

The hydrogen economy: a threat or an opportunity for lead–acid batteries?

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Available online 8 January 2005

Abstract

There is mounting concern over the sustainability of global energy supplies. Among the key drivers are: (i) global warming, ocean surface acidification and air pollution, which imply the need to control and reduce anthropogenic emissions of greenhouse gases, especially emissions from transportation and thermal power stations; (ii) the diminishing reserves of oil and natural gas; (iii) the need for energy security adapted to each country, such as decreasing the dependence on fossil fuel imports (in particular, the vulnerability to volatile oil prices) from regions where there is political or economic instability; (iv) the expected growth in world population with the ever-increasing aspiration for an improved standard-of-living for all, especially in developing and poor nations. Hydrogen is being promoted world-wide as a total panacea for energy problems. As a versatile carrier for storing and transporting energy from any one of a myriad of sources to an electricity generator, it is argued that hydrogen will eventually replace, or at least greatly reduce, the reliance on fossil fuels. Not unexpectedly, the building of a ‘hydrogen economy’ presents great scientific and technological challenges in production, delivery, storage, conversion, and end-use. In addition, there are many policy, regulatory, economic, financial, investment, environmental and safety questions to be addressed. Notwithstanding these obstacles, it is indeed plausible that hydrogen will become increasingly deployed and will compete with traditional systems of energy storage and supply. Moreover, the case for hydrogen will be greatly strengthened if fuel cells, which are the key enabling technology, become more reliable, more durable, and less expensive. This paper examines the prospects for hydrogen as a universal energy-provider and considers the impact that its introduction might have on the present deployment of lead–acid batteries in mobile, stationary and road transportation applications.

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Keywords: Energy; Fuel cell; Hydrogen economy; Lead–acid battery; Mobile and stationary power; Road transportation

1. Energy in transition

The world relies heavily upon fossil fuels (coal, oil, natural gas) as its major sources of energy for heating, mechanical power and electricity generation. There is now, however, overwhelming evidence that the unfettered use of such fuels will not deliver ‘energy sustainability’ that is will not provide the energy required to meet humankind needs on an indefinite basis without causing irreversible degradation of the environment.

1.1. Energy security

Coal is by far the most abundant fossil fuel; it is estimated that there are 250 years of economically recoverable

reserves at today’s rate of usage. By contrast, over the past 30 years there have been many pessimistic forecasts of oil reserves. According to early projections, production should now have peaked and be in decline. In fact, this has not happened because of advances in geo-prospecting and in the technology of drilling and tapping off-shore oil wells in deep water. Whereas, there appears to be no serious danger of resource depletion in the near-term, it is self-evident that this situation cannot continue indefinitely and, sooner rather than later, petroleum will be in short supply. Huge quantities of natural gas, a desirably cleaner fuel, have been discovered and globally no shortage is expected for several decades to come. Even so, this fuel too will ultimately become scarce and will need to be replaced—most probably, by gasification of the vast reserves of coal. There are also inequalities in the geographic distribution of these natural resources that make some countries wealthy and others relatively poor. Thus,

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unabated consumption will intensify political, economic and social tension.

There are two other significant sources of energy, namely, nuclear power and hydro power, both of which are manifest as electricity. In the minds of many, nuclear power is perceived to be surrounded by issues of safety and security, whereas the limitation to hydroelectric power is set by the availability of suitable sites. It is worth noting, however, that only one-quarter of the world's 45,000 dams produce electricity and that only 6% of Africa's, 21% of Asia's and 35% of South America's hydro capability has been put into practice.

1.2. Atmospheric pollution and climate change

Of equal concern are the destructive effects of the growing levels of energy conversion and usage on the earth's biosphere. At the local level, energy use in motor vehicles has been a major contributor to the degradation of urban air quality. The exhaust pollutants include carbon monoxide (which displaces oxygen in the blood), nitrogen oxides (NO_x , which combine with water to form corrosive nitric acid) and unburnt hydrocarbons (which react with NO_x in the presence of sunlight to form ozone, and thereby, photochemical smog—a lung irritant). Recent developments in vehicle exhaust catalysts, and in environmental regulations in many countries, have resulted in major declines in the levels of these pollutants in urban air. Energy use in large stationary applications, such as thermal power stations is also a serious source of both sulfur oxides (SO_x) and NO_x , which are the major precursors to 'acid rain'.

In global terms, the energy sector is the single largest source of anthropogenic 'greenhouse gases' through emissions of: (i) carbon dioxide from the combustion of coal, oil and natural gas in electricity generation, in transport, and in the direct consumption of such fuels by industry, commerce and households; (ii) methane from the production, transport and end-use of natural gas, and from coal mining; (iii) nitrous oxide, which is one of the NO_x formed during the combustion of fossil fuels. Greenhouse gases are so-called because, like the glass panes of a greenhouse, they allow sunlight to penetrate but absorb the infra-red radiation (heat) that is re-radiated from the earth's surface. Thus, enhanced levels of such gases in the atmosphere will result in more heat being trapped and accordingly will cause an increase in ambient temperature. Most authorities believe that carbon dioxide evolved from burning fossil fuels is mainly responsible for the 0.5 °C rise in the global average temperature over the past 100 years during which fossil fuels have been extracted and burnt on a substantial scale. Moreover, the phenomenon of climate change may be accelerating. In many parts of the world, records have been broken for the warmest ever temperatures. If this trend continues, it is predicted that storms and major floods (and droughts elsewhere) will become commonplace. Progressive melting of the polar ice-caps would lead to a rise in sea levels and the inundation of low-lying

areas with the prospect of large areas of land suitable for cultivation being lost and populations displaced. If the Arctic or Antarctic ice sheets were to melt, then the consequences would be inordinately worse.

In essence, the challenge facing world society today is to move progressively from the fossil fuel age to renewable forms of energy that are secure in supply and non-polluting. This is the concept of 'energy sustainability'.

2. Why hydrogen?

Fossil fuels are remarkable in that they are not just fuels, but are also energy stores. Once mined and processed, fossil fuels may be transported and stored at the designated location. It is this vital storage capability that is lacking in most renewable forms of energy. Without such a facility, there is often a mismatch between where and when renewable energy is available, and where and when it is required. For instance, wind turbines work well when the wind is blowing, but electricity is also needed on windless days. Solar power is available during daylight hours, but much electricity use is at night. Finding an economic means for storing energy, particularly electricity, lies at the very heart of the renewables problem.

Electricity can be stored either in a physical form (i.e., as thermal, potential, kinetic, electromagnetic, or electrostatic energy); or it can be stored as chemicals, especially as electrochemical materials in rechargeable batteries, such as the lead-acid battery. Recently, however, there has been intense scientific, industrial and governmental interest in the development of a further form of chemical storage—hydrogen. (Despite being the most abundant element in the universe, it is a mistake to consider hydrogen as an energy 'source' that exists freely in nature like coal, oil, or natural gas; similar to electricity, it is an energy 'carrier' that has to be generated.)

The widespread use of hydrogen as an energy-storage medium, the so-called 'hydrogen economy', would offer the following advantages:

- hydrogen is a sustainable form of energy in that it can be produced from many primary sources, e.g., fossil fuels, renewables, and nuclear power; this flexibility reduces the chances of creating a hydrogen cartel similar to that set up by the Organization of Petroleum Exporting Countries (OPEC);
- by virtue of its exceptionally low density in both the gas and the liquid state, hydrogen has the best energy-to-weight ratio ('heating value') of any fuel (note, however, the heating value of liquid hydrogen per unit volume is less than that of other liquid fuels);
- hydrogen may be transmitted over long distances in pipelines that to some degree provide a storage component;
- hydrogen is ideal for use in fuel cells to regenerate electricity; this would enable the decentralization of power generation;

- hydrogen is colourless, odourless, tasteless and non-toxic; it is also oxidized cleanly to water, thereby, the cycle is closed and no significant pollutants are formed;
- hydrogen can also be used as a fuel for engines, and it does double duty as a raw material in a myriad of other uses.

A more detailed discussion of the hydrogen economy and the importance of developing a strategy for the world's future energy supply is given in [1].

It should be acknowledged that hydrogen has a poor safety reputation, largely on account of the Hindenburg airship disaster in 1937. It has been recently shown, however, that the Hindenburg fire was more to do with the flammability of the fabric chosen for the airship's envelope than with the fact that it was filled with hydrogen. Nowadays, there is considerable industrial experience of the safe handling of hydrogen gas in bulk, both in refineries and in chemical plants. The general opinion of those involved in such operations is that hydrogen is safe provided that its properties are clearly understood and well-defined safety regulations are followed. A positive safety feature of hydrogen is that, in the event of a fire, the low luminosity of the flame restricts the emission of thermal radiation to less than one-tenth of that from hydrocarbon flames. Thus, bystanders are much less likely to suffer radiation burns. Furthermore, the low density and high diffusivity of hydrogen results in the very rapid dispersal of liquid hydrogen after a spillage, so that the risk of fire persists for a much shorter period than with other liquid fuels.

While a hydrogen economy represents a visionary strategy for our future energy security, its successful implementation is subject to two major requirements:

- the individual technical steps must be connected by an infrastructure that provides seamless, safe and environmentally acceptable transitions from production, to distribution and storage, and then to use;
- hydrogen as an energy carrier must be economically competitive.

Before addressing the potential impact of a hydrogen economy on the prospects for lead–acid batteries, it is appropriate to review briefly the present status of the functional areas that would facilitate such a radical change in global energy supply.

3. Hydrogen production

Of the present world-wide production of hydrogen (around 50 million tonnes per annum), over 90% comes from raw fossil materials. In energy terms, hydrogen equates to around 5% of the world's oil consumption. The hydrogen is used mainly in making nitrogen fertilizers and, increasingly, in converting low-grade crude oils into transport fuels. Lesser applications are found in the manufacture of other chemicals, as well as in the food, plastics, metals, electronics, glass, electric power and space industries.

3.1. Hydrogen from fossil fuels

The gasification of coal is the oldest means of obtaining hydrogen from fossil fuels. When heated in a restricted supply of air (so-called 'destructive distillation' or 'pyrolysis'), coal is converted to mixture of hydrogen, methane and carbon monoxide (typically, 50, 35 and 8%, respectively), together with coal tar and coke. Alternatively, when heated coal is reacted with steam the 'water-gas reaction' occurs, i.e.,

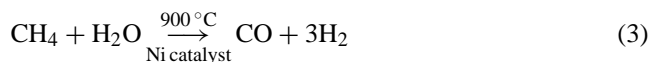


Water gas found widespread use before World War II in producing hydrogen for the manufacture of ammonia via the Haber process. The water-gas reaction is highly endothermic (heat absorbing), and thus, soon ceases unless heat is supplied. Conversely, the combustion of coal or coke in air is highly exothermic (heat evolving). It is, therefore, usual to pair off the two reactions so as to balance the heat evolved with that absorbed. The two reactions may be conducted consecutively in short bursts or, more usually, simultaneously by feeding a mixture of air and steam to the heated bed. The resulting gas is a mixture of CO, H₂, CO₂, and N₂. This may be upgraded in terms of hydrogen content by the 'water-gas shift reaction'. The gas is reacted with steam over a catalyst that converts carbon monoxide to carbon dioxide and increases the amount of hydrogen, i.e.,



The carbon dioxide can be removed by a variety of gas-scrubbing techniques. The process engineering of coal gasification is quite complex. Nevertheless, several large-scale gasifiers have been developed. Research is also being conducted on similar technology for the processing of biomass and organic waste.

The steam reforming of natural gas is the most efficient and widely used process for making hydrogen. At present, it is also the cheapest route. The methane is reacted with steam and air over a nickel-based catalyst, i.e.,



The resulting product is known as 'synthesis gas' (or 'syn-gas') because it may be used for the preparation of a range of commercial products that include hydrogen, ammonia, methanol, and various organic chemicals. As with the gasification of coal, steam reforming can be combined with the water-gas shift reaction (reaction (2)) to increase the yield of hydrogen. Steam reforming is very energy-intensive since it operates at high temperatures (850–950 °C) and high pressure (3.5 MPa). The thermal efficiency can reach 60–70%.

A third method is 'partial oxidation' in which fuel and oxygen are combined in proportions such that the fuel is converted into a mixture of hydrogen and carbon monoxide. The amount of hydrogen is only about 75% of that produced by steam reforming (but of course the content can be increased

via the water-gas shift reaction). Depending on the composition of the fuel and the required processing rate, the partial oxidation process is carried out either catalytically or non-catalytically. The latter approach operates at high temperatures (1100–1500 °C) and can be applied to a range of feedstocks that include heavy residual oils and coal. By contrast, the catalytic process is performed at a significantly lower range of temperatures (600–900 °C) and, in general, is used for light hydrocarbon fuels, e.g., natural gas and naphtha. The drawback to partial oxidation is that it requires the use of expensive oxygen (rather than air, which would dilute the product hydrogen with nitrogen). In ‘autothermal reforming’, the exothermic process of partial oxidation is combined with endothermic steam reforming so that the gasification process requires virtually no input of external energy.

Whereas, it is likely that natural gas will provide the earliest affordable feedstock for hydrogen, today’s costs are prohibitively high for applications, such as transportation, while petrol is still comparatively cheap. Moreover, the fact that processes based on the use of fossil fuels produce carbon dioxide in addition to hydrogen appears to be self-defeating on environmental grounds. Clearly, their future will depend on developing efficient means to separate this greenhouse gas and then sequester it, possibly in underground chambers or by chemical loops. Therefore, efforts are underway to develop technology that will reduce both costs and emissions. For example, the FutureGen Project in the USA aims to develop coal-fired plants for the cogeneration of electricity at only 10% above today’s prices and hydrogen that is competitive in price with petrol, together with 90% sequestration of the attendant carbon dioxide.

Hydrogen can also be produced by the direct thermocatalytic decomposition (‘cracking’) of methane or other hydrocarbons. The energy requirement per mole of methane is, in fact, less than for steam reforming, although only half as much hydrogen is produced, and the process is simpler. In addition, a valuable by-product—clean solid carbon—is produced, which obviously can be captured and stored more easily than gaseous carbon dioxide. There is, however, the problem of progressive catalyst deactivation through carbon build-up; reactivation would result in unwanted CO₂ emissions.

3.2. Hydrogen from water

Water is the other huge storeroom of hydrogen. Breaking down water to hydrogen also requires energy. Electrical, chemical, light or thermal energy can be employed.

3.2.1. Electrolysis

Although electrolysis is a mature technology, only a few percent of world hydrogen is obtained by this method, and mostly as a by-product of the chlor-alkali process for the manufacture of chlorine and sodium hydroxide. Electrolysis is extremely energy-intensive—the faster the generation of hydrogen, the greater is the power required per kilogram

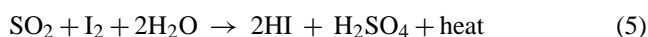
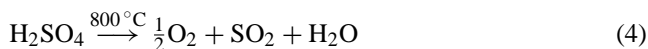
produced. The practical operating voltage exceeds the theoretical or ‘reversible’ value of 1.229 V due to ohmic losses in the electrodes and electrolyte, and to electrochemical kinetics (‘overpotential’) losses at the electrodes. Thus, electrolyzers are most effective when operating at low current densities, i.e., at low production rates. Large-scale units using alkaline electrolyte can run at 70–75% efficiency, while smaller systems with polymer electrolytes reach 80–85%. Steam electrolyzers, in which some of the energy required to split water is supplied by heat, can achieve very high efficiencies (over 90%) but are presently not commercially feasible. Consideration has also been given to operating fuel cells in reverse as electrolyzers. The dual-function system is termed a ‘regenerative fuel cell’. Such technology would save on weight and costs compared with a power system that employs a separate fuel cell and electrolyzer. It would also offer the prospect of using renewable energy (e.g., solar, wind, geothermal) to generate hydrogen that would be stored in the same unit for subsequent production of electricity. To date, however, reliability problems with bifunctional electrodes and efficiency limitations of the ‘charge–discharge’ process (ways have to be found to optimize the catalyst for both processes) have delayed progress on these devices.

It should be noted that when using electricity generated from thermal power stations the overall efficiency of converting fossil fuel to hydrogen via electrolysis would, typically, be only about 30%. This is not a very attractive return on the invested energy. And again, there is the problem of capturing the emissions. Of course, this issue would not arise if hydro or geothermal power were to be available, as in Iceland, but few countries are blessed with such renewable energy. Photovoltaic electricity is similarly limited and is very expensive. Wind power has gained some supporters, but the supply of electricity would be variable and at best would only be suitable for small-scale electrolyzers. Given the state-of-the-art, the concept of employing electrolysis-produced hydrogen for the storage of electricity derived from renewables presents energetics that are grossly unfavourable, and this deterrent is compounded by economics that are not commercially viable. It is for these reasons, that many scientists, and even the eminent environmentalist James Lovelock, now argue that the only ‘green solution’ is to conduct electrolysis with electricity derived from nuclear fission. After all, there would be no fugitive pollution—the radioactive waste is easily held captive. Clearly, the time has come to rethink our relationship with the awesome power of the atom. Further into the future, there is every hope that initiatives such as the International Thermonuclear Experimental Reactor (ITER) Programme will hasten the practical realization of nuclear fusion, which is widely acknowledged to be the ultimate provider of sustainable energy.

3.2.2. Thermochemical production

It is also possible to decompose water to form hydrogen without generating electricity first. This would remove the need for an electrolyzer and avoid the problem of emissions.

For example, thermal energy can be used via ‘thermochemical cycles’. In each of the leading processes, heat is used to decompose sulfuric acid to oxygen and sulfur dioxide. There are then several possible cycles. The most promising employs iodine to produce hydrogen iodide exothermically, which in turn dissociates endothermically to hydrogen and iodine, and the cycle is then repeated, e.g.,



Efficiencies of around 40% have been demonstrated in the laboratory, but the processes are still far from practical realization. Thermochemical cycles are, however, obvious candidates for coupling with the waste heat from nuclear power plants.

3.2.3. Photoelectrolysis

Photoelectrolysis is one of three possible methods (v.i.) for the direct production of hydrogen via the harnessing of solar radiation. Light is converted to electrical and chemical energy by using a semiconducting oxide, such as titanium dioxide (TiO_2), to absorb photons and provide oxygen and electrons. The electrons flow through an external circuit to liberate hydrogen at a metal counter electrode, such as platinum. By virtue of its relatively low cost, titanium dioxide is most attractive as a photovoltaic material. It does, however, have a somewhat high band-gap energy (~ 3.2 eV), and therefore, absorbs light energy in the ultraviolet rather than in the optical part of the spectrum. Accordingly, present efficiencies are only 1–2%, i.e., well below the commercial target of 10%. To achieve improvements in performance, research efforts are being directed principally towards finding a means to shift the spectral response of titanium dioxide into the optical region through modification of band-gap and light-absorption properties.

The possible benefits to be gained by using a photoelectrochemical cell in tandem with a dye-sensitized solar cell (‘Grätzel cell’), to absorb complementary parts of the solar spectrum, are also being explored. The latter also employs titanium dioxide as a photovoltaic material and overcomes the band-gap problem by means of a subterfuge. This involves separating the optical-absorption and charge-generating functions by using a dye that is capable of being photo-excited in the optical spectrum, and thereby, acting as an electron-transfer reagent. Such redox cells have demonstrated sunlight-to-electricity efficiencies of 10% in the laboratory but only 5% in the field. Again, this cell technology is still under development. An overall conversion efficiency from standard solar light to hydrogen generation of 4.5% has been reported for the tandem devices. There are, in fact, many different possibilities for photoelectrochemical cells and this area of research is attracting much scientific interest.

3.2.4. Biophotolysis

Photosynthesis is the basis for almost all life on earth. The first step involves splitting water into oxygen and hydrogen, and then hydrogen is mixed with carbon dioxide and turned into carbohydrates. There are, however, some groups of micro-algae that are capable of releasing hydrogen. For example, green algae contain an enzyme, hydrogenase, that manages the dark-to-light transition that the micro-organisms face daily; it catalyzes the reduction of protons by electrons to form hydrogen. Biologically, however, the system is not designed for continuous operation. This is because the enzyme is very sensitive to oxygen and is only synthesized after several hours of dark pre-incubation under anaerobic conditions. Thus, when oxygen is produced by the algae after a short period in sunlight, the rate of hydrogen evolution decreases. To overcome this, two-stage ‘indirect biophotolysis’ processes are being investigated in which a photosynthetic carbon dioxide fixing stage that generates oxygen is followed by a dark anaerobic fermenting stage that produces hydrogen. Clearly, fundamental molecular research into genetically engineered micro-organisms, together with the technological development of efficient and inexpensive photobioreactor designs, has to be undertaken before such light harvesting can become a practical proposition.

3.2.5. Thermolysis

The temperature required for breaking down water directly into hydrogen and oxygen can be achieved by focusing the sun rays from a large number (up to thousands) of individual mirrors on to a thermal receiver mounted on top of a central, tall ‘solar tower’. The key scientific challenges are to find catalysts that will reduce the dissociation temperature, and to provide an improved means for separating the gases so as to prevent recombination. Large-scale production in areas with poor road or rail links is not practical—the hydrogen should be generated close to where it is needed. To this end, CSIRO in Australia is designing and building ‘mini’ solar towers with smaller footprints for the decentralized generation of hydrogen. This type of infrastructure would be easier to install and is flexible in that units can be added over time to meet any growth in demand. It has also been suggested that solar–thermal radiation could facilitate and improve the photoelectrochemical decomposition of water by enabling the process to be conducted at high temperatures and pressures. Much of solar radiation lies in the infra-red part of the spectrum and is of too low energy to be utilized in photoelectrochemical reactions so that it is wasted. Radiation received by the solar tower would, therefore, be separated into an infra-red component to heat pressurized water to at least 300°C , and into optical/ultraviolet radiation to effect the water-splitting reaction. Thermodynamic calculations suggest that the required energy is substantially reduced at high temperature and pressure, and that it should be possible to reach overall efficiencies approaching 20% for the conversion of solar energy to hydrogen. There is, however, a drawback in that regions of the world where insolation is both high and per-

sistent are often those where water is in short supply. (Note, solar towers may also be used for the steam reforming of coal gas or natural gas.)

4. Hydrogen distribution and storage

Given that plentiful supplies of hydrogen can be produced economically, the next issues relate to its distribution and storage.

4.1. Gaseous and liquid hydrogen

In the gaseous state, the most obvious method for distributing hydrogen would appear to be via pipeline. Indeed, 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:

- materials problems (e.g., blistering, embrittlement and decarburization of metals) may not allow the use of natural gas facilities;
- 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);
- 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;
- 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 3–4 MJ dm⁻³. This approaches the 2010 target (5.4 MJ dm⁻³) set by the US FreedomCAR Partnership for fuel-cell vehicles, but is far below the 2015 target (9.7 MJ dm⁻³). Incidentally, the corresponding gravimetric

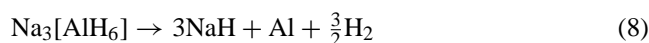
targets (7.2 and 10.8 MJ kg⁻¹) will be even more difficult to reach. In this respect, liquid hydrogen would be more attractive; its density is 850 times greater than that of the gaseous form. Liquid hydrogen is routinely transported by road and by sea, but about 30% of the energy in the hydrogen is wasted 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.

4.2. 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 metal hydrides can be categorized as high-, medium- or low-temperature systems. Clearly, hydrides operating close to ambient are preferred. Unfortunately, however, the maximum gravimetric storage of low-temperature hydrides (<150 °C) is quite low, typically 1–2 wt.%. (Note, 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⁻¹ based on the higher heating value for hydrogen.) Moreover, the best high-temperature hydrides (magnesium-based hydrides, such as Mg₂NiH₄ at >300 °C) offer a maximum storage of only 3.6 wt.% (5.1 MJ kg⁻¹). By contrast, hydrides have a comparatively good hydrogen storage capacity when expressed on a volumetric basis, namely, 0.1 kg dm⁻³ (6.7 MJ dm⁻³); both mass and volume are critical factors when considering storage on board a vehicle. Obviously, the major research challenges are to develop new alloying techniques for low-temperature hydrides that have increased gravimetric density.

4.3. Chemical storage

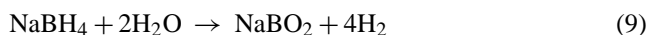
Hydrogen may also be stored chemically in the form of ionic salts that are composed of sodium, aluminium or boron, and hydrogen—the so-called ‘complex hydrides’. The alanates Na[AlH₄] and Na₃[AlH₆] are the preferred reagents. Thermal decomposition of Na[AlH₄] takes place in two steps, i.e.,



The reactions are reversible only at elevated temperatures and pressures. The first step, at 50–100 °C, corresponds to the release of 3.7 wt.% hydrogen and the second step, at 130–180 °C, 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[AlH₄] has thermodynamic properties that are comparable with those of low-temperature hydrides (e.g., LaNi₅H₆ and TiFeH). By contrast, Na₃[AlH₆] requires higher temperatures for hydrogen liberation.

Sodium borohydride, NaBH₄, is stable up to about 400 °C, and is therefore, not suitable for providing hydrogen through a thermal-activation process. It does release hydrogen, however, on reaction with water, i.e.,



This is an irreversible reaction, but has the advantage that 50% of the hydrogen comes from the water. In effect, NaBH₄ acts as a ‘water-splitting’ agent. Based on the mass of NaBH₄, 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., CaH₂, LiAlH₄, LiH, LiBH₄, KH, MgH₂, 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 and involves the input of a considerable quantity of energy, probably electrical.

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 (v.i.).

4.4. 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 (m² g⁻¹). 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 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. 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 60 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 0.7–3 nm. ‘Multi-walled’ nanotubes consist of multiple, concentric, graphite layers and show diameters of 30–50 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 °C).

5. Hydrogen utilization: fuel cells

The realization of a hydrogen economy is linked irrevocably with that of the fuel cell. This device is essentially a water electrolyzer working in reverse; a fuel is fed to the negative electrode and oxygen (or air) to the positive electrode. An electrochemical reaction takes place—fuel is oxidized, oxygen is reduced, water is formed—and a voltage is generated across the cell so that a direct current may then be drawn. The six principal types of fuel cell can be categorized in terms of their temperature of operation, i.e.,

- low-temperature (50–150 °C): alkaline (AFC), proton-exchange membrane (PEMFC) and direct methanol (DMFC) fuel cells;
- medium-temperature (around 200 °C): phosphoric acid fuel cell (PAFC);
- high-temperature (600–1000 °C): molten carbonate (MCFC) and solid oxide (SOFC) fuel cells.

The DMFC differs from the other five types in that it uses a liquid fuel. The low-temperature cells (AFC and PEMFC) require pure hydrogen, free of sulfur and carbon monoxide because these impurities act as electrocatalyst poisons. The hydrogen supplied to AFCs must also be free of carbon diox-

ide, which otherwise would react with the alkaline electrolyte to form solid carbonates that reduce the conductivity of the electrolyte and severely decrease the performance of the cell. (Obviously, if air is used at the positive electrode, this too must be purged of carbon dioxide.) The medium-temperature fuel cell (PAFC) does not pose quite so rigorous a purity specification, while the high-temperature fuel cell types (MCFC and SOFC) can burn carbon monoxide, and therefore, can accept fairly impure hydrogen derived, for example, from coal or natural gas (reactions (1)–(3)). Fuel cells are of interest for stationary, portable and mobile applications.

5.1. 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 Teflon-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 °C enables the platinum electrocatalyst to tolerate up to 1 wt.% (100 ppm) 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 over 250 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 airport terminals, hospitals, hotels, military facilities, office buildings, and schools.

Proton-exchange membrane fuel cells (PEMFCs) are also 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 versus 1–4 h). The central component of a PEMC is the so-called ‘membrane electrode assembly’, in which a sulfonated polymer membrane (usually, Nafion™) 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). The latter is an all-solid-state device with no liquid components. Both present difficult materials science and technology problems. Molten alkali carbonate at 600–700 °C is a most aggressive medium and corrosion problems are se-

vere 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 700–1000 °C 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 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.

Although steady progress is being made in the technology and engineering of fuel cells, it is unlikely that they will prove to be major competitors to lead–acid batteries in the field of stationary energy provision, both in the immediate future and beyond. This is because, despite the reliability, durability and cost limitations that have still to be overcome with fuel cells, it is likely that the two technologies will provide quite different services on account of the difference in the method by which they supply electricity. Fuel cells make electricity and require a continuous supply of fuel from an outside source, whereas conventional batteries, such as lead–acid, store electricity and require a supply of outside electricity to function. Thus, the capacity of a fuel cell is limited only by the size of the fuel and oxidant supply and not by the cell design, while the energy-storage capability is built into a lead battery during manufacture. (Note, for this reason, fuel cells are rated by their power output, kW, rather than by their capacity, kWh, as is the case for a battery.) Clearly, therefore, fuel cells are best suited to situations where sustained periods of power are required locally in, for example, distributed energy networks and base-load operations. By contrast, batteries are more appropriate for short-term storage/delivery applications, such as the provision of back-up power via ‘uninterruptible power supplies’ and the capture of electricity from renewable energy sources (principally, solar and wind). Moreover, the fast response of batteries makes them particularly attractive as emergency power sources.

5.2. 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.

Already, 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. These encouraging prospects for portable fuel cells will have little impact on the future business of lead–acid batteries as it has long been established that there are no substantial opportunities for this battery technology in portable-power applications.

5.3. 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.

Hybrid electric cars are of two basic types. The ‘series-hybrid’ has a purely electrical transmission and drive that is powered by a rechargeable battery that is recharged by a small ICE (typically, about 1-L capacity) via a generator. The engine–generator combination provides sufficient power to maintain the vehicle at a steady cruising speed, but is insufficient for acceleration or hill-climbing. In the latter two operations, the battery provides the necessary power boost. The series-hybrid has a comparatively large traction battery and may be operated with the engine switched-off as a pure electric vehicle in sensitive urban environments. The ‘parallel hybrid’ has a conventional mechanical transmission that links the engine to the wheels. The engine is sized for cruising and is boosted when required by an electric motor. The electric drive-train may be totally independent, e.g., with electric motors in the wheels, or may be integral with the mechanical drive-shaft. Parallel hybrids range from ‘full hybrids’, in which the electric drive provides a major part of the power when required, to ‘mild hybrids’ where the drive is essentially mechanical with the electric boost being limited to a few extra horsepower. In both designs of HEV, the battery system may be augmented by the inclusion of a supercapacitor, which provides an efficient means for the capture of energy from regenerative braking (during deceleration or hill descent, the motor converts the vehicle’s potential energy into electrical energy and puts charge back into the supercapacitor and/or battery). To date, most hybrids have been produced with a parallel configuration. In the final analysis, the choice of hybrid system depends on the required duty cycle of the vehicle, the degree of engineering complexity, the capital and running costs, and the emission regulations that have to be observed.

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. In the longer term, the ‘Holy Grail’ for road transportation is that of deriving hydrogen from water by electrolysis with electricity generated from renewable energy sources. This would provide a global transportation system that is truly sustainable, i.e., one that is supported by abundant energy supplies and has no environmental impact.

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. These factors have a 'theoretical' basis just as sound as the thermodynamic analysis of fuel-cell efficiency. They cannot be dismissed as temporary practical impediments that are simply waiting to be overcome by further development.

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 fuel cells, as for electrolyzers, there is a trade-off between size and capital cost on the one hand, and efficiency and running cost on the other. The larger the unit, the higher is the capital cost of construction—but the resulting low current density leads to high efficiency of operation. 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

fuel cell 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:
 $0.65 \times 0.9 \times 0.9 = 53\%$;
- hydrogen to low-voltage dc electricity: $0.50 \times 0.9 = 45\%$;
- low-voltage dc electricity to tractive effort: $0.9 = 90\%$;
- well-to-wheels efficiency (natural gas to tractive effort):
 $0.53 \times 0.45 \times 0.9 = 21\%$.

In other words, FCVs based on reformed natural gas have an overall efficiency that is close to that of present high-performance ICEVs, 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. If the natural gas is steam reformed regionally or locally, rather than centrally, then there would be some savings in the energy otherwise lost in distribution, but this would be offset by the lower efficiency (not to mention the higher cost) of the smaller reformers. Also, the sequestering of the carbon dioxide would become more complicated.

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 0.75–0.6 V, as determined by the current density. Thus, the electrolyser 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-fired or nuclear-fired) to 55% (combined-cycle gas turbine). The well-to-wheels efficiency from primary fuel to traction effort is then:

- coal or nuclear plant: $0.3 \times 0.45 \times 0.9 \times 0.9 = 11\%$;
- natural gas plant: $0.55 \times 0.45 \times 0.9 \times 0.9 = 20\%$.

Note, in these 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. If and when renewable electricity is available on a large scale, the overall efficiency figures should improve.

Table 1
Anticipated improvements in ICE technology [2]

	Fuel	Fuel consumption	
		MJ km ⁻¹	l 100 km ⁻¹
1996 Reference car	Petrol	2.73	8.46
2020 Technology			
Advanced spark ignition engine	Petrol	1.54	4.79
Advanced compression engine	Diesel	1.36	4.20
Hybrid spark ignition engine	Petrol	1.07	3.32
Hybrid spark ignition engine	CNG	1.03	3.20
Hybrid compression engine	Diesel	0.92	2.86

This is because the conversion of mechanical energy (e.g., wind or wave power) to electrical energy does not involve a Carnot cycle and the efficiency should be 80–90% rather than 30–55%. The extent to which such a move to renewable electricity is possible will be determined by cost considerations, by political acceptability and, ultimately, by having a practical means of electricity storage within the grid system.

In the meantime, it should be noted that the efficiency of ICEs is expected to improve rapidly, as demonstrated by the projections given in Table 1 for various configurations of family-sized cars in 2020 [2]. The data suggest that by converting to HEVs—a perfectly feasible proposition by 2020—it should be possible to reduce fuel consumption by two-thirds compared with the 1996 model family car. 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.

A key step towards the wider penetration of HEVs into transportation markets is the development of a low-cost battery. Present models are fitted with nickel–metal-hydride 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. Despite this common problem, these two battery chemistries will constitute a serious threat to automotive lead–acid batteries should they prove, on performance grounds alone, to be the only option for the desired new generation of road vehicles. Although the lead–acid battery offers a more affordable option, it suffers premature failure under the special duty demanded by HEVs [3]. If this limitation can be overcome, then the threat presented to lead–acid by the widespread introduction of HEVs could, in fact, be turned into an opportunity—such vehicles are likely to command a greater degree of energy storage than that required by present-day 12-V automotive systems. This, then, is the challenge facing the lead–acid battery industry—to develop a fully satisfactory battery for use in new-generation road vehicles, and then to expand production capability so as to meet the very large market that is likely to develop.

References

- [1] R.M. Dell, D.A.J. Rand, *Clean Energy*, The Royal Society of Chemistry, Cambridge, UK, 2004, <http://www.rsc.org>.
- [2] M.A. Weiss, J.B. Heywood, E.M. Drake, A. Schafer, F.F. AuYeung, *On the Road in 2020: A Life-cycle Analysis of New Automobile Technologies*, Energy Laboratory Report #MIT EL 00-003 Massachusetts Institute of Technology, Cambridge, MA, USA, October, 2000.
- [3] A. Cooper, L.T. Lam, P.T. Moseley, D.A.J. Rand, in: D.A.J. Rand, P.T. Moseley, J. Garche, C.D. Parker (Eds.), *Valve-Regulated Lead–Acid Batteries*, Elsevier, Amsterdam, The Netherlands, 2004, pp. 549–565.