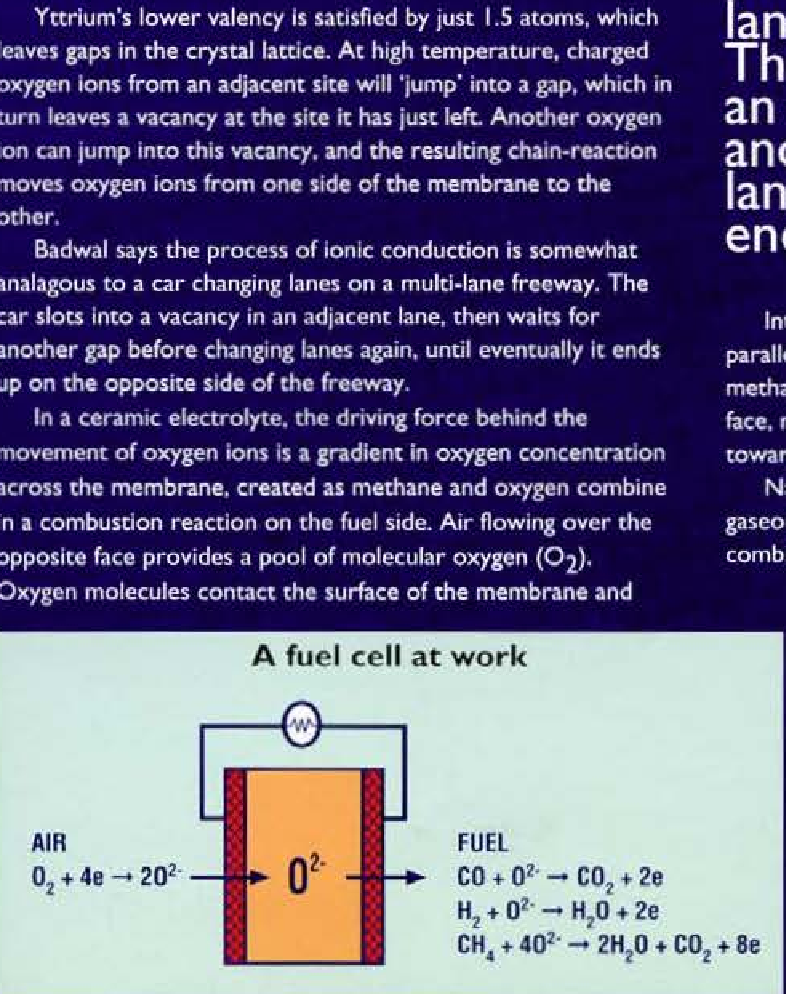
Interconnects have a second, vital function. Through shallow, parallel channels in each surface, they simultaneously supply methane to the fuel face of the electrolyte, and oxygen to the air face, maintaining a an oxygen gradient that keeps ions flowing towards the fuel face.

Natural gas consists of about 92% methane and 8% of other gaseous hydrocarbon molecules. When methane (CH_4) combines with oxygen during combustion, the by-products are water vapour (H_2O) and carbon dioxide (CO_2).

The final exhaust stream consists mainly of steam and carbon dioxide and little else. The low operating temperature of 800°C in the the stack minimises reactions between atmospheric nitrogen and oxygen, so nitrogen oxide emissions are low. The carbon dioxide emissions are also substantially lower than those from a conventional coal or oil-fired power station. Since both carbon dioxide and nitrogen oxides are greenhouse gases, when solid-oxide fuel cells come into widespread use next century, they will produce much 'cleaner' energy than conventional power stations and help nations limit greenhouse-gas emissions.

A fuel cell at work



All for the want of a durable nozzle

IN THE late 1960s, a paper mill at Burnie, Tasmania, approached Bob Stringer of CSIRO's former Division of Tribophysics in Melbourne to see if he could develop a more durable nozzle for slurry pipes carrying hot, corrosive alkaline fluids.

Metal nozzles corroded rapidly, so the division's scientists experimented with a coarse, refractory ceramic, zirconia, or zirconium oxide. Research continued at a relatively low level until the early 1970s, when serendipity intervened.

A foreman of a metal-extrusion company brought a zirconia die into the division, one of a batch of imported dies. This die had resisted wear and cracking far longer than all its batchmates in the face of the extreme heat, abrasion and thermal shock involved in forcing red hot metal billets through a small aperture. Could the division make other dies like it?

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Brittleness is the weakness of virtually all ceramics. Anybody who has observed the crazing patterns in a thick china mug has seen the aftermath of the stresses imposed by differential thermal expansion. The exposed surface heats rapidly and expands, while deeper material remains cool. Fine porcelain cups tend not to crack because they are of higher quality and free of defects. Nevertheless, they shatter even in small impacts. Generally, ceramics resist corrosion well and have high melting points, but they are not attractive for engineering applications because, unlike metals, they lack the toughness to absorb impacts.

In 1975, Hannink, Ron Garvie, and Dr Terry Pascoe of CSIRO announced they had developed the world's first tough engineering ceramic: a fine-grained material produced by mixing zirconia with other oxides to produce a ceramic alloy. They demonstrated the exceptional toughness of the new ceramic, called transformation-toughened, partially stabilised zirconia, by showing that it would not crack or chip even under a vigorous sledgehammer blow.

In 1977, CSIRO signed an agreement with a Melbourne company, Nilsen Sintered Products, to commercialise the new technology. CSIRO's Advanced Materials Laboratory, headed by Dr Mike Murray, continued to work closely with Nilsen to improve PSZ. Bob Hughan of CSIRO and Mike Marmach of Nilsen collaborated at this time, with considerable inputs from others in their respective teams to scale-up the PSZ process for commercialisation. Once yields of 90% and better were obtained, the company established a niche market for PSZ nozzles, dies and bearings in the minerals, oil and chemicals industries.

Murray recalls sending a batch of custom-made PSZ bearings to Mt Isa Mines in Queensland, to be used in a bag house dust conveyor system whose abrasive environment was renowned for chewing through cast iron bearings in mere weeks.

'The maintenance workers were skeptical because cast-iron bearings are cheap, but they decided to install a trial batch of our PSZ bearings,' Dr Murray says. 'A few months later, the mining company flew us up to Mt Isa and feted us like heroes.

'When we asked why they had changed their minds, the maintenance workers told us that replacing the bearings was one of the dirtiest jobs at the mine, and the PSZ bearings lasted so long that the task was all but eliminated.

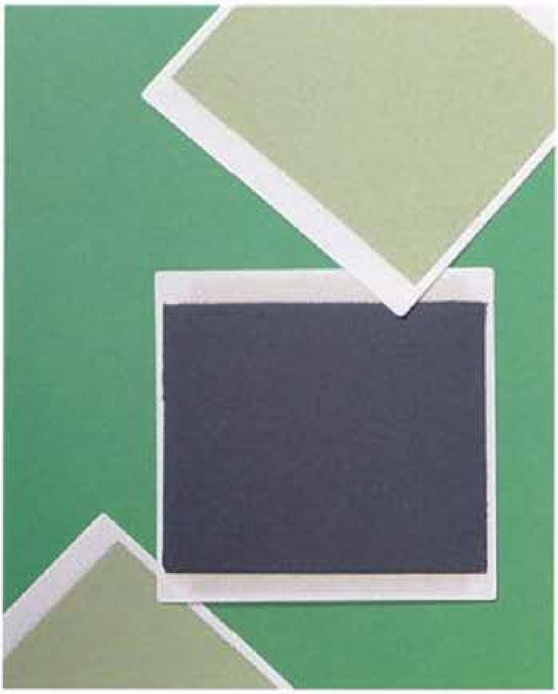
The big United States diesel engine manufacturer Cummins also experimented with PSZ as cylinder liners to improve the efficiency of its engines, but the dream of an all-ceramic engine that would run without cooling or lubrication is still unrealisable.

In 1984, Nilsen was joined by CRA in a joint venture. Four years later the rights to PSZ were sold to ICI Australia. ICI is in the process of selling off its interest to Carpenter Technologies of the US. It is expected that the new company will continue and expand its Australian production capacity.

In 1984, Murray and his colleagues sought support for a major research project to develop a solid-oxide fuel cell based on PSZ's properties as an electrolyte. Initially the response was cool, but in 1989 the recently privatised NSW company Pacific Power was enthusiastic. BHP's Dr John Parrott and the Strategic Research Foundation, (set up by the Victorian Government to promote the commercialisation of research) also took an interest and invited Victoria's State Electricity Corporation, the Gas and Fuel Corporation, BHP, and the Commonwealth Government's Energy Research and Development Corporation to form a research consortium with CSIRO. In 1991, together with Pacific Power, the partners launched Ceramic Fuel Cells Limited.

The consortium now includes CSIRO, BHP, the Energy Research and Development Corporation, the Strategic Industry Research Foundation, and five electricity utilities: the Electricity Corporation of New Zealand, the Electricity Trust of South Australia, Pacific Power, Western Power Corporation and South East Queensland Electricity Corporation.

Research and development is carried out at the company's Noble Park premises and a a purpose-built laboratory at Churchill in Victoria's Latrobe Valley, and at two Clayton sites: CSIRO's Division of Manufacturing Science and Technology and BHP's Melbourne Research Laboratories. To June this year, consortium members had invested $32 million in the project.



Complete fuel cells with air (black) and fuel (green) electrodes coated on the electrolyte plate (white).

Fired PSZ is a solid, creamy colour, but the company has succeeded in making membranes just 50 microns thick, (one micron is one thousandth of a millimetre), so thin that they are translucent. Badwal demonstrates this by laying a square of PSZ on a magazine page, and showing that print and photographs are clearly visible through the membrane.

At this exceptional thinness, even PSZ is brittle, but still tough enough to survive what Badwal and his colleagues dubbed the 'Schacht test', named after a former Federal Science Minister, who, when shown one of the sheets, alarmed scientists by flicking it vigorously with a fingernail.

PSZ membranes can flex without shattering, but in fuel cells they are sandwiched between rigid layers of stainless steel (see story on page 25). The main requirement is that they do not shatter when heated from room temperature to 800°C as the stack is fired up. Wafers of PSZ easily resist the relatively balmy 800°C operating environment of the solid-oxide fuel cell stack.

The fuel cell's Achilles heel is the metal interconnect. The researchers experimented with a high-temperature alloy from Austria, consisting of iron, yttrium and chromium. This alloy tolerates temperatures of 1000°C, but is too expensive for mass-produced fuel cells. So Badwal and his colleagues compromised by dropping the stack's operating temperature to 800°C and using relatively cheap stainless steel to connect the individual cells.

The individual ceramic wafers used in the 5 kW prototype are 100 mm square (100 cm^2), but Dr Badwal says commercial stacks may employ membranes up to 150 mm square (225 cm^2). A silk-screen process is used to apply electrodes to the surface of the ceramic – a black electrode on the air side, and a green electrode on the combustion side – which make good electrical contact with the metal interconnects.

Each unit in the stack – a membrane plus its interconnect – is about 3 mm deep, so the 50-unit prototype stack is 15 cm tall. The induction and exhaust manifolding is internal, and designed so that the gas flow enters at the base of the stack and flows upwards, then sideways through the channels in the interconnects.

Optimum air and fuel flow through the interconnect channels was achieved through computer modelling. Because fuel and air never mix inside the stack, (the PSZ membrane only conducts oxygen ions), there is no opportunity for nitrogen and oxygen to react to form environmentally unfriendly nitrogen oxides.

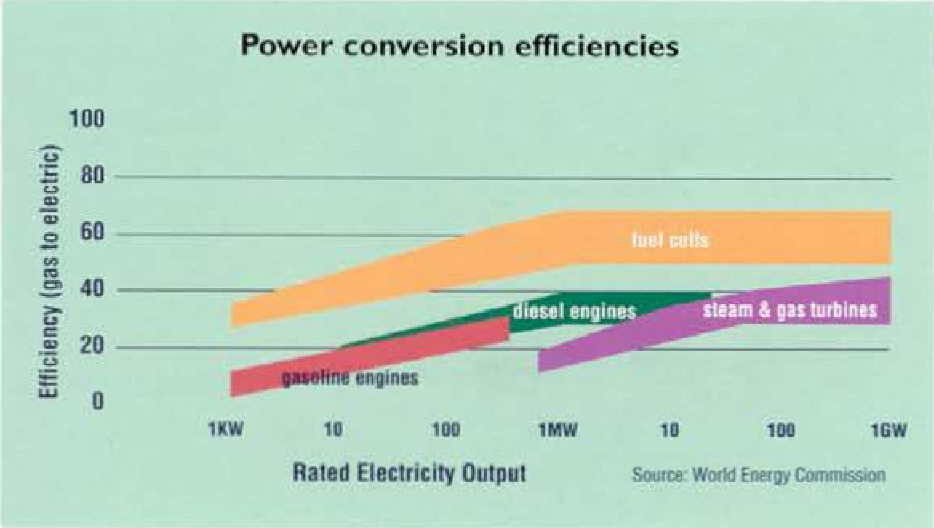
But wait, it's more efficient!

Badwal says generating electricity directly from the combustion of natural gas is exceptionally efficient. The 'first pass' energy yield is equivalent to 60% of the potential chemical energy in methane, making solid-oxide fuel cells much more efficient than diesel engines (less than 40%) and combined cycle and steam turbines (about 50%). But this is just for starters. The 800°C gas from the exhaust can be fed into a turbine to extract even more electrical energy on the second pass. After recycling through the plant, the steam and carbon dioxide that finally emerge from the turbine can be passed through a heat exchanger to extract even more energy for process heat, space-heating and hot water.

An integrated or combined cycle system – a solid oxide fuel cell stack linked to a turbine and heat exchanger – could, in theory, achieve an electric efficiency approaching 70%, more than twice that of a black coal-fired power station.

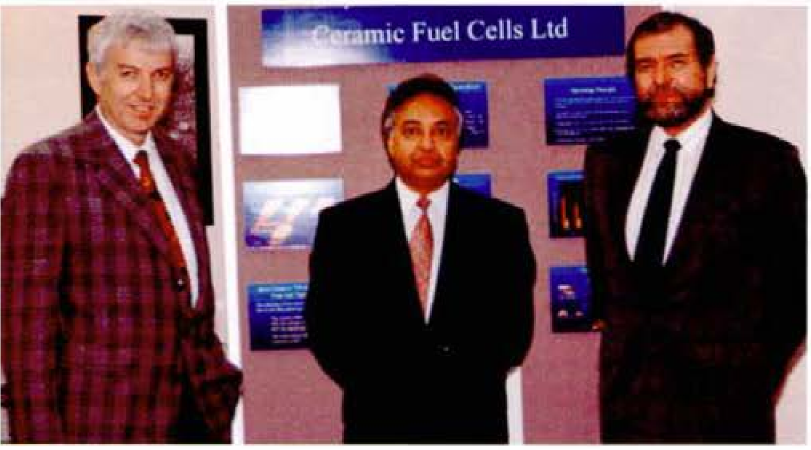
And because solid-oxide fuel cells utilise hydrogen-rich methane fuel, rather than carbon-rich coal or oil, their greenhouse gas emissions will be substantially lower. A comparison of total emissions of pollutants from a fuel-cell stack (sulfur dioxide, nitrogen oxides, hydrocarbons and particulates) relative to conventional power stations shows the enormous environmental benefits in prospect (see diagram on page 28). The emission of carbon dioxide is reduced by a factor of two and other pollutants, such as nitrogen oxide and sulfur dioxide, are reduced to a fraction, compared with conventional coal-fired power plants.

But, as the salesman says, there's more. Because solid oxide fuel cell stacks are compact and self-contained (apart from needing to be connected to a natural gas supply) they can be installed in



Power conversion efficiencies

Source: World Energy Commission



Initiators of Australia's ceramic fuel cell venture: Dr Karl Foger, Dr Sukhvinder Badwal and Dr Mike Murray of CSIRO.

office towers, factories and shopping centres to provide both electricity, space heating and hot water.

Dr Bruce Godfrey, who succeeded Dr John Parrott as managing director of Ceramic Fuel Cells Limited in July, says the system's ability to produce energy – electricity and heat – at the point of consumption, instead of transmitting it from power stations remote from major cities, is 'revolutionary'.

Australia's power stations traditionally have been constructed on or near major coal deposits to reduce the cost of transporting coal (in Victoria's brown coal fields in Gippsland, 60% of the weight of the coal is water). High-tension power lines heat up because of resistance in the metal wires, and lose heat energy to the surrounding atmosphere. Over distances of hundreds of kilometres, losses can run as high as 30%. In-situ solid-oxide fuel cell stacks would avoid these losses.

A vision for 2000

Godfrey, a director of the company since 1992, says its vision is to establish its solid-oxide fuel cell technology globally through strategic alliances that will maximise returns to members of the Australian consortium backing the project.

'We want to build a billion dollar industry out of this technology,' Godfrey says. 'To do that, we will have to establish a major new company and a major new industry in this country: that's the potential.

'We are not going to be able to service all world markets from Australia, so we probably will establish strategic alliances in different regions.

'We know we have a world competitive solid-oxide fuel cell technology, and that we are probably ahead of the competition in certain areas of the technology.'

Godfrey says with the first five-year phase of the research and development project completed in June this year, the next three-and-a-half-year phase, ending in December 2000, will focus on refining and scaling up the technology, proving its reliability and durability in sustained operation, and reducing manufacturing costs.

'Our goal, like that of our competitors, is to demonstrate a 100 kW stack by 2000', he says. 'If we succeed, we will seek to raise funds to establish production facilities, and look to enter the market around 2002.'

Godfrey says the aim will be to develop a stack that can be incorporated into modular systems. First-generation systems will probably be assembled from either 10 kW or 25 kW stacks, with a basic module size of 100 kW. Customers will then scale up in increments of 100 kW, depending on their requirements.

Sukhvinder Badwal's research team has so far met all its research, development and demonstration deadlines on time or well within schedule.

'For four successive years we have brought our project milestones forward, and set even more difficult targets,' Badwal says. 'We have achieved all our milestones under budget, and demonstrating the 5 kw stack was the last milestone in our first phase.

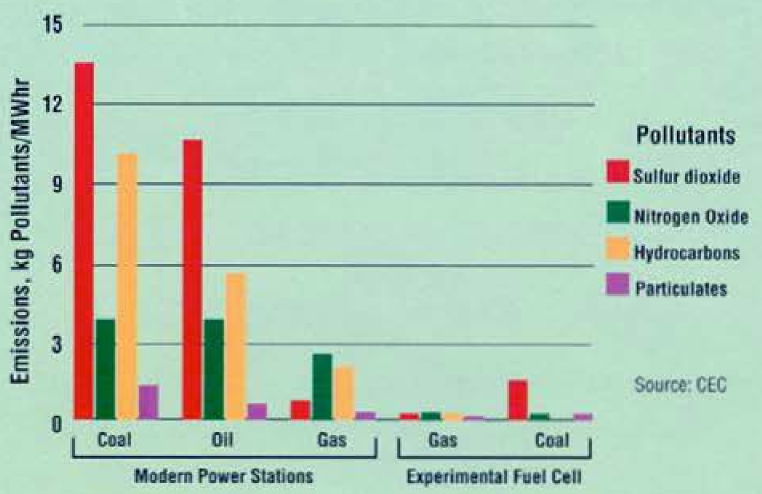
'We have agreed on another set of equally ambitious targets for the second phase. We haven't solved all the technical challenges yet, but then neither has anyone else.'

abstract

Melbourne-based company Ceramic Fuel Cells Limited has successfully tested a prototype five-kilowatt solid-oxide fuel cell stack module. These devices generate electricity directly from fuels such as hydrogen and natural gas, and combine unprecedented efficiency with low emissions of carbon dioxide and other greenhouse gases.

Keywords: Fuel cells; Solid-oxide fuel cells; Ceramic alloys; Power generation; Energy efficiency; Partially stabilised zirconia

Emissions from stationary power sources



Source: CEC