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# Electrochemical power sources: key agents for energy sustainability (Ⅱ)

D. A. J. Rand

(CSIRO Energy Technology, Box 312, Clayton South, Victoria 3169, Australia)

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## 3　Hydrogen distribution and storage

### 3.1　Gaseous and liquid hydrogen

In the gaseous state, the most obvious method for distributing hydrogen would appear to be via pipeline. This has long been the practice in Germany to supply hydrogen for chemical processes. More recently, other networks have been installed in Northern France, the USA, South Korea, and Thailand. The pipelining of hydrogen as a universal energy vector is a more difficult proposition since the distances would be much greater and the allowable costs much less. Apart from the huge capital investment that would be required, there are many technical difficulties, such as (i): materials problems (e.g., blistering, embrittlement and decarburization of metals) may not allow the use of natural-gas facilities; (ii) the small molecular size of hydrogen renders it easily diffusible so that it could escape through existing natural-gas pipes (but mixtures similar to synthesis gas could be used in the interim); (iii) the low volumetric energy density of hydrogen means that, to deliver a given amount of energy, the flow rate must be about three times greater than that for natural gas, and therefore more energy is required to move hydrogen; (iv) over long distances, there will also be a need to re-pressurize regularly, which will cause further loss of energy.

To some degree, pipelines themselves would provide a storage component. Large-scale storage underground in natural or anthropogenic cavities is also a possibility, e.g., in aquifers, limestone caves, salt domes, depleted oil and gas fields, or abandoned mines. Inevitably, local geology is the deciding factor in taking up this storage option.

On a much smaller scale, compressed hydrogen may be stored in pressure vessels. Steel cylinders are used for stationary storage at pressures of up to 80 MPa. For portable and mobile applications, however, cylinder weight and volume must obviously be minimized. There has been some success with the development of lightweight vessels composed of carbon-fibre shells with aluminium liners that can withstand a pressure of 55 MPa and thereby provide a hydrogen storage density of 3 to 4 MJ/dm$^3$. This approaches the 2010 target (5.4 MJ/dm$^3$) set by the US FreedomCAR and Fuel Partnership for fuel-cell vehicles, but is far below the 2015 target (9.7 MJ/dm$^3$). Incidentally, the corresponding gravimetric targets (7.2 MJ/kg and 10.8 MJ/kg) will be even more difficult to reach. In this respect, liquid hydrogen would be more attractive; its density is 850 times greater than that of the gaseous form. Liquid hydrogen is routinely transported by road and by sea, but about 30 % of the energy in the hydrogen is wasted in the liquefaction process, the cryogenic and filling-emptying equipment is both complex and costly, and the boil-off rate is such that the liquid can only be stored for a few days at most. Overall, therefore, this storage option is not practical for most potential applications.

### 3.2　Metal hydrides

Certain metals and alloys can repeatedly absorb and release hydrogen under moderate pressures and temperatures via the formation of hydrides. Heat must be removed during absorption of the hydrogen, but has to be added to effect desorption. This feature provides a safe method of storage, i.e., when the heat source is removed, the hydride ceases to expel hydrogen. The direction of the hydrogen absorption-desorption process is determined by the pressure of the hydrogen gas. If the pressure is above the equilibrium value, then the hydride will be formed. Conversely, below the equilibrium pressure, hydrogen is released and the metal/alloy returns to its original state. The equilibrium pressure depends on temperature; it increases with increasing temperature and vice versa. This relationship is expressed by the van't Hoff equation, i.e.,

$$\ln P = \Delta H/RT - \Delta S/R \qquad (7)$$

where: $P$ is the dissociation pressure; $\Delta H$ is the change in enthalpy; $R$ is the gas constant; $T$ is the absolute temperature; $\Delta S$ is the change in entropy. The value of $\Delta H$ can vary widely from metal/alloy to metal/alloy. By contrast, $\Delta S$ does not vary as much. For a given metal hydride, the van't Hoff plot of $\ln P$ *vs.* $1/T$ is a straight line and provides a useful illustration of the hydrogen absorption-desorption characteristics.

The dissociation pressure curves for a number of metal hydrides are presented in Fig. 12. These plots show that hydrides can be broadly classified into three categories, namely: high-temperature (HT), medium-temperature (MT) and low-temperature (LT) hydrides. The LT category is the most useful in that such hydrides offer hydrogen storage closest to ambient temperature and are therefore convenient for supplying fuel cells. In this case, the

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**作者简介**:

D. A. J. Rand, Chief Research Scientist, CSIRO Energy Technology, Australia.

required enthalpy of hydrogen desorption would be provided by the waste heat from the fuel cell. Unfortunately, however, the maximum gravimetric storage of low-temperature hydrides ( < 150 ℃) is quite low, typically 1 wt. % to 2 wt. %. (Note that wt. % is the hydrogen-to-metal weight ratio, as a percentage, in the hydride and the system weight is not included: 1 wt. % = 1.42 MJ/kg based on the higher heating value for hydrogen.) Moreover, the best HT hydrides (magnesium-based hydrides, such as $Mg_2NiH_4$ at > 300 ℃) offer a maximum storage of only 3.6 wt. % (5.1 MJ/kg). By contrast, hydrides have a relatively good theoretical volumetric performance of 0.1 kg/$dm^3$ (6.7 MJ/$dm^3$). Obviously, the major research challenges are to develop new alloying techniques for LT hydrides that have increased gravimetric density.

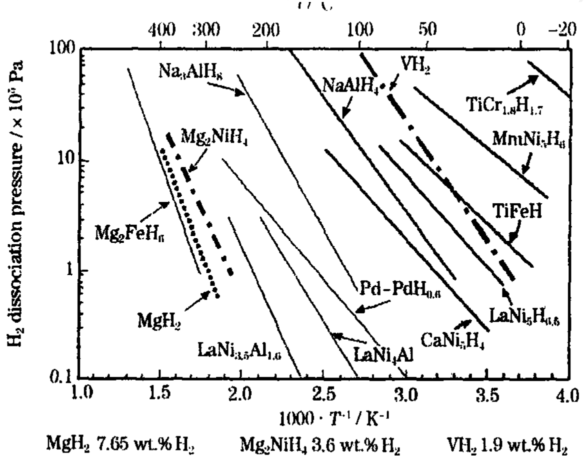

Fig. 12 Dissociation pressures of various metal hydrides

### 3.3 Chemical storage

Hydrogen may also be stored chemically in the form of ionic salts that are composed of sodium, aluminium or boron, and hydrogen —the so-called 'complex hydrides'. The alanates $Na[AlH_4]$ and $Na_3[AlH_6]$ are the preferred reagents. Thermal decomposition of $Na[AlH_4]$ takes place in two steps, i.e.,

$$3Na[AlH_4] \longrightarrow Na_3[AlH_6] + 2Al + 3H_2 \tag{8}$$

$$Na_3[AlH_6] \longrightarrow 3NaH + Al + 3/2H_2 \tag{9}$$

The reactions are reversible only at elevated temperatures and pressures. The first step, at 50～100 ℃, corresponds to the release of 3.7 wt. % hydrogen and the second step, at 130～180 ℃, to a further 1.9 wt. % hydrogen. Research has shown that, in the presence of a titanium catalyst, the temperatures for discharge and recharge of hydrogen may be brought down to acceptable levels. Titanium-catalyzed $Na[AlH_4]$ has thermodynamic properties that are comparable with those of low-temperature hydrides (e.g., $LaNi_5H_6$ and TiFeH). By contrast, $Na_3[AlH_6]$ requires higher temperatures for hydrogen liberation.

Sodium borohydride, $NaBH_4$, is stable up to about 400 ℃ and is therefore not suitable for providing hydrogen through a thermalactivation process. It does release hydrogen, however, on reaction with water, i.e.,

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2 \tag{10}$$

This is an irreversible reaction, but has the advantage that 50 % of the hydrogen comes from the water. In effect, $NaBH_4$ acts as a 'water-splitting' agent. Based on the mass of $NaBH_4$, the hydrogen released is 21 wt. % —a remarkably high output —but in practice this is lowered to around 7 wt. % when the total system weight is taken into account. Several of these so-called 'chemical hydrides', e.g., $CaH_2$, $LiAlH_4$, LiH, $LiBH_4$, KH, $MgH_2$, NaH, are being evaluated for their reactivity with water. One approach to preparing the storage medium is to mix the hydride with light mineral oil and a dispersant to form an 'organic slurry'. The oil coats the hydride particles and thereby offers protection from inadvertent contact with water, moderates the reaction rate of the hydride with water when desired, and avoids thermal runaway. The disadvantage of using chemical hydrides is that the storage of hydrogen is not rechargeable; the spent solution has to be returned to a processing plant for regeneration of the hydride. This procedure is similar to that proposed for zinc-air traction batteries.

Organic liquids, such as cyclohexane or methanol, can serve as chemical carriers of hydrogen. The gas is subsequently recovered by catalytic decomposition.

Methanol is usually manufactured from synthesis gas [reaction (3)]. It is therefore unlikely that it would be manufactured from electrolytic hydrogen and then decomposed back to hydrogen for use in a fuel cell. The overall energy efficiency of such a cycle would be very poor. Methanol derived from fossil fuel is, however, a prime candidate for fuel cells in portable applications (see below).

### 3.4 Nanostructured materials

Considerable research is being carried out on materials that have structural elements with dimensions in the nanoscale range. The materials have high specific surface-areas ($m^2$/g). This attribute can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared with the amount of bulk support material. It has been found that carbon and boron nitride nanostructures, clathrates and metal-organic frameworks (Fig. 13) can store hydrogen in the molecular state via weak molecular-surface interactions. The physisorption of hydrogen is considered to be more desirable than absorption in metal hydrides (in which the hydrogen molecules are dissociated into atoms that bond with the lattice of the storage medium) as it would moderate both the pressure and the temperature required for the respective uptake and release of hydrogen.

Various types of graphitic nanofibres have been investigated. These are grown by the decomposition of hydrocarbons or carbon monoxide over bi- and tri-metal catalysts of iron, nickel and copper. The nanofibres consist of graphene sheets aligned in a set direction (dictated by the choice of catalyst) and three distinct structures may be produced: platelet, ribbon, and herringbone (Fig. 13). The structures are flexible and can expand to accommodate the hydrogen. Carbon nanotubes are created by using a laser evaporation technique and are cylindrical or toroidal varieties of fullerene (the generic term used to describe a pure carbon molecule that consists of an empty cage of sixty or more carbon atoms) with lengths of up to about 100 μm. Each end is capped with half a spherical fullerene molecule. 'Single-walled' nanotubes are formed by only one graphite layer and have typical inner diameters of 0.7 to 3 nm. 'Multi-walled' nanotubes consist of multiple, concentric, graphite layers and show diameters of 30 to 50 nm. Various pretreatments have been suggested to enhance the storage capacity, which may amount to several wt. % of hydrogen. There is, however, considerable controversy over the findings because of the difficulty in preparing homogeneous, well-defined, pure and reproducible samples. Moreover, contrary to expectation, hydrogen storage requires either high pressure ( > 10 MPa) or low temperature (at least 100 ℃).

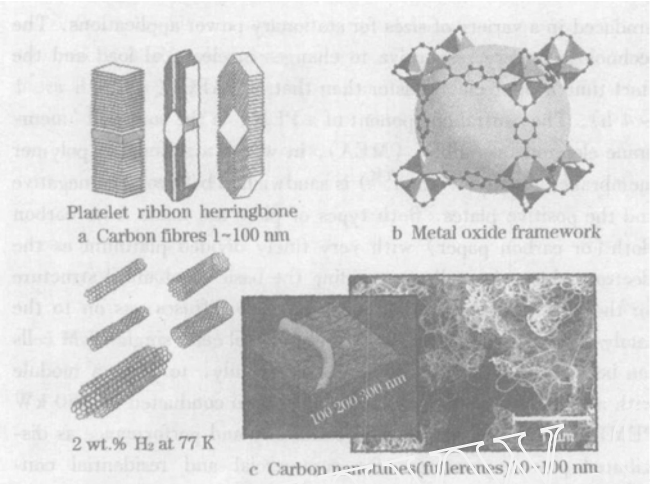

Fig. 13　Schematic representations of (a) carbon nanofibres, (b) single crystal structure of $Zn_4O$ (1,4-benzene decarboxylate)$_3$ and (c) carbon nanotubes, with electron micrographs of a single and bundle of such nanotubes

## 4　Hydrogen utilization: fuel cells

The realization of a hydrogen economy is linked irrevocably with that of the fuel cell, which is an electrochemical power source of interest for stationary, portable and mobile applications. Clearly, therefore, the fuel cell is a key agent for energy sustainability. The device is the converse of the electrolyzer —it converts chemical free energy into electricity. Fuel is oxidized at the negative electrode with the release of electrons that pass through the external circuit and reduce oxygen at the positive electrode. The flow of electrons is balanced by the ionic current (i.e., the electrical charge carried by ions) in the electrolyte. When hydrogen is the fuel, the reversible voltage under standard conditions is 1.229 V at 25 ℃, just as for the electrolyzer. On drawing current from the cell, however, the voltage developed is much lower, typically 0.6～0.8 V, as a result of electrokinetic limitations at the electrodes (often called ‘polarization’ losses), ohmic losses due to the resistance of the electrolyte and the current-carrying components, and the occurrence of side-reactions (cf., Fig. 7). Because these effects are experienced by each unit cell, it is customary to build up the voltage by stacking fuel cells in series, using the same bipolar ‘plate-and-frame’ arrangement that is employed for electrolyzers. The half-cell reactions of the six major types of fuel cell are summarized in Fig. 14. The systems can be broadly categorized in terms of their temperature of operation, namely: (ⅰ) low-temperature (50～150 ℃): alkaline electrolyte (AFC), proton-exchange membrane (PEMFC) and direct methanol (DMFC) fuel cells; (ⅱ) medium-temperature (around 200 ℃): phosphoric acid fuel cell (PAFC); (ⅲ) high-temperature (600～1 000 ℃): molten carbonate (MCFC) and solid oxide (SOFC) fuel cells. Some operational data on each type are given in Table 1.

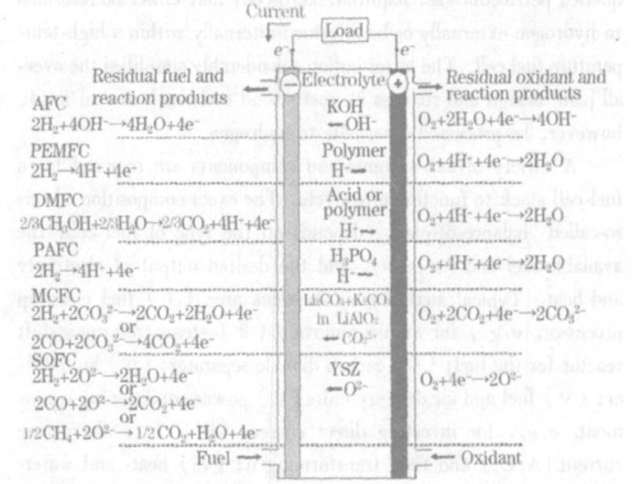

Fig. 14　Electrochemical reactions occurring in different types of fuel cell

The DMFC differs from the other five types in using a liquid (methanol) rather than hydrogen as the fuel. This is far more convenient to transport and handle than a gas. Unfortunately, the methanol molecule is much more difficult to activate than hydrogen, and this necessitates a higher loading of platinum in the negative electrode. Other alcohols, notably ethanol, have also been explored as potential fuels and this has led to the generic term ‘direct alcohol fuel cell (DAFC)’, but comparatively little progress has yet been made with these alternatives.

The level of purity of the hydrogen required by the remaining five types of fuel cell becomes progressively less stringent given the increasing operational temperature of the systems. Both AFC and PEMFC units are poisoned by quite small quantities of sulfur and carbon monoxide (e.g., ～$10^{-3}$ % CO) and therefore have to use hydrogen of high purity. By contrast, the PAFC is somewhat more tolerant to carbon monoxide, while the high-temperature designs (MCFC and SOFC) will accept carbon monoxide and a variety of

**Table 1**　Principal types of fuel cell

| Fuel-cell technology | Electrolyte | Temperature range/ ℃ | Electrocatalyst |  | Fuel | Efficiency[a] / %HHV | Start-up time/ h |
|---|---|---|---|---|---|---|---|
|  |  |  | Positive electrode | Negative electrode |  |  |  |
| PAFC | $H_3PO_4$ | 150～220 | Pt supported on C | Pt supported on C | $H_2$ (low S, low CO, tolerant to $CO_2$) | 35～45 | 1～4 |
| AFC | KOH | 50～150 | NiO, Ag, or Au-Pt | Ni, steel, or Pt-Pd | Pure $H_2$ | 45～60 | < 0.1 |
| PEMFC | Polymer[b] | 80～90 | Pt supported on C | Pt supported on C | Pure $H_2$ | 40～60 | < 0.1 |
| DMFC | $H_2SO_4$ | 60～90 | Pt supported on C | Pt supported on C, Pt-Ru | $CH_3OH$ | 35～40 | < 0.1 |
| MCFC | Polymer[b] $Li_2CO_3$ | 600～700 | Lithiated NiO | Sintered Ni-Cr and Ni-Al alloys | $H_2$, variety of hydrocarbon fuels (no S) | 45～60 | 5～10 |
| SOFC | Oxygen-ion conductor | 700～1 000 | Sr-doped $LaMnO_3$ | Ni- or Co-doped YSZ cermet | Impure $H_2$, variety of hydrocarbon fuels | 45～55 | 1～5 |

a. Reported values of the efficiency of a given type of fuel cell vary widely and often no information is provided on whether the higher (HHV) or the lower (LHV) heating value is used. The va-lues that are taken here from the literature should be treated with caution as to their exact meaning and are simply included to provide an approximate comparison of the performance of the respective systems; b. Proton-conducting polymer: perfluoro-sulfonic acid polymer.

hydrocarbon fuels provided that they are free of sulfur-containing compounds. Liquid fuels that are comparatively ‘clean’ (e.g., liquefied petroleum gas, naphtha, kerosene) may either be reformed to hydrogen externally or be reformed internally within a high-temperature fuel cell. The latter option considerably simplifies the overall plant design and reduces its cost. Solid fuels such as coal must, however, be processed externally to hydrogen.

A variety of sub-systems and components are required for a fuel-cell stack to function effectively. The exact composition of this so-called ‘balance-of-plant’ depends on the type of fuel cell, the available fuel and its purity, and the desired output of electricity and heat. Typical auxiliary sub-systems are: (i) fuel clean-up processor, e.g., for sulfur removal; (ii) steam reformer/shift reactor for the fuel; (iii) carbon dioxide separator; (iv) humidifier; (v) fuel and air delivery units (vi) power-conditioning equipment, e.g., for inverting direct current (D.C.) to alternating current (A.C.) and then transforming it; (vii) heat- and water-management facilities; (viii) overall system controls. Individual components include fuel storage tanks and pumps, compressors, pressure regulators and control valves, fuel and/or air pre-heaters, heat-exchangers and radiators, voltage regulators, motors, and batteries.

Sub-systems (i) to (iii) above involve the preparation of pure hydrogen and may be remote from the fuel cell (or not needed if pure, electrolytic hydrogen is used). Alternatively, they may be integral with the fuel cell, but this adds considerably to the complexity, maintenance and cost of the installation, as well as to its size and mass. Heat and water management are particular problems that have to be addressed in the engineering design. Often the balance-of-plant may account for 60 % to 80 % of the total capital cost. For this reason, the fuel-cell system should have a long operational life (about 25 years) in order to be economical. The modules themselves are required to last for 40 000～50 000 h for stationary applications and 3 000～5 000 h for transportation duty. In the case of a small vehicle, such as a car, it is impractical on the grounds of both size and cost to accommodate on-board reformers (with the possible exception of a methanol reformer) and therefore the fuel supplied must be pure hydrogen. For larger vehicles, such as buses or trucks, on-board reforming of primary fuels is a possibility.

### 4.1 Stationary power

The phosphoric acid fuel cell (PAFC) is the most advanced for moderately large stationary power units. This fuel cell typically has electrodes made from PTFE-bonded platinum and carbon, and uses hydrogen that is reformed externally from natural gas. The concentrated phosphoric acid electrolyte allows the cell to operate well above the boiling point of water, which is a limitation on other acid electrolytes that require water for conductivity. Moreover, the high operating temperature of around 200 ℃ enables the platinum electrocatalyst to tolerate up to 1 wt. % ($10^{-2}$ %) of carbon monoxide and this broadens the choice of fuel. On the other hand, the use of phosphoric acid requires the other components to resist corrosion. Turn-key systems are available commercially and several hundred PAFCs, each rated at 200 kW, have been installed at locations in Asia (principally Japan), Europe, and the USA. These systems supply combined heat and power to major building complexes such as airports, hospitals, hotels, military facilities, office buildings, and schools.

Proton-exchange membrane fuel cells (PEMFCs) are being produced in a variety of sizes for stationary power applications. The technology is very responsive to changes in electrical load and the start-time is appreciably faster than that of PAFCs (< 0.1 h *vs*. 1～4 h). The central component of a PEMC is the so-called ‘membrane electrode assembly’ (MEA), in which a sulfonated polymer membrane (usually, Nafion$^{TM}$) is sandwiched between the negative and the positive plates. Both types of plate are made from carbon cloth (or carbon paper) with very finely divided platinum as the electrocatalyst. As well as providing the basic mechanical structure for the electrode, the carbon substrate also diffuses gas on to the catalyst. In common with other types of fuel cell, single PEM cells can be stacked together, in series electrically, to form a module with a higher voltage. Field trials have been conducted on 250 kW PEMFC plants to evaluate their suitability and performance as distributed power generators for commercial and residential consumers.

There are two high-temperature fuel cells, namely, the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC); both present difficult materials science and technology problems. Molten alkali carbonate at 600～700 ℃ is a most aggressive medium and corrosion problems are severe in this fuel cell. A further issue is the introduction of carbon dioxide and its control in the air stream since this gas is consumed at the positive electrode and transferred to the negative. The SOFC operates at even higher temperatures, in the range 700～1 000 ℃ as dictated by the composition of the solid oxide electrolyte employed, but at least has no liquid components to cause corrosion.

The high-temperature operation of the MCFC and the SOFC systems does, however, offer some advantages, namely: (i) removes the need for a precious-metal electrocatalyst, which reduces cost; (ii) allows the reforming of fuels internally, which enables the use of a variety of fuels, simplifies the engineering (especially heat balancing), and reduces the capital cost; (iii) provides high tolerance to carbon monoxide poisoning. Despite the technical problems they pose, considerable research progress has been made, and prototypes of both MCFC (300 kW～3 MW) and SOFC (100～250 kW) plants have been built and tested in several countries. Given their long start-up times (1～5 h and 5～10 h, respectively) and the slow response to changing power demands, the two technologies are seen as base-load generators and as candidates for combined heat and power (‘co-generation’) systems. The high operating temperatures result in exhaust heat of good quality that may be used to drive steam or gas turbines.

### 4.2 Portable power

Rechargeable batteries are well-suited to portable-power applications where the energy requirement between recharges is relatively small. In recent years, for example, lithium-ion batteries have proved their worth in mobile communications (cellular phones) and in laptop computers. With the advent of mobile broadband computing, however, the next generation of portable electronic equipment will demand ever-greater amounts of stored energy, most probably at levels that are well beyond the capabilities of batteries. For this reason, attention is turning to so-called ‘micro fuel cells’ that promise an energy-storage capability of over an order of magnitude greater than that of the best batteries, albeit with a lower power output. It is therefore widely thought that the first major markets for fuel cells will be established in the field of portable power.

There has been a surge of interest in the development of units that generate just a few watts to power a wide range of consumer electronics, as well as in larger cells (up to a few hundred watts) that are suitable for military equipment such as man-pack radios, helmet-mounted image displays, night-vision sights, laser range finders, and sophisticated communications systems. At present, the direct methanol fuel cell (DMFC) is the preferred technology because, as a liquid fuel, methanol is more readily dispensed and carried than hydrogen. Replacement of a spent methanol cartridge in a micro fuel cell will only take a few seconds. By comparison, rechargeable batteries require periods of hours to be replenished. Furthermore, liquid methanol has a higher stored energy than hydrogen. Applications requiring higher power levels are stimulating the development of hybrid fuel-cell-battery combinations, in which the battery provides the peak power when required and is recharged by the fuel cell. The ultimate in miniaturization would be a ‘nano fuel cell’ on a micro-chip. Self-powered chips would give birth to a new generation of self-sufficient devices such as remote sensors that could telemeter data from the field back to a central station.

Despite the above advantages of DMFCs for portable-power applications (viz., the ready availability, low cost, ease of storage and handling of methanol, and the high specific energy of methanol fuel cells compared with batteries), there are also a number of problems and challenges in bringing the technology to market. In brief, these are as follows.

**Improved kinetics at the negative electrode**. Research to date has found that platinum-based electrocatalysts are the only materials that are able to activate methanol. Even then, the overall reaction at the negative electrode is sluggish, particularly at low temperatures. This is because the electrochemical oxidation of methanol to carbon dioxide is quite complex. Partial electron transfer results in the formation of surface-adsorbed species on the electrocatalyst that, in turn, lower the activity for methanol oxidation. The main ‘poison’ is linearly-bonded carbon monoxide (Pt-CO). Subsequent reactions are thought to involve oxygen transfer (from water) to the Pt-CO species to produce carbon dioxide that desorbs from the platinum surface, i.e.,

$$\mathrm{Pt} + \mathrm{H_2O} \longrightarrow \mathrm{Pt\text{-}OH_{ads}} + \mathrm{H^+} + \mathrm{e} \tag{11}$$

$$\mathrm{Pt\text{-}OH_{ads}} + \mathrm{Pt\text{-}CO_{ads}} \longrightarrow 2\mathrm{Pt} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e} \tag{12}$$

These reactions occur at a very slow rate on pure platinum and this has resulted in a large research effort to find better electrocatalysts. At present, platinum-ruthenium offers the best performance.

**Higher temperature operation**. Particular attention is being directed towards improving the kinetics at the negative electrode by finding the means to allow cells to operate at higher temperatures (e.g., 150～180 °C). This essentially requires the development of new membrane materials that have a higher resistance to dehydration and can therefore operate with less humidification, or do not require water to maintain their proton conductivity. Other essential attributes include low permeability for methanol (see following discussion), long-term thermal and chemical stability, high flexibility, and good mechanical strength.

**Mass transport effects**. Proton-exchange membranes are permeable to both methanol and water. The ‘crossover’ of methanol, which is caused by protonic drag and is similar to the electro-osmotic drag of water, will result in a loss of cell performance and efficiency due to unproductive fuel consumption by direct reaction with oxygen at the positive electrode. In addition, migration of water across the membrane floods the positive electrode and thus inhibits the access of oxygen. Methanol crossover can be reduced to more manageable levels by using dilute aqueous solutions of less than 10 % methanol by volume, but this will cause a decrease in power density. New membrane materials and improved MEA designs are being investigated as more effective means to moderate the transfer of both methanol and water. Methanol crossover deactivates the positive electrode and this, together with the above-mentioned poor kinetics of methanol electrooxidation at the negative electrode, requires a DMFC to have at least ten times more precious-metal electrocatalyst than a PEMFC to achieve a comparable power output.

Micro fuel cells will obviously have little direct implication for the international energy scene, although they may impact upon it indirectly, for example by powering sensors and monitors. Their real significance, however, is in getting developers to address the generic and basic problems associated with the DMFC, as well as in improving public awareness and acceptance of fuel cells in general. If micro fuel cells can be brought to a successful solution then extrapolation of DMFC technology to larger sizes may prove possible.

### 4.3 Power for road transportation

Conventional internal-combustion-engined vehicles (ICEVs) are frequently designed for power rather than for economy. The result is that these vehicles have engines that are too large and inefficient for steady driving, in order to have power in reserve for acceleration and overtaking. The way to avoid this profligate waste of petroleum, and thereby to reduce vehicle emissions which cause urban air pollution and add to the growing inventory of greenhouse gases, is to divorce steady-state performance from acceleration by having two separate energy sources, i.e., one for cruising and one for power. Accordingly, many automotive companies are putting sizeable efforts into the development of hybrid electric vehicles (HEVs) that have electrical or electromechanical drive-trains. As a consequence, around 200 000 HEVs are presently being driven on the world's roads.

The fuel-cell vehicle (FCV) operating on hydrogen, most probably with a PEMFC, is seen as the ultimate solution to the increasing energy security and environmental problems that are confronting road transportation. As discussed above, hydrogen can be manufactured from a wide range of primary feedstocks, even from cheap coal of which the world has almost unlimited quantities. Such vehicles would release nations from the costs and political uncertainties of importing petroleum.

The appeal of FCVs to manufacturers is less obvious. At their present stage of development, PEMFC power systems are hugely more expensive than ICEs (up to 60 times greater per kW of power produced) and the ability to reduce the costs to a competitive value must be questionable. In addition, there are numerous technical difficulties still to be resolved before FCVs can become commercially viable. Above all, there are the over-riding problems of where to manufacture the hydrogen, how to convey it to the vehicle-refuelling sites, and how to store it on-board.

The efficiency of fuel cells (the fraction of the fuel's energy converted into useful output) is also a critical issue. Much is made of the fact that fuel cells are not heat engines like ICEVs, so their efficiency is not limited by the Carnot cycle and therefore must be high. This reasoning promotes much interest and investment in fuel-cell technology. The thermodynamic (‘theoretical’) efficiency, defined as the ratio of reaction free energy to enthalpy, can be above 80 %. Nevertheless, electrochemical kinetic theory says that this ratio is an upper limit that is only reached at equilibrium when the current is zero. In practice, the efficiency must be smaller. How much smaller is difficult to calculate and depends on numerous kinetic and other parameters such as overpotential and ohmic losses, the occurrence of side reactions, fuel loss via the electrolyte, partial fuel usage, and energy consumption by the auxiliary components.

When comparing different transportation fuels, different motive-power units and different vehicles, it is essential to speak of ' well-to-wheels ' efficiency. This concept takes into account: ( i) all of the energy consumed in extracting the fossil fuel from the ground (e. g. , oil and gas from wells, coal from mines) and in refining and transporting the fuel to the service station; ( ii) the combined efficiency at which the fuel is combusted in the engine and the resulting heat energy is transformed to mechanical energy at the wheels, with due regard to the friction losses in the drive-train. It is well known that ICEs are rather inefficient (presently 20 %～25 %, at best), whereas electrochemical generators such as fuel cells are substantially more efficient (50 %～60 %, subject to the current density). The dependence of fuel-cell performance on current output is especially important in vehicle applications. For small vehicles, such as cars, where size and capital cost are at a premium, it is likely that the fuel cell will operate at high current density and, therefore, at relatively low efficiency.

In comparing FCVs with HEVs, account has to be taken of the energy losses incurred in manufacturing the hydrogen fuel. If the hydrogen is derived from fossil fuels, there are the losses in chemically reforming the feedstock (natural gas or coal); while if it is produced by electrolysis there are the losses in generating and transmitting the electricity. The steam reforming of natural gas to hydrogen on a large scale is 60 %～70 % efficient (say 65 %). It is reasonable to assume at least a further 10 % energy loss in compressing the hydrogen, as well as 10 % in transporting it from the centralized steam-reformer to the vehicle-refuelling depot. The PEMFC is 40 %～60 % efficient electrochemically (say 50 %), but allowances have also to be made for parasitic losses in the fuel-cell system (power for pumps, heaters, blowers, controllers, etc.), and for energy losses in the vehicle's electrical system (losses in inversion to alternating current, in the transformer, and the traction motor). In round figures, again, the collective losses in each system can be taken as 10 %. Thus, the well-to-wheels efficiency from natural gas to traction effort, via hydrogen, is calculated as follows:

natural gas to distributed hydrogen: 0.65 ×0.9 ×0.9 = 53 %
hydrogen to low-voltage D.C. electricity: 0.50 ×0.9 = 45 %
low voltage D.C. electricity to tractive effort: 0.9 = 90 %
well-to-wheels efficiency (natural gas to tractive effort):
0.53 ×0.45 ×0.9 = 21 %.

In other words, FCVs based on reformed natural gas have an overall efficiency that is close to that of the present high-performance ICEV, namely, 18 %～22 % when the energy losses in oil recovery and refining (typically, 13 %) are taken into account. As discussed above, however, FCVs would offer the benefit of zero harmful emissions during driving.

What if the hydrogen is produced by electrolysis rather than directly from natural gas? Here the situation is even worse. The practical cell voltage for the electrolysis of water is around 1.47 V. The voltage of a PEMFC lies in the range of 0.75～0.60 V, as determined by the current density. Thus, the electrolyzer and fuel cell combination is likely to be 40 %～50 % efficient at best (say 45 %). Although this is higher than for a high-performance automobile (20 %～25 %), as emphasized by advocates of FCVs, the losses incurred in producing hydrogen from primary fuels have yet to be included. The efficiency of a conventional power station lies in the range of 30 %(coal or nuclear) ～55 % (combined-cycle gas turbine). The well-to-wheels efficiency from primary fuel to traction effort is then:

coal or nuclear plant: 0.3 ×0.45 ×0.9 ×0.9 = 11 %
natural gas plant: 0.55 ×0.45 ×0.9 ×0.9 = 20 %

Note that in these two calculations, the 10 % energy loss in compressing the hydrogen has been retained, while the 10 % loss in distributing hydrogen has been replaced with a 10 % loss in the electricity-supply system that would result from distribution, voltage reduction, and rectification operations.

The above are only approximate calculations. Nevertheless, from the viewpoint of overall energy efficiency, the analysis clearly shows that there is no incentive to replace internal-combustion engines with fuel cells in road vehicle applications.

In the meantime, serious analyses have predicted that the efficiency of the ICE is expected to improve rapidly through technological innovation. The combination of such advances together with conversion to HEV drive-trains is predicted to reduce fuel consumption by two-thirds compared with the 1996 model family car, Fig. 15. On both energy efficiency and cost grounds, this appears to be a much more realistic option than the introduction of fuel-cell cars. Hybrids are attractive to the automotive industry since a paradigm shift in technology is not required, and to the users because such vehicles are reasonably cost-competitive with conventional automobiles and will deliver superior fuel economy. Nevertheless, for HEVs to achieve deep penetration into road transportation markets, and thereby make a make a major contribution to the saving of precious oil and the reduction of carbon dioxide emissions, a high-performance, low-cost battery must be developed. Thus, this electrochemical power source is yet another key agent for energy sustainability.

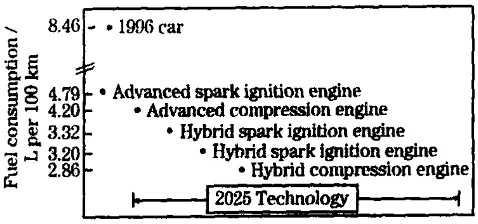

Fig. 15 Anticipated improvements in ICE-based cars

A HEV battery has to supply significant amounts of electrical energy for on-board electrical functions and, in several of the electrical systems proposed for the new-generation vehicles, will have to accommodate charge returned via ' regenerative braking ' as part of the scheme to save fuel. Under such duty, the battery will have to operate continuously at a partial-state-of-charge (PSoC) and accept charge at extremely high rates. In addition, high-rate discharge is necessary for engine cranking, acceleration and hill-climbing (i. e. , ' power-assist '). Overall, the battery is said to undergo high-rate partial-state-of-charge duty, or more briefly ' HRPSoC duty '.

Present HEVs are fitted with Ni/ MH batteries; these provide adequate performance but are expensive. Rapid progress is being made with rechargeable lithium batteries, but again there will be a cost penalty. Although the valve-regulated lead-acid (VRLA) battery offers a more affordable option, it suffers premature failure under the HRPSoC duty demanded by HEVs. Specifically, high-rate discharge causes a compact layer of lead sulfate to form on the surface of the negative plate and this ' hard ' sulfate is difficult to recharge. On the other hand, high-rate charge promotes the early evolution of hydrogen and, therefore, reduces the charging efficiency of the plate. To overcome this problem, CSIRO has developed the valve-regulated UltraBattery. To explain the configuration and operating principles of this innovative device, it is first necessary to provide a brief review of supercapacitor technology.

Supercapacitors differ from conventional electrostatic and electrolytic capacitors in that they store electrostatic charge in the form of ions, rather than electrons, on the surfaces of materials with high specific areas ($m^2/g$), see Fig. 16 (a). In the ' symmetric ' design, the electrodes are usually prepared as compacts of finely-divided, porous carbon, which provide a much greater charge density than is possible with non-porous, planar electrodes. Supercapacitors can store vastly more energy than conventional capacitors and much of the storage capacity is due to the charging and discharging of the electrical double-layers that are formed at the electrode | electrolyte interfaces. The voltage is lower than for a conventional capacitor, while the time for charge, as well as that for discharge, is longer because ions move and reorientate more slowly than electrons. In these respects, the supercapacitor begins to take on some of the characteristics of a battery, although no electrochemical reactions are involved in the charge and the discharge processes. The ' asymmetric ' design of supercapacitor moves one step closer to a battery, see Fig. 16 (b). Here, an electrode material with a large specific surface-area (e. g., carbon) is combined with a ' battery-like ' material that can be reversibly oxidized and reduced over a wide potential range. The energy is stored both by ionic capacitance and by surface (and near-surface) redox processes that occur during charge and discharge. The latter are electrochemical reactions (i. e., faradaic processes) in which surface ions are reduced and oxidized. This enhances the amount of stored energy; the capacitance is twice that of the symmetric counterpart, see Fig. 16. Moreover, because the ions are confined to surface layers, the redox reactions are rapid and are fully reversible many thousands of times and this makes for a long cycle-life.

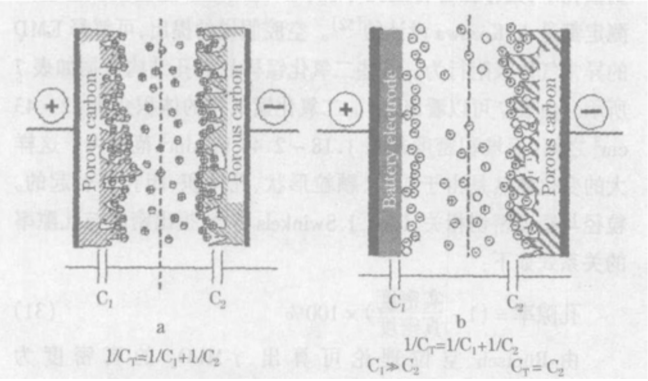

Fig. 16　Schematic of (a) symmetric supercapacitor and (b) asymmetric supercapacitor

The CSIRO valve-regulated UltraBattery combines a VRLA battery with an asymmetric supercapacitor into a single unit without the need for extra electronic control. The hybrid structure is shown schematically in Fig. 17. A VRLA cell, which has one lead-dioxide positive plate and one sponge-lead negative plate, is combined with an asymmetric supercapacitor, which is composed of one lead-dioxide positive plate and one carbon-based negative plate (i. e., a capacitor electrode). Since the positive plates in the VRLA cell and the asymmetric supercapacitor have the same composition, they can be integrated into one unit by connecting internally the capacitor electrode and the VRLA negative plate in parallel. Both these electrodes now share the same positive plate. With this design, the total discharge or charge current of the combined negative plate is composed of two components, namely, the capacitor current and the VRLA negative-plate current. Accordingly, the capacitor electrode can now act as a buffer to share current with the negative plate and thus prevent it from being discharged and charged at high rates. Prototype batteries have been constructed by a leading battery manufacturer and are presently undergoing evaluation in both laboratory and field trials.

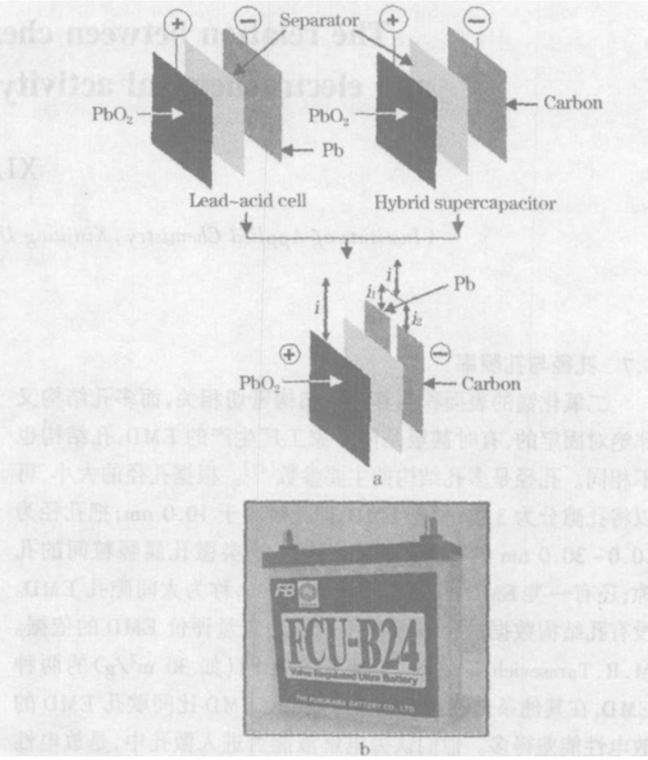

Fig. 17　(a) Configuration of the CSIRO valve-regulated UltraBattery; (b) prototype battery

## 5　Concluding remarks

By virtue of its physical and chemical properties, it is clear that hydrogen has the potential to occupy a unique position in the future world energy scene. Not only could it become ultimately a universal means of conveying and storing energy ——especially if renewable energy is to become dominant ——but also an entirely novel fuel with attributes that are quite distinct from those of other fuels. Hydrogen is the obvious choice for a low-carbon economy in that it would liberate no pollutants to the atmosphere and, when coupled to carbon sequestration or derived from non-fossil primary energy sources, no carbon dioxide to contribute to climate change. This study has attempted to show that the various technologies now being advanced by electrochemists are vital contributors to the realization of clean and secure global energy.

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