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Electrochemical energy — progress towards a cleaner future: lead/acid batteries and the competition

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Abstract

Electric vehicles (EVs) with conventional architecture may be capable of a range of 72–80 km (45–50 miles) with a 35 Wh kg^{-1} lead/acid battery with a weight equal to 25% of that of the vehicle. An improved vehicle (such as the GM Impact) with lower energy utilization and architecture that allows greater battery weight may attain 160 km (100 miles). A battery corresponding to the mid-term goal of the US Advanced Battery Consortium in an Impact-type vehicle could allow 480 km (300 miles) range. It remains to be seen if this will be technically and economically attained. The EV is more likely to be made practical with the development of a satisfactory polymer-exchange-membrane (PEM) fuel cell, which will involve the same recharging logistics as those of a gasoline vehicle, with much improved energy efficiency. Considerable progress is still required, but one major problem, the amount of platinum catalyst required per vehicle, appears to have been overcome. A loading of 0.15 g/kW now appears to be feasible, so major production of such vehicles will allow platinum producers to keep pace. The advent of the PEM-fuel-cell/battery hybrid vehicle will open up a larger market for rechargeable batteries than that for vehicles which use traction batteries alone. Economics seem to point to the fact that such vehicles will use lead/acid batteries for the hybrid peak power and regenerative braking element.

Keywords: Electrochemical energy; Lead/acid batteries; Future

1. Transportation emissions

On 13 December, 1989, the California Air Resources Board introduced new rules on vehicle emissions to take effect later in the coming decade. These involved new categories of vehicles, including transitional low-emission vehicles (TLEVs), low-emission vehicles (LEVs), ultra-low-emission vehicles (ULEVs), and zero-emission vehicles (ZEVs). The latter were to produce no 'tailpipe' emissions at all, and would be electrically-powered. The requirement would be that all manufacturers selling more than 35 000 vehicles per year in California in the category below 3750 lbs (1.70 metric tons) curb weight would be required to sell 2% ZEVs in model years 1998–2000, 5% in 2001 and 2002, and 10% in 2003 and beyond. This was later modified to 'offer for sale', on the legal grounds that the state could not force the sale of any product to the public, however desirable it might pretend to be.

State law mandated that companies unable to offer for sale ZEVs would be fined $5000 per vehicle not provided for retail. The rule about ZEVs was sustained in May, 1994. According to present sales, the manufacturers involved will be General Motors (GM), Ford, Chrysler, Toyota, Nissan, Honda, and Mazda.

Even though the situation in the Atlantic States north of the Carolinas (the six New England States: New York, New Jersey, Delaware, Pennsylvania, Maryland, Virginia; and the District of Columbia) is not comparable with that in California, the Ozone Transport Commission (OTC) representing these jurisdictions was leaning towards adopting the California regulations. Massachusetts and New York had decided to go ahead, with Connecticut proposing the same, and other jurisdictions would follow if the decision were unanimous.

The OTC was established by the Clean Air Reauthorization Act of 1990 to allow coordination of activity between the different jurisdictions in a regional strategy to combat clean air problems along the 'Amtrack Corridor'. Whereas nitrogen oxides and reactive hydrocarbons, which photochemically generate ozone, are produced in the Los Angeles basin area, the North-

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eastern States receive windblown ozone from the Midwest, along with nitrogen oxides produced in Midwestern coal-fired power plants, which react with locally-generated hydrocarbons and make the situation worse. About 50% of nitrogen oxides are produced by power plants, about 26% is produced by heavy vehicles and locomotives, and about 12% is produced by older model automobiles. The last-mentioned represent about 10% of the total automobile fleet. The remaining automobiles are much cleaner, as they are for non-methane hydrocarbon (NMHC) or reactive organic gas (ROG) emissions. This is also true for CO emissions, which do not give rise to photochemical ozone. The ultimate sink of transported ozone and its precursor gases, along with CO and sulfur oxides also produced by coal-burning power plants, is the Atlantic Ocean.

The Northeastern States decided to accept California regulations in February 1994, but were threatened with lawsuits by the big three automakers, who pointed out the differences between the situations in these states and in California. In the Northeast, pollution incidents are less frequent and less severe than in the Los Angles basin. In addition, if the region adopted California cars, these were designed to operate on California gasoline, which is very low in sulfur and which was also specially tailored for pollution reduction in the Los Angeles climate. Finally, ZEVs using lead/acid batteries under California conditions would have their range degraded by only 25% in January, whereas cold days with 5 cm of snow in the Northeast could reduce the range by 50%. An electric heater could reduce it a further 30%, but in practice a chemical heater would be used. They also pointed out that a 2% mandate would be difficult to achieve. In California, only four GM models exceed 2% (Saturn SL, Pontiac Grand Am, Geo Metro, and Chevrolet Camaro). All are sub-compact to compact cars. An EV would therefore have to be a very popular model to sell well [1].

With New York and Massachusetts already being sued, the remaining states decided in May to ask the Environmental Protection Agency (EPA) to force them to adopt California regulations, so that the automakers would have to sue the Federal Government. Each state must devise a plan to comply with Clean Air Act regulations by 15 November, 1994, or risk being cut off from considerable federal funding. The states are now somewhat divided on the issue. Delaware, Virginia, and Pennsylvania have questioned the constitutionality of the OTC, which can petition the EPA on behalf of the region. The EPA had already interpreted the 1990 Clean Air Act in such a way as to not force the States to require ZEVs if they adopted California rules. The ZEV requirement would be optional. In consequence, New York and Massachusetts stated that they would require ZEVs, whereas Connecticut would only encourage their use.

The automakers offer a 'compromise' plan to sell second-tier LEV cars in the 49 states if California rules are not adopted, to avoid producing five tiers of vehicles with progressively tighter emissions. On 13 September, 1994 it was stated that the EPA was leaning towards this compromise. New York representatives stated, however, that they did not intend to back down from California regulations. If a compromise is not reached by 10 November, 1994, the whole region will be forced to accept the EPA's interpretation of California regulations (Note added in proof: the EPA missed this deadline.) If the 49-state plan is adopted now, individual states may adopt California rules when (and if) the EPA decides to half-present Federal emissions rules to the proposed 'Tier II' levels, if declining air quality makes this necessary. These would be (in grams per mile over weighted urban and highway driving): NMHCs, 0.125; CO, 1.7; and NO_x, 0.2. Nevertheless, the Clean Air Act prohibits this before 2003, and the voluntary 1999 plan proposed by the automakers would be both legally unenforceable and may not improve air quality sufficiently in the Northesat. How the situation evolves is important, since the twelve states and the District of Columbia account for 20% of total US car sales, the same as California itself.

2. Automobile fuel economy

The April 1992 report of the National Research Council committee on Fuel Economy, chaired by Richard A. Meserve, criticized the methods by which the Federal gasoline mileage standard (27.5 mpg in 1990) was established. It proposed higher taxes either on gas guzzlers or on gasoline, with subsidies for efficient cars. They could be in the form of increased registration fees on larger cars, with 'feebates' (a fee or rebate on registration, as was approved by the California legislature in 1990) for efficient cars. The report considered that a reasonable goal would be a Corporate Average Fleet Efficiency (CAFE) standard of 33 mpg by 2001 and 37 mpg by 2006, with only a 10% weight reduction with a modest cost in safety, and at a cost of $500 to $2500 per vehicle. Sub-compacts might obtain a realistic 39 mpg by 2006, averaged over the entire class of vehicles. Developments such as variable valve-timing would only add 6% to gasoline mileage, and not as much as 10%, as claimants had alleged. With less confidence, 44 mpg might be achievable using emerging technology. The Meserve report also pointed out that the majority of the American public did not want small cars. They required cars with four full-size seats, automatic transmission and air-conditioning. Indeed, the public preferred large cars, and the 27.5 mpg CAFE requirement had penalized the manufacturers of large cars, who had left the small car market to the Japanese. It called small Japanese vehicles such as the Honda

Civic 'specialty cars' that would not achieve their EPA rating of 59 mpg when they were fitted with automatic transmission and air-conditioning. The figure would be closer to 47 mpg.

During the Vice-Presidential Debate of the 1992 Presidential Campaign, Senator Al Gore called for a CAFE standard of 40 mpg, following suggestions taken from his book 'Earth in the Balance' [2]. This mentions Japanese progress in lean-burn engines which have high fuel efficiency, but which produce NO_x emissions which are too high. He was countered by Vice-President Quayle, who cited the Meserve report to demonstrate that this was not feasible.

On 29 September, 1993, President Clinton and Vice-President Gore, together with the Chief Executives of the big three automobile manufacturers, representing the United States Council for Automotive Research ('USCAR'), announced the formation of a new partnership for the non-competitive R&D stage of work to develop 'a new generation of vehicles'. The goals of the Partnership for a New Generation of Vehicles (PNGV), which was also nicknamed the 'Supercar' or 'Clean Car' Initiatives, were three-fold. The first was to improve national competitiveness and productivity in manufacturing by using 'agile and flexible' technologies with reduced costs and lead-times. The second would increase recycleability of vehicle components from 75 to 80%. The third was to improve fuel efficiency by using commercially viable technologies that reduce demand for energy from the engine and drive-train, with the ultimate aim of developing a vehicle that would achieve three times the average fuel economy in BTUs per mile of today's 'comparable' vehicle in the largest market segment, i.e., the 1994 Chevrolet Lumina, Ford Taurus, and Chrysler Concorde. The plan was to have concept cars by about 1999, and Production Prototypes by 2003. The vehicle should at least achieve proposed Clean Air Act Tier II emissions standards (see earlier). The programme would set new goals for competitiveness in the auto industry, which represents 13% of gross domestic product (GDP) overall, of which domestic assembly is 4.5%, and almost 25% of total energy demand. It would increase US competitiveness worldwide, reduce oil imports, and help greatly in achieving the goals of the 1992 Rio de Janeiro Greenhouse Warming Treaty by giving an easy way of reducing CO_2 emissions, if it can be implemented.

The stated aims were therefore to develop and demonstrate not 40 mpg, but three times today's gas mileage in a comparably-sized vehicle, i.e., 80–82.5 mpg or the equivalent, with very low tailpipe emissions. If the vehicle weight, aerodynamics, and rolling resistance remained the same, this would require a prime mover efficiency averaged over the urban and highway driving cycles of about 54%, compared with 34.2% today. This assumes that idling losses are eliminated, that drive-train losses are reduced by 50%, and that 50% of the braking energy can be recovered. These figures are considered in more detail later.

It was argued that the above aims could be carried out by using a hybrid motor with on-board energy storage that allows regenerative braking. The motor would operate at constant load at peak efficiency. Energy storage and drive-train coupling might be: purely mechanical, as with a flywheel, shafts, and gears; or electrical, with a secondary battery and/or an ultracapacitor, with final electric drive. The motor might be an advanced reciprocating engine operating on the Otto, Diesel, or other cycles, some other intermittent compression-internal combustion engine (e.g., a rotary Wankel engine), or a Brayton cycle gas turbine with heat recuperation. For the Otto and Diesel cycles, the emphasis was on lean burn, if NO_x emissions could be controlled. The Stirling cycle does not seem to have been suggested as an alternative, perhaps because of earlier experiences of the auto industry in attempting to develop it. On the other hand, the fuel cell was considered to be an alternative to the above.

A White House Conference, sponsored by Vice-President Gore, was held on 27 July, 1994 to discuss the feasibility of fuel cell technology for vehicle applications. The general consensus was that fuel cells, with their high intrinsic efficiency within the prime mover (the electrochemical engine) stood the best chance of achieving the required goals.

3. Automobile energy losses

The average mid-size car has an Otto-cycle spark-ignition engine that operates at a gross efficiency of 37.6% under urban conditions, and at about 30.8% under highway cruise, on a fuel lower-heating-value basis. This is because it operates at low engine revolutions under cruise conditions, and at higher average revolutions and at higher thermal efficiency in the city. These figures are degraded significantly, however, by idling losses that amount to 17.2% under urban conditions, and only 3.6% on the highway, giving 20.4 and 27.2% overall. Accessories necessary for vehicle operation (not including air-conditioning) are 2.2 and 1.5%, respectively, giving net efficiencies of 18.2 and 25.7% overall. Drive-train efficiencies are about 69 and 79%, respectively, so that overall efficiency (power out to tires) is 12.6% (Federal urban conditions) and 20.2% (Federal highway conditions), respectively. These must supply the kinetic energy for acceleration, which itself is lost in the form of heat by braking. The latter represents 5.8% of total energy under urban conditions, and 2.2% under highway cruise. The remainder of the energy must overcome the aerodynamic and rolling resistances of the vehicle. Under urban conditions, these

are 2.6 and 4.2%, respectively, whereas under highway conditions they are 10.9 and 7.1%. The losses are shown schematically in Fig. 1.

The energy per mile to overcome rolling resistance is largely independent of velocity, whereas that for overcoming aerodynamic drag increases as the square of velocity. Based on the above figures, the total energy required at the wheels per mile in urban use will be in the ratio 1:0.62:1.38, for rolling resistance, aerodynamic resistance, and acceleration/braking, respectively, whereas the corresponding ratios for highway driving will be 1:1.54:0.31. Since the rolling energy requirements per mile are similar in both cases, then the total energy requirement per mile (in dimensionless units) is 3.0 under urban conditions, and 2.85 for highway driving. Using the motor-drive train efficiencies of 12.6% (urban) and 20.2% (highway), the fuel consumption per unit distance on the highway should be 59% of that under urban conditions.

An industry-typical mid-sized car with the smallest engine offered (usually 3.0–3.1 liter V6) is rated by the EPA at 19 mpg (urban), 29 mpg (highway) [3] [1]. The treadmill duty cycle used by the EPA to determine urban gasoline mileage (the Federal Urban Driving Schedule, FUDS) simulates an average speed of 19.68 mph (31.67 kph) over a 1372 s driving cycle with 18 stops, with 17.9% of the time at idle. Higher speeds (up to 56.7 mph, 91.2 kph) are reached during the first 505 s of the cycle [4]. It is identical to the FTP 72 (Federal Test Procedure 72) test cycle used to determine US exhaust emissions in model years 1972–74, and which has been adopted by Australia, Mexico, Sweden, and Switzerland. This cycle is based on actual measurements in Los Angeles rush-hour traffic. The FTP 75 cycle, which has been used to measure legally-established emissions in the United States since 1975 and which is now used by Canada, consists of the FTP 72 cycle from a cold start, followed by a 600 s period with the engine off, which is again followed by the higher-speed part (the first 505 s) of the FTP 72 cycle (the hot transient). Emissions are determined for the first 505 s (the 'cold transient', average speed: 25.7 mph, 41.3 kph), the 867 s 'stabilized' part (average speed: 16.2 mph, 26.0 kph), and for the 'hot transient'. They are then multiplied by a factor of 0.43, 1.00, and 0.57, respectively. The results are added, and divided by the total distance (11.1 miles) to determine overall emissions.

The Federal highway cycle (FHDS) simulates rural roads and freeways with no intermediate stops, at an average speed of 48.5 mph (78.0 kph) over 10.3 miles in 765 s [4]. The laboratory results obtained under urban and rural highway conditions on a treadmill are then adjusted downwards by 10 and 22%, respectively, to give a better accounting of real-world driving [3]. Even so, experience shows that the typical urban rating it too high [2]. If 29 mpg is a correct figure for highway operation, and if this is 59% of the corresponding value under urban conditions, then 17 mpg may be a better estimate for city driving. Thus, the average energy use at the wheels under urban conditions (12.6% overall efficiency) will then be 0.25 kWh/mile (0.13 kWh/km). The corresponding value under highway conditions (20.2% efficiency) is 0.23 kWh/mile. It will be seen below that these figures give a better account of measured energy use per mile in electric vehicles.

[1] These figures refer to 1995 reformulated gasoline, containing up to 2.7% of oxygen by weight, depending on location and time of year. This is intended to help reduce CO emissions. The lower-heating-value of this gasoline is taken to be 114 132 BTUs per US gallon [18], less than the traditional rule-of-thumb value of 125 000 BTUs per US gallon.

[2] Ref. [1] uses unadjusted mean urban-highway mileage of 26.6 mpg for the various 1994 Chevrolet Lumina/Ford Taurus/Chrysler Concord models, i.e., the values which would be expected on treadmill tests.

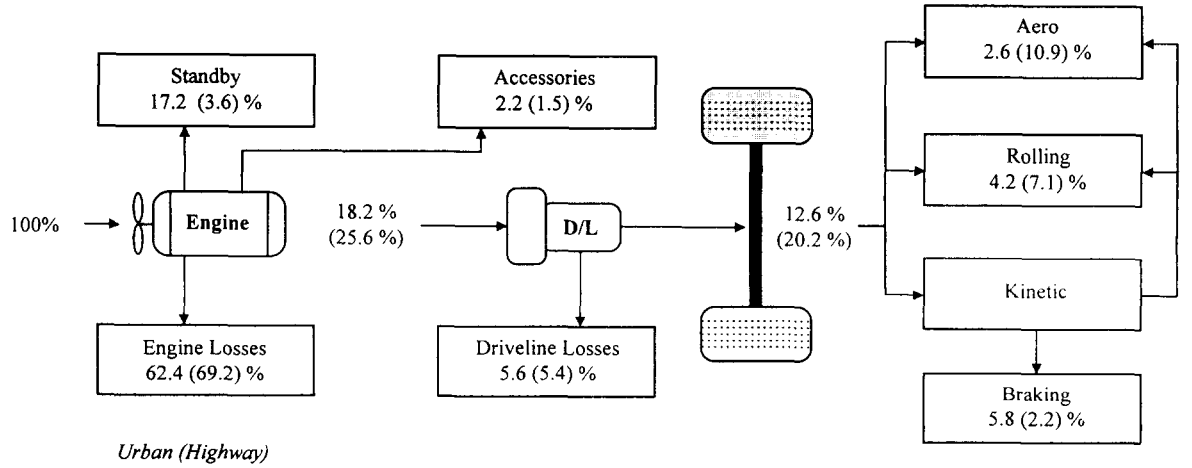

Fig. 1. Energy balances in typical mid-size cars under urban and highway driving conditions (cf. Ref. [18]).

4. A three-fold reduction in energy use

Without the mechanical losses for stand-by and accessories, the useful work output of today's engine corresponds to a gross mechanical efficiency of 37.5% under urban conditions, and 30.8% on the highway. Assuming that there are no improvements to the vehicle to decrease energy use at the wheels, and that the mechanical stand-by and accessory losses are proportional to engine efficiency, under a 55–45% mix of urban and highway miles, a mean engine efficiency of about 100% will be required to improve the energy use per mile of today's automobile by a factor of three. Clearly, the only way to effect this is first by reducing or eliminating losses outside of the engine, at the same time increasing engine efficiency. One loss that must be reduced or eliminated is idling at stand-by. Another loss that can be reduced, if not eliminated, is that due to braking. Some of the energy may be recuperated via electric or mechanical recovery of energy. For example, if regenerative braking can be used at 50% efficiency, urban energy requirements per mile measured at the wheels fall by 23% to 0.19 kWh per mile, and highway requirements fall by 5.5% to 0.22 kWh per mile. If idling at stand-by is eliminated by similar energy recovery at 67% efficiency, it and regenerative braking will reduce total energy requirements by 53% under urban conditions (i.e., 36 mpg), and by 13.5% (34 mpg) under highway conditions. This represents an improvement of 50% in overall gasoline mileage.

Without redesign of tires and aerodynamics and/or a reduction in vehicle weight, a further doubling would require a net engine thermal efficiency of about 59% (urban) and 56% (highway). It is unlikely that this can be achieved in any conceivable thermal engine. It may be achievable, however, in a vehicle that uses electric drive and an electrochemical engine (i.e., a fuel cell) as the prime mover in a hybrid configuration with a battery for energy storage.

One major advantage of a fuel cell (or indeed of all electrochemically-powered drive-trains) is the elimination of stand-by idle losses (with the exception of certain auxiliary power requirements). The electric drive (motor plus electronic controller) may be assumed to have an overall average efficiency of 0.84. Accessories are assumed to require 0.044 kWh per mile under urban conditions and about 0.017 kWh per mile under highway conditions (about 800–900 W, as in the gasoline-powered vehicle). With regenerative braking to the above specifications, 0.27 kWh per mile including accessories will be required under urban conditions at 19.68 mph average speed. This represents an average net power output of only 5.7 kW, with instantaneous power reaching approximately 50 kW (cf., Ref. [5]). On the highway at 48.5 mph average speed, 0.28 kWh per mile and 13.6 kW will be similarly required. Both the energy and power requirements are measured at the fuel-cell terminals.

Thus, a fuel-cell engine operating at a net average thermal efficiency of 55% should allow an energy consumption (in BTUs per mile) in a 55–45% mix of urban and highway driving equal to one-third of that in a gasoline-powered automobile of the same weight and design under realistic conditions. Whether this can be achieved at a realistic cost, and using which fuel, are discussed in a following section.

5. Fuel cells for transportation

Fuel cells are reviewed in Ref. [6]. Because of fuel-cell chemistry and electrochemistry, there are a limited number of choices of fuel-cell electrolyte, which determines the performance and operating temperature of the various systems [7]. All fuel cells operate internally on hydrogen fuel, which must be manufactured from conventional carbon-containing fuels, usually by steam-reforming followed by water-gas-shifting. At the present time, only low-temperature fuel cells operating at less than 200 °C are potentially suitable for transportation applications. If phosphoric acid electrolyte (PAFCs), proton exchange membrane electrolyte (PEMFCs), and alkaline electrolyte (AFCs) are used, fuel processing must be carried out outside of the fuel cell itself. The three systems require feedstock with increasing levels of purity. The AFC (operating at about 70 °C) requires pure, CO_2-free hydrogen (and oxygen or air) to avoid carbonatation of the electrolyte. The anode catalyst of the PEM (60–90 °C) is poisoned by CO in the parts per million by volume (ppmv) range, so this component must be removed by successive shift reactors, followed by a final polishing, normally by oxygen or air injection over a selective oxidation catalyst. The higher operating temperature of the PAFC (about 200 °C) allows it to tolerate up to 1.5% CO, so only low-temperature water-gas-shifting is required.

Fuel-cell systems have zero emissions from hydrogen fuel, and ultra-low emissions from natural gas fuel. For the stationary 200 kW ONSI PC25A PAFC (International Fuel Cells, South Windsor, CT), NO_2 emissions from the lean reformer burner have been measured at 0.45 ppmv [8]. This corresponds to 2.4 g/MWh, or 7×10^{-4} g/mile, based on the energy requirements given above. The present requirement for light-duty vehicles in the 49 US mainland states is 0.4 g/mile. Other emissions (CO, reactive organic gases, particulates) are below background [8]. If reformers similar to those used in the PAFC are used to make hydrogen from natural gas, the emissions for the overall fuel cycle will be negligible. If, however, fuel processing is carried out aboard the vehicle, the size and 800 °C operating temperatures of reformers for hydrocarbon fuels make their use unsuitable. By contrast, methanol fuel can be reformed at 250 °C in a relatively compact reformer.

All of the above fuel cells have attractive features. The operating temperature of the PAFC is high enough to supply excess steam for reforming, which increases system efficiency [9]. On the debit side, its stack materials are heavy, which makes the system suitable only for heavy vehicles. In addition, its high operating temperature is appropriate only for continuous duty. It is currently being used in an urban methanol-powered but demonstration project in Georgetown, Washington DC [10]. Attractive features of the AFC are high cathode performance and the ability to operate with non-noble cathode electrocatalysts [11]. Nevertheless, these features must be weighed against the requirements for pure hydrogen fuel and the problems of management of the liquid electrolyte (KOH solution) [11]. It would certainly not be practical to separate pure hydrogen from methanol reformate aboard a vehicle, and circulating KOH electrolyte has many practical difficulties.

6. The PEMFC

Up to the early 1990s, the PEM system, which uses fluorinated sulfonic acid polymer as the electrolyte (Nafion™, Du Pont de Nemours and Company; Aciplex™-S, Asahi Chemical Industry Company; XUS 13204.10, the Dow Chemical Company) was considered to be unsuitable for widespread use because of its high platinum catalyst requirements [12]. They were typically a total of about 8 mg cm^{-2}, or about 1.7 troy ounces (53 g) per kW in 1985. Thus, if a 20 kW fuel cell would be modestly required for a hybrid vehicle, it would have used more than 1 kg of platinum, worth more than $14 000 at present prices. An annual product of 100 000 vehicles, which would have had little overall impact on air quality or energy use, would have consumed the entire annual world production of platinum.

The problems reported between 1985 and 1986 involved very low platinum utilization due to the almost linear contact overlap between the comparatively thick electrodes and the pressure-bonded electrolyte film. Improved electrodes required impregnation with electrolyte material to increase the internal area of contact [13]. In recent times, however, platinum loadings have dropped by a factor of about 100, and performance has not been significantly compromised by the use of electrodes of improved structure. The effect is shown in Fig. 2, which has two plots showing the logarithm of platinum utilization as a function of time, and the value of a dimensionless function $\log f(1-f)$, where f is the estimated platinum utilization in the desirable cell voltage (or overall efficiency) range. Both represent excellent examples of learning curves. It is predicted that, by 1997, platinum utilization will approach 50%.

The best performance on hydrogen and air at atmospheric pressure reported to date on ultra-low-loading electrodes (0.05 mg cm^{-2}) has been obtained in the author's laboratory. It is illustrated in Fig. 3. It represents a platinum utilization at the cathode of about 20% in the 0.7 V range. The data should be compared with those of Fig. 4, which shows the corresponding performance of electrodes with 3 mg cm^{-2} of pure

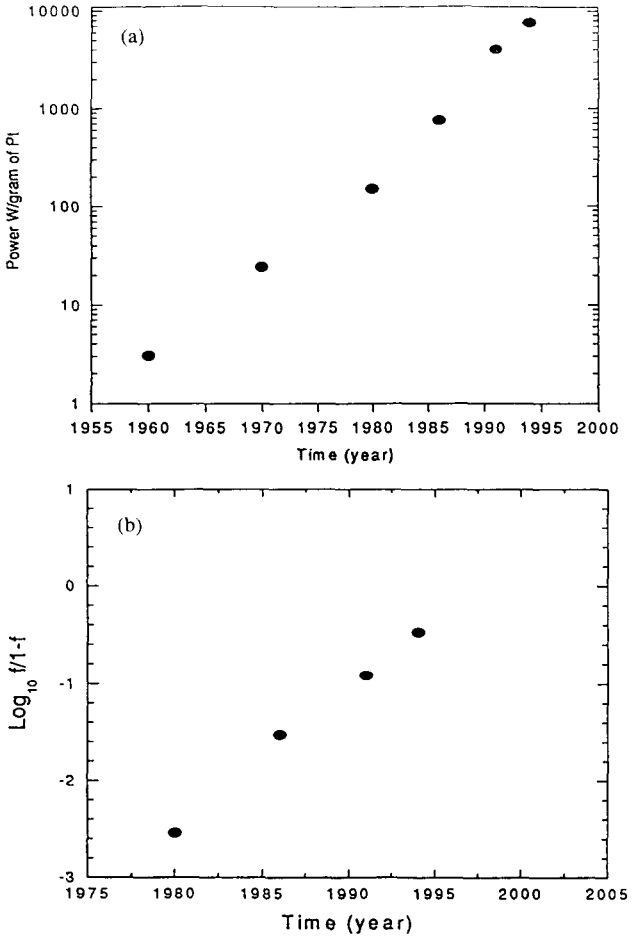

Fig. 2. (a) Power output per gram of platinum catalyst in PEMFCs under typical operating overpotential conditions as a function of calendar year of operation. (b) Plot of $\log_{10} f/(1-f)$ as a function of calendar year of operation, where f is utilization of platinum cathode catalyst under typical overpotential operating conditions.

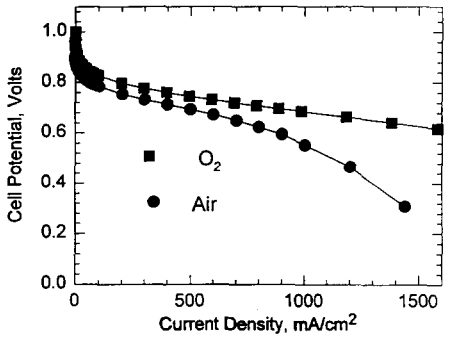

Fig. 3. Late 1993 performance of 5 cm^2 fuel cell operating at 1 atm absolute (atma) on pure hydrogen and air at low utilization, using 0.05 mg cm^{-2} of platinum (20 wt.% on carbon) at 70 °C with Asahi Chemical Industry Company Aciplex™-S membrane (from Ref. [14]).

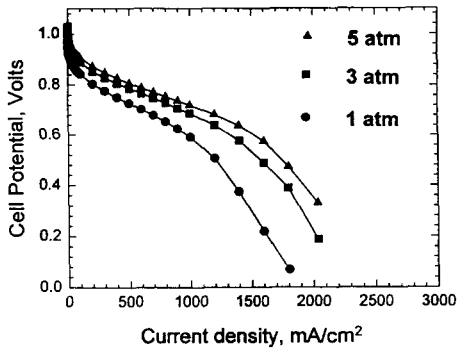

Fig. 4. Performance obtained in 1992 with 3 mg cm^{-2} pure platinum black electrodes on hydrogen–air as a function of pressure.

platinum (non-carbon-supported) on hydrogen and air at 1 atm absolute (1 atma), 3 atma, and 5 atma. It is of interest to compare the voltage–current density slope in the linear region at 1 atma in Fig. 4 with the corresponding range in Fig. 3, which indicates an improvement in the diffusion performance of thinner electrode active layers.

Based on the performance shown in Fig. 3, and assuming that the less exigent anode can use 0.025 mg cm^{-2} of platinum catalyst, approximately 3 g of platinum will be required in a 20 kW fuel cell rated at 0.6 V, 0.88 A cm^{-2} under these conditions (0.53 W cm^{-2}). By contrast, 0.74 V and 300 mg cm^{-2} might be available under cruise conditions (0.22 W cm^{-2}). This corresponds to a total power output of 8.3 kW, which is sufficient for a small car (see below).

7. PEM water management

PEM membranes only conduct protons if they contain water. Since small laboratory cells must often be operated with a large excess of reactant gases, these must be humidified to avoid drying and loss of conductivity of the PEM film. Humidification of reactant gases is not practical in a vehicle fuel cell unless elaborate engineering is used. For example, the Ballard Technologies fuel-cell stack contains a built-in membrane humidifier for the reactant gases. A better solution would be the use of product water for internal humidification.

A major step forward has been a patented PEM structure that proposes the use of thin cast PEM layers on the electrodes to allow rapid water transport from cathode to anode [15]. The cell must be operated at temperatures and oxygen utilizations so that the membrane is always in contact with an adequate partial pressure of water vapour. Fig. 5 shows results in a cell that is not fully optimized from the membrane-electrode assembly (MEA) viewpoint, since it uses Nafion® 115 electrode and 1.5 mg cm^{-2} platinum electrodes. It does show, however, that this method of operation is satisfactory on hydrogen and air at 2.4 atma at current densities up to 1.0 A cm^{-2}. Fig. 6 gives a similar plot, this time for hydrogen and oxygen at pressures of 1 to 2.4 atma, at both 50 and 70 °C, with 0.4 mg cm^{-2} electrodes. It shows that internal water transport into the membrane is satisfactory up to current densities of 3.0 A cm^{-2}. In several current PEMFC stacks (e.g., Siemens, Ballard), humidification is conducted through membranes in special cells in the stack that contain cooling water. This must be pure water, which is a great disadvantage for vehicle operation under subfreezing conditions.

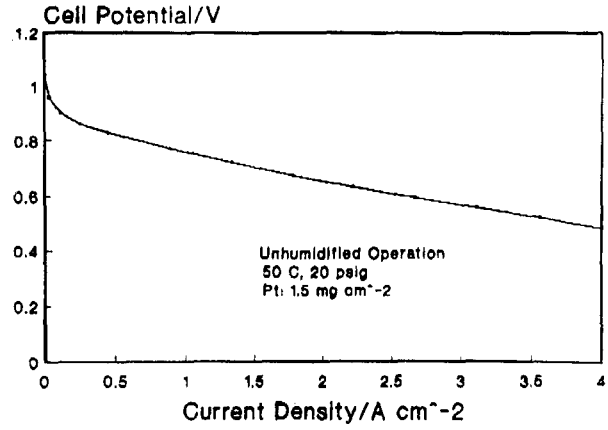

Fig. 5. Cell with Nafion® 115 membrane and 1.5 mg cm^{-2} platinum electrodes. Performance on hydrogen–air at 2.4 atma at current densities up to 1.0 A cm^{-2}.

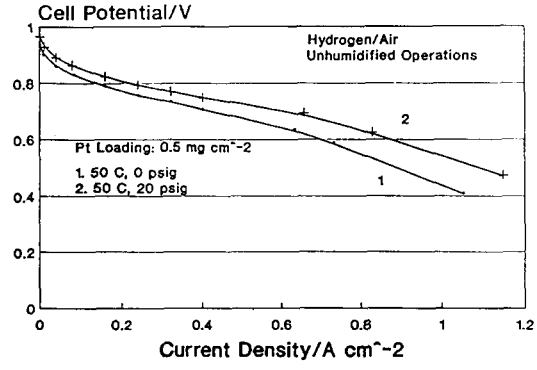

Fig. 6. Performance plot for hydrogen and oxygen at 1 atma to 2.4 atma at 50 and 70 °C for 0.4 mg cm^{-2} electrodes. This demonstrates that internal water transport into the PEM is satisfactory up to current densities of at least 3.0 A cm^{-2}.

8. Choice of fuel and operating conditions

Ref. [5] gives an extensive presentation of PEM fuel-cell system designs for a range of GM vehicles. They are based on the use of a PEMFC pressurized to 3 atma to increase current density at rated power to 1.0 A cm^{-2} at 0.7 V. Using a compressor and expander with efficiencies in the 70% range, the compression

requirements for two stoichiometric equivalents of air are about 9.3% of total electrical output at 0.7 V, corresponding to 65 mV. This increases to 75 mV at 85% motor-controller efficiency. Inspection of Fig. 4 shows that pressurization is essentially self-defeating in systems that are intended to operate at constant efficiency, since the current density at 0.625 V at 1 atma is about the same as that at 0.7 V and 3 atma. Consequently, optimization for atmospheric pressure operation may be the best choice for the designer of PEM fuel cells for automobiles. This also decreases system complexity, and can reduce fuel cell weight by elimination of heavy components in a filter-press configuration, or that of a heavy pressure vessel.

The weight and volume of the proposed electrochemical engine in Ref. [5] corresponds to 3.7 kg kW^{-1} and 6.01 l kW^{-1}. The compressor and methanol fuel processing system in Ref. [5] is about two-thirds of the total volume. Its relative mass is presumably somewhat less than this. The proposed system operates on hydrogen-rich gas with an anode that is resistant to CO-poisoning in the few ppm range; this reflects the potential for reverse water-gas-shifting in the fuel cell when CO levels are reduced below the equilibrium shift level by partial oxidation. The loading of platinum–ruthenium catalyst required to effect this over long periods of operation has yet to be established. The system is designed to operate at 80% hydrogen utilization, so that anode effluent can be burned to provide reforming heat (which requires 50% of the total) and heat of evaporation of methanol and water. The reformer efficiency is about 93%, and represents the lower heating value (LHV) of output hydrogen divided by the total LHV of methanol plus hydrogen plus anode exhaust. At 0.608 V (the effective cell voltage after allowing for parasitic work), the fuel-cell 'in-cell' efficiency for hydrogen use is (0.608/1.255) or 48.4%, where 1.255 V is the LHV of hydrogen under standard conditions. Corrected for hydrogen utilization, this is reduced to 38.8%. Since one equivalent of methanol produces one of hydrogen, this must be multiplied by the ratio of the LHV values of hydrogen and methanol to give the overall system efficiency, i.e., by (1.255/1.1028), to yield 44% overall.

The methanol is produced from natural gas by reforming and catalytic combination in a process that produces the by-product hydrogen. The process thermal efficiency is about 67%, if it is assumed that the hydrogen can be used elsewhere. Thus, the above electrochemical engine has an approximate rated efficiency of 29.5% based on primary energy, from natural gas. By contrast, an electrochemical engine operating at atmospheric pressure and 0.7 V on hydrogen produced from natural gas by steam-reforming and pressure-swing absorption at 70% efficiency would have an overall efficiency of 37% based on natural-gas primary energy LHV input. This assumes 99% utilization of 'pure' hydrogen in the cell to allow for purging of impurities, and 3.8% of electrical output required as parasitic cooling work. The upper limit of CO_2 impurity has yet to be established, since it will depend on the kinetics of the reverse water-gas shift reaction on the anode, and the degree of hydrogen loss permitted in the purge or bleed. A fraction of 1% (perhaps 0.25%) seems to be allowable.

No allowance has so far been made for compression work in this simple analysis. If hydrogen is to be compressed from 20 atma (294 psia) to 340 atma (5000 psia) at 80% compressor efficiency, about 3.6% of the LHV will be required (as work). If this is provided by electricity produced from natural gas at 40% efficiency, the overall production efficiency of compressed hydrogen falls from 70 to 64%. Work should be partially recovered from compressed hydrogen aboard the vehicle, at an expander efficiency of, for example, 70%. The recovered energy may be used to supply auxiliary requirements. This will effectively increase the net efficiency of the fuel cell by 2.5% to 55.6%. Thus, the overall LHV system efficiency (natural gas to fuel cell terminals) will be about 35.5%.

9. Lightweight fuel cells in vehicles

It is now possible to operate a PEMFC with ultra-low platinum loading at atmospheric pressure without extensive pre-humidification. This is a major step forward. A practical vehicle, however, requires an inexpensive, lightweight fuel cell design, which is a major challenge. Any on-board system must be ultimately air-cooled, and direct air-cooling can be used with a lightweight atmospheric pressure stack. The product water in the PEMFC has a pH in the range 4.5–6.4, and dense graphite is therefore not necessary for a corrosion-resistant bipolar plate, as it is in the PAFC [6,9]. The membrane-electrode assembly in today's PEMFC using carbon cloth with 40 wt.% Teflon® as both electron support and current collector[3] weighs 600 g m^{-2}, or 0.27 kg kW^{-1} at 0.74 V.

The bipolar plates and flow fields in a lightweight PEMFC must be designed commensurately. It is anticipated that the membrane electrode assembly and the electrode flow fields may weigh about 1.5 kg m^{-2} of active area. Lightweight conducting plastic bipolar plates would weigh about 0.2 kg m^{-2}. The repeat unit, two such cells with a cooling plate, should weigh about 4.7 kg m^{-2}. All cells will be bonded (as in the zinc/bromine battery) to avoid the use of heavy end-plates and tie-bars. Each cell could produce 0.22 mW cm^{-2} at 0.74 V (59% LHV efficiency on hydrogen), 0.30 mW

[3] Textron Specialty Materials, Inc., Lowell, MA. Weight 135 g m^{-2}.

cm^{-2} at 0.7 V (gross 56% LHV), 0.48 mW cm^{-2} at 0.6 V (48% LHV), with a peak power of about 0.58 mW cm^{-2} at 0.48 V (38% HHV).

10. Power and energy requirements – Geo Metro electric vehicle

The power and energy requirements used in the author's work were based the General Motors Geo Metro, a four-seat sub-compact built by Suzuki, which is powered by a three-cylinder 1.0 l 45 kW IC engine that conforms to California emissions standards. An electric conversion of this car was fitted at Texas A&M University with a 375 kg zinc/bromine battery developed by SEA in Austria in 1991–92. The battery stored 22.5 kWh, and the car consumed 18.0 kWh in 120 min at 95.0 kph on the Chrysler test track in Phoenix, AZ, i.e., it required 9.0 kW from the battery terminals at this cruise speed, giving an energy consumption of 0.094 kWh/km (0.15 kWh/mile). With regenerative braking, the corresponding energy consumption in typical city driving was close to 0.1 kWh/km (0.16 kWh/mile). The total weight of the vehicle with driver and passenger was 1250 kg, about 25% more than that of the original loaded IC-engined version. It is noted that the generic, mid-size car discussed earlier has a weight with driver and passenger of about 1725 kg. The energy consumptions at the battery terminals for the Geo Metro, corrected for vehicle weight, correspond to 0.13 and 0.14 kWh/km (0.21 and 0.22 kWh/mile) for highway and urban use for a mid-size car. Assuming 84% average controller-motor-drive efficiency, these consumptions are about 26 and 23% less at the wheels than the values estimated earlier for a generic mid-sized car on the FUDS and FHDS cycles. This is explained by the fact that: (i) driving involved light-use regimes, with less heavy acceleration and maximum speeds than the FUDS cycle, and with very little highway acceleration; (ii) electrical auxiliaries are not included; (iii) the Geo Metro was fitted with special Goodyear low-rolling resistance high-pressure tires. Calculations show that each of these three factors contributed about equally to the lower estimated energy use per mile.

For a Geo Metro class vehicle, it is proposed that a fuel-cell stack with 20 kW rated power would be sufficient. It should be capable of supplying 8.5 kW for efficient cruise of a Geo Metro at 90 kph (55 mph) and hybridized with a small traction battery for regenerative braking, start-up, auxiliary power, and for extra power for hill-climbing and high acceleration. The fuel cell would operate at a lower average load in the FUDS cycle than in cruise. With an allowance for on-board partial recovery of hydrogen compression work for auxiliaries (e.g. about 3.8% of output for a cooling fan), and assuming 99% hydrogen utilization to allow for purging to remove impurities, operation at 0.74 V corresponds to 56% LHV efficiency. A 3 kWh, second-generation battery capable of producing a peak power of 24 kW (8*C*) would suffice as a hybrid This may be itself hybridized with an ultracapacitor to allow short bursts of power. This battery is likely to be an advanced lead/acid battery that weighs about 85 kg.

An air-cooled fuel-cell stack with a peak power of 20 kW might have 4.17 m^2 of active area, with a total weight of platinum equal to 3.1 g, assuming 50 μg cm^{-2} at the cathode and 0.025 μg cm^{-2} at the anode. With a ΔT of 20 °C, it will require a cooling flow equal to 36 times the process air flow at 50% oxygen utilization, to give a velocity of a few m s^{-1} through the cooling plates. Such a stack would weigh about 14.7 kg overall and could be rated at 20 kW at 0.6 V.

An electric Geo Metro with driver and passenger, but without batteries, weighs about 880 kg. With the above fuel cell, battery, and composite pressure tanks weighing 62 kg and storing 5 wt.% (3.1 kg, 103.4 kWh thermal) of hydrogen, the vehicle would weigh about 1050 kg, compared with 990 kg for a gasoline version [4]. Because of its lower weight, it would use 90% of the energy per km of the 1250 kg battery vehicle, i.e., 4.6 g/km (7.4 g/mile) of hydrogen averaged over the Federal mix of highway and urban driving. This will allow 670 km (416 miles) range under these conditions, about 10% more than the PNGV requirements outlined in Ref. [18]. The average energy use per mile (measured as compressed hydrogen) would be 0.248 kWh (thermal) per mile, compared with 0.706 kWh (thermal) per mile using the EPA corrected FUDS (55%) and FHDS (45%) gasoline mileages (i.e., 46 and 49 mpg). Whether these high values are correct in real driving is of course open to question, since the corresponding figures for a three-speed automatic model are 36 and 39 mpg, or 0.895 kWh (thermal) per mile. Thus, even if the above figures are discounted by 20% to allow for greater accelerations, the hydrogen fuel cell car will consume 2.35 times less energy per mile than the five-speed manual version, and 3.0 times less than the three-speed automatic.

In a mid-size gasoline car under FUDS conditions, an air-conditioner operating at an average load of 2 kW will require about 0.27 kWh (thermal) per mile of

[4] The latest pressure tank design, with an interior metallized mylar film for sealing, with aerospace-quality graphite fibres wound on an inflatable mandrel, is capable of storing 14.3% of hydrogen by weight. Its safety factor is 2.25, the same value as that used for today's compressed natural gas tanks. The use of such a tank would reduce vehicle weight by 40 kg, and would improve performance correspondingly. The total weight of fuel plus tank will be about 23 kg, compared with 32 kg for a gasoline vehicle giving the same range. At 340 atma pressure, the volume of the tank plus hydrogen would be about 125 l, compared with about 35 l for gasoline. For a methanol fuel-cell vehicle, the corresponding figure for the fuel plus tank would be about 25 kg and 25 l. (Compressed gas tank data are from Ref. [16], cf., Ref. [17]).

gasoline, and 0.134 kWh/mile under highway conditions, to give an averaged value of 0.21 kWh/mile. This degrades average gas mileage by 12–15%. A similar air-conditioning load will increase gasoline consumption substantially in a subcompact; the exact amount depends on the engine speed range, i.e., on gearing. For the Geo Metro with manual transmission, it will be reduced by about 23%, averaged over the FUDS and FHDS cycles. In an automobile with an electrochemical engine operating on hydrogen, the corresponding energy requirements for a 2 kW air-conditioning load will be about 0.18 kWh (thermal) per mile and 0.074 kWh/mile of hydrogen, to yield an average of 0.14 kWh/mile. Thus, operating with air-conditioning will degrade average energy use by 36%. Clearly, this problem will require attention, for example, the use of improved insulation (aerogels), double thin-panel glazing, reflective coatings, with improvements in the air-conditioning cycle and coefficient of performance.

11. Conclusions

The amount of noble metal per small vehicle with a hydrogen-powered electrochemical engine is now projected to be similar to that in a catalytic converter. At present prices, the cost of the platinum it would contain would be about $40.00 (i.e., $2.00/kW). The production of 10 million small vehicles per year could be supplied by 25% of the platinum presently mined, or 30 tonnes per year. The remaining materials, except for the PEM membrane, are inexpensive, and cost about $2.00/kg. Depending on the manufacturer, the PEM membrane costs between $650 m^{-2} and about $2150 m^{-2}, or approximately $6.00 and $20.00 per gram, the cost of a new generation of pharmaceutical products. The manufacturers state that if production increases by two orders of magnitude, then the cost of the membrane will fall by one order of magnitude. A cost of $650 m^{-2} corresponds to $135 kW^{-1} (estimated at 0.6 V) or $325 kW^{-1} (at 0.74 V). A reduction in cost to $13.50 kW^{-1} at 0.6 V would be acceptable, and would give a total materials cost for the fuel cell stack of $17.00 kW^{-1}, 80% of which would be the PEM electrolyte.

When and how can this cost be achieved? The PEM membrane for the vehicle fuel-cell corresponds to only one layer of a multilayer structure used by the Chlor-Alkali industry. The total amount of PEM material produced by all manufacturers today for Chlor-Alkali applications is about 25 000 m^2 per year, i.e., the equivalent of an annual production of about 60 000 small vehicles. An increase of 2.2 orders of magnitude for a production of ten million vehicles per year may result in a decrease in cost by a factor of 13. The constraints on price are less restrictive for heavy vehicles, that will require larger membrane areas. In the meantime, other improvements can be anticipated, such as the introduction of thinner membranes to reduce cost further and increase performance. Electrolyte costs are likely, however, to be the pacing item. A concerted effort to develop alternative and less expensive membrane chemistry seems indicated.

An affordable price for the electrochemical engine appears to be eventually feasible. The fuel, i.e., hydrogen, should also be affordable. At natural gas future costs of $2.20/MMBTU (compared with US spot prices of only $1.60 in September, 1994), the cost of the natural gas fuel itself would be $3.15/MMBTU of hydrogen. If a gas-station production unit requiring no labor input (as is the case of the ONSI 200 kW PAFC fuel-cell reformer) has fixed costs equal to twice those in a refinery-scale production unit (i.e., about $6.00/MMBTU), then the total cost would be $9.15/MMBTU. This is the equivalent of gasoline at $1.05 per gallon. With the promised economies of energy use per mile, this would be welcomed by consumers.

Calculations based on known vehicle energy utilization under real operating conditions, which are close to the FUDS and FHDS cycles, indicate that a three-fold improvement in energy utilization per unit distance in a car whose architecture is similar to that of today's may eventually be close to being achievable. A vehicle with the architecture of the GM Impact with its excellent aerodynamics and low rolling resistance would perform better. It appears to have an energy use that represents about a 20% improvement over that of the Geo Metro considered in this paper.

While the fuel-cell-powered small car seems to be economically attainable, especially if an operating lifetime of only 3000–5000 h will suffice, the first application may well be in heavy vehicles. This will have the advantage of reducing the high NO_x emissions of large diesels, which represent about 57% of NO_x emissions in the total ground transportation sector (including trains). For heavy vehicles, the prime mover should have an operating lifetime of 50 000 h, and a much higher initial cost per kW is permissible. Volume and weight restriction per kW are also much less than for small vehicles. Whether the PAFC (with methanol fuel) or the PEM (with methanol or hydrogen) will be most advantageous remains to be seen.

The final question concerns the hybrid battery. It is widely admitted that the lead/acid battery has energy density and lifetime limitations that will reduce the performance and effectively increase the operating cost of electric vehicles that rely entirely on battery traction. Nevertheless, lead/acid is still the system of choice over nickel/cadmium, because its first cost is 2.5 to 4 times less. Even so, nickel/cadmium offers a 50% higher energy density, and increases the range of a vehicle powered only by traction batteries. The only other aqueous battery that may show reasonable cycle life and whose cost

may be feasible (i.e., equivalent to that of nickel/cadmium if materials recovery is allowed for) appears to be nickel/metal-hydride. It may have a somewhat higher energy density than that of nickel/cadmium. It is not yet, however, a definable system. The same is true for zinc/air, which has yet to be proven rechargeable. Rechargeable zinc/manganese dioxide, which is attractive on paper, still must show proven cycle life. High-temperature batteries (sodium/sulfur, sodium/nickel-chloride, possibly lithium/iron-sulfide) may offer a 50% higher energy density than that of nickel/cadmium, but at an indeterminate (and high) cost, and with indeterminate reliability. Lithium/organic systems with liquid or polymer electrolyte may (again on paper) show higher energy densities, but they will be limited in rate and will have strongly rate-dependent energy density. Lithium-ion batteries will show the same limitations, but will also have lower energy densities, perhaps only 50% greater than that of nickel/metal-hydride.

Hybrid vehicles with electrochemical engines present a different series of options. To avoid over-sizing the fuel cell, a hybrid vehicle must have a battery of some type even if storage of regenerative-braking energy for acceleration is provided by an ultracapacitor of limited storage capacity. The battery will no longer be the controlling factor over vehicle range. The battery must be reliable and affordable. An advanced lead/acid battery is the logical choice in the new market that may be opened up by the fuel-cell electrochemical engine.

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