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BATTERY SYSTEMS FOR ELECTRIC VEHICLES — A STATE-OF-THE-ART REVIEW

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Summary

The future economy demands the development of more efficient power sources for urban vehicles. These sources could be electrochemical systems, *i.e.*, batteries or fuel cells or battery—fuel cell hybrids. The purpose of this paper is to review the current world effort being directed towards developing advanced battery systems for electric vehicle power source applications.

The relative merits of the various battery types under examination will be discussed in terms of their efficiency, performance, convenience, cost, and the availability of their component active materials. These factors are important in deciding whether a particular system will be suitable for use in electric vehicles.

SUMMARY

1. Introduction

The need to introduce electric vehicles into the transportation sector as replacements for the petroleum-powered lorry, delivery van, and domestic motor car has been the subject of world-wide debate during the last few years. In the United States the first Bills dealing with electric vehicles were introduced in the 89th Congress in 1966. Original interest in electric vehicles arose mainly from the concern over atmospheric pollution attributable to exhaust emissions from petroleum-powered cars. Recently [1], a survey by 300 civic environmentalist groups operating 22 000 monitoring points in and around Tokyo showed that auto emissions, and not industrial plants, were the main cause of air pollution in that city. Criticism that noxious pollutants are not avoided by the introduction of electric vehicles, but are merely moved to a central power plant, can be answered by a report [2] by Electric Vehicle Associates in which emissions associated with the electric vehicle (calculated by taking standard Environment Protection Agency emission figures for coal-fired power stations and dividing by the number of electric vehicles serviced) were compared with those from the conventional car. It was found that 0.25 and 0.87 g/km of hydrocarbons and nitrogen oxides, with a negligible amount of carbon monoxide, were attributable to the electric vehicle, whereas the amounts emitted from the internal combustion-engined (i.c.e.) car were 0.93, 1.93 and 9.32 g/km, respectively. E.P.A. studies in the U.S.A. have shown that transportation contributes approximately 42% of the total emissions, with the car being the largest single polluter of the atmosphere. In Australia, stationary sources are responsible for only 10 - 15% of the total pollution. Large-scale introduction of electric vehicles will certainly increase emissions from power stations, but in the cause of a cleaner environment it is easier to limit and/or control the pollution from the central power source for electric vehicles than the pollution from the multiple, mobile sources associated with conventional transport. Replacement of i.c.e. vehicles by their electric counterparts would also result in an abatement in acoustic pollution, since battery-powered vehicles are exceptionally quiet.

The case for electric vehicles was further strengthened by the Oil Crisis of 1973 which reminded the world that fossil fuel supplies were, indeed, finite. A recent study [3] by the West German Institute for Geophysics and Raw Materials concluded that world resources of fossil fuels will be exhausted by the year 2080. The decision of the O.P.E.C. countries to restrict the supply of oil, and the later quadrupling of crude oil prices, caused consumer countries to become conscious of their vital dependence upon fossil fuels. In the United States, over 95% of the energy input to the transportation sector is from oil, and transport accounts for nearly 55% of the petroleum consumption, with passenger vehicles accounting for 80% of the oil used by road vehicles [4]. In Australia, land transport accounted for 47% of the total petroleum consumed in 1975/1976 [5], and the September 1977 Report of the National Energy Advisory Committee stated [6] that motor cars and station wagons use over half of Australia's transport fuels, with 25% of the

fuel being consumed by private cars for travel to and from work, mostly with driver only or driver plus one other passenger. In the U.K., a recent report [7] by the Department of Energy has claimed that battery power could replace some 70% of the fuel used by cars and light vans, which at present consume three-quarters of this nation's total transport fuels. These considerations, together with world-wide determination to seek ways of conserving existing fossil fuel supplies and to develop alternative forms of energy (*e.g.*, solar, aeolian, tidal, geothermal, etc.), suggest a future "Electric Economy" with good prospects for a viable electric vehicle industry.

Electric vehicles, even at their present stage of development, appear to be economically attractive, for instance, for the indoor industrial transport of materials, products and personnel, and for house-to-house distribution of dairy products and postal items, that is, for a variety of short-haul, multiple stop, pickup and delivery services needing light commercial vehicles running on established duty cycles with known mileages. Electric delivery vans have been used successfully for many years in the U.K., and currently about 40 000 are operating on the nation's roads. It also appears possible to run electric vehicles within a large bus fleet [8], and more than thirteen different kinds of electric buses are in operation in England, France, Germany, Japan, and Australia [9]. Compared with oil-run vehicles, battery-powered work vehicles offer low maintenance costs, as well as low running costs due to the lower cost of electricity and the use of off-peak power for recharging. For example, tests carried out by the U.S. Postal Service on 31 electric vans showed that energy and maintenance costs averaged $142* and $172 per year, respectively, compared with $251 and $363 per year for petrol vehicles in the same service. Other reports [10, 11] have shown a cost comparison index, taking the electric vehicle as the base at 100, of 138 - 169 for the comparable diesel vehicle and 147 - 183 for the petrol-powered equivalent. Electric work vehicles also offer benefits for indoor operations in reduced fume and noise levels, and in greater safety through simple controls and reduced fire hazard.

The economic feasibility of electric vehicles for private travel has yet to be proved. However, in a recent study of future transport fuels, Chapman *et al.* [12] conclude that electric cars with high energy density batteries (*v.i.*) will be the most likely choice for road transport in Britain about the year 2025 when oil supplies are expected to be exhausted. The only other strong candidate would be an i.c.e. running on a synthetic liquid fuel derived from coal, although this would only be an interim solution whilst coal supplies last.

The heart of an electric vehicle is its battery and the key to the future of the electric vehicle industry is a better battery — one that weighs less, is more compact, stores more energy, lasts longer, can be recharged more rapidly, and costs less than existing ones. However, the long-awaited break-through in battery development has not taken place, and the electric passenger

*All monetary values reported in this paper are given in U.S. dollars.

vehicles being tested today operate mostly on the lead–acid system. This battery will remain dominant in the near-term, but even with improvements in battery performance, technological advances in vehicle design, and more efficient transmission and control systems, it is unlikely that lead–acid powered vehicles will provide the private owner with the speed and the range that he has come to expect from the petroleum-run car. The National Academy of Sciences recently completed a market study of electric vehicles and concluded that a competitive family model would need a range of 322 km (200 miles) and a cruising speed of 88.6 km/h (55 m.p.h.).

The performance of present electric vehicles is limited mainly by the low energy and limited power densities of the lead–acid battery. The weight penalty thus imposed limits the range of 4-seat passenger cars to about 150 km* and the cruising speed to about 55 km/h (Table 1) — a performance still well below that advocated in the N.A.S. study. Also, the ranges of all types of vehicle are reduced under the stop/start conditions of urban driving, and this will be more serious for electrics because of their initial short range and the long recharge time of the batteries. The range of the CDA Town Car fell from 166 km at a constant speed of 64 km/h to 118 km at a maximum speed of 56.4 km/h with 2 stops per 1.6 km. Considerable attention has been paid to establishing minimum performance standards for electric vehicles by defining driving patterns that are truly representative of the particular environment in which the vehicle is intended to be used. Several versions of urban, suburban, and intercity driving schedules have been proposed during the past few years, and the most widely adopted are those formulated by the Society of Automotive Engineers, Inc., in the U.S.A., *i.e.*, Test Procedure SAE J227a, schedules B (fixed-route urban), C (variable-route urban) and D (variable-route suburban).

An i.c.e. vehicle can be refuelled in a minute or so, but refuelling (recharging) a battery vehicle takes hours and this is inconvenient for private travel. There is a limit to the rate at which a battery can accept charge, and unless careful control is exercised, high rates of charging lead to raised temperatures which will, in turn, cause rapid deterioration of the battery. Present opinion is somewhat sceptical of the advantages claimed for rapid recharging techniques and tends to favour methods that maximize charging efficiency and prolong battery life.

Lead–acid batteries available now have energy densities in the range 22 - 30 W h/kg (at the 1-hour rate), whereas the Chapman Report [12] suggests that batteries with energy densities greater than about 80 W h/kg are required to give an electric vehicle a range of between 200 and 250 km. Each "authority" in the field appears to have his own idea on the size, performance, cost, comfort, and handling and safety characteristics that a

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*In comparing the performances of different models it should be remembered that the range depends on the terrain, the cruising speed, and the payload — these details are often not supplied by manufacturers. A recent track test of 22 electric vehicles (including some listed in Table 1) by the Department of Energy in the U.S.A. gave [13] range/speed results that were 25% lower for most cases and 50 - 60% lower in a few.

TABLE 1

Lead—acid powered passenger vehicles: state-of-the-art 1978

Model	Year	Origin	Seats	Power pack (V)	Max. speed (km/h)	Cruise speed (km/h)	Max. range (km)
Flinders MkII Investigator	1977	Australia	4	144	75	60	65 - 70
Marathon C-300	1977	Canada	2	72	–	55 - 70	80
Pininfarina Ecos	1978	Italy	4	96	–	80	90
PGE — 3P	1978	Italy	3	62	60	–	70
Zagato 2000	1976	Italy	2	48	60	40	80
EV1	1977	Japan	4	96	90	40	130 - 150
EV2	1977	Japan	5	192	95	40	180 - 200
EV2P	1977	Japan	4	144	85	40	180
Volvo	1977	Sweden	4	72	70	–	100
Pilcar	1978	Switz.	4	84	90	–	115
THEV III	1978	Taiwan	4	96	75	40	110 - 120
Rickshaw	1977	U.K.	4-5	72	50	–	90 - 105
Tropicana	1977	U.K.	3	72	60	–	80 - 100
CDA Town Car	1976	U.S.A.	2	108	95	65	165
CitiCar	1974-6	U.S.A.	2	48	60	55 - 60	65 - 80
Sundancer	1970-2	U.S.A.	2	72	100	50	160
EVA Pacer	1977	U.S.A.	4	120	100	40	90
XDH-1	1977	U.S.A.	2	120	120	75	145
EXAR-1	1976	U.S.A.	5	144	110	90	160
Endura	1977	U.S.A.	4	240	100	55	185
Electricar	1977	U.S.A.	4	144	130	100	90
CDA Runabout	1978	U.S.A.	4	72	95	65	115
GE Centennial	1978	U.S.A.	4	108	100	65	120

given vehicle must possess if it is to be accepted by the public, and, of course, these criteria will vary from country to country. However, the power, energy, and cycle life requirements proposed by Arthur D. Little, Inc. [14] for six common types of vehicle (Table 2) are generally taken to be realistic for transport applications in most developed countries. It can be seen that city cars, vans, and buses require power sources in the region of 50 - 180 W h/kg and 60 - 130 W/kg (peak). For an urban electric car, about 0.14 - 0.16 kW h/tonne/km of energy is required from the battery for typical urban driving profiles such as the SAE J227a driving schedule [15]. The private family car requires a battery of high specific power (~ 200 W/kg peak) to provide adequate acceleration and hill-climbing capability, and a high specific energy (>150 W h/kg) to give the vehicle a practical range (*e.g.*, 200 - 300 km). For traction applications, the lead—acid battery appears most suitable for use in the small utility car which requires only a short range per cycle, for local commuting, shopping excursions, etc.

TABLE 2

Specifications for electric car power sources

	Small utility car	City car	Delivery van	Delivery truck	City bus	Family car
Energy density (W h/kg)	30 - 70	50 - 100	60 - 120	60 - 100	60 - 180	150 - 300
Peak power density (W/kg)	60 - 80	70 - 110	80 - 130	60 - 120	60 - 90	140 - 250
Cycle life	← ————————— >1 000 deep discharge cycles ——————— →					

There are many other battery systems with substantially higher theo-retical energy densities* than that of the lead–acid system (171 W h/kg), and the viable electric vehicle application of one of these advanced (or "super") batteries has become a goal of battery technologists, manufacturers, and scientists throughout the world.

2. Available power sources

There are two types of electrochemical power source available for vehicle propulsion, namely, the secondary (or rechargeable) storage battery and the fuel cell. A storage battery consists of an assemblage of secondary cells which are chemically reversible to a degree that permits electrical recharging. A fuel cell consists of two electrodes (usually porous) which can catalyze the conversion of a particular fuel (hydrogen, methanol, hydrazine) and an oxidant to electricity. Power can be drawn from the cell as long as fuels are supplied and the reaction products are removed. Thus, batteries store electricity and require a plentiful supply of outside electricity to function, whereas fuel cells make electricity and require a plentiful supply of fuel.

Although fuel cells have a considerable advantage over storage batteries in that they can be refuelled in a matter of minutes in much the same way as an i.c.e., fuel cell systems are not suitable for the high-rate, short-duration discharges needed to start and accelerate vehicles. There are also problems in finding cheap organic fuels, and more especially in discovering an inex-pensive and efficient catalyst to replace noble metals for the oxidation of low-grade hydrocarbon fuels. Nevertheless, there is some world-wide effort to develop battery–fuel cell hybrid vehicles in which acceleration and grade-

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*Theoretical energy densities given in this review are based on the energy content of all the active materials taking part in the cell reaction and assuming 100% utilization. Further, the theoretical values are calculated using the open-circuit cell voltage, and this is higher than the voltage observed under load conditions because of losses due to electro-chemical kinetic factors, concentration gradients, and internal cell resistance.

ability modes are powered by a secondary battery and the range provided by a fuel cell. The purpose of this review is to discuss only current research on storage batteries. Of course, different battery systems may be coupled to give an all-electric-driven hybrid vehicle; the development of such hybrids in Japan has produced [16] passenger vehicles with impressive road performances. For example, a passenger car powered by a zinc–air system for long range and lead–acid for acceleration had a 455 km range at 40.2 km/h on a single charge.

Over thirty different battery systems have been proposed for electric road vehicles (for an excellent review see ref. 17), and they can be classified by the nature of the electrolyte used, *i.e.*, aqueous solution (acidic or alkaline), molten salt, organic liquid or solid compound. The present review considers only those systems that are the most developed, or the most promising, candidates in each of these four categories of batteries for electric road vehicles.

3. Battery systems under development

3.1 Aqueous electrolyte batteries

This group of batteries includes lead–acid, nickel-based (Ni–Zn, Ni–Fe, Ni–H_2, Ni–Cd), metal–air (Fe–air, Zn–air, Pb–air, Cd–air, Li–air, etc.), and zinc–halogen (Zn–Cl_2, Zn–Br_2) systems. Of the nickel-based batteries, nickel–cadmium may be dismissed, principally on the grounds of cost due to the limited world supply of cadmium; this metal is obtained only as a by-product of lead and zinc refining processes. Nickel–cadmium batteries have energy densities only slightly higher than lead–acid systems, and are generally employed in electronic applications and in equipment requiring high power pulses. The Ni–H_2 battery has been developed by COMSAT, E.R.C., Hughes and S.A.F.T. for space applications, and prototypes with lifetimes of 1 000 - 2 000 cycles and energy densities of 50 - 88 W h/kg have been built [18]. The main problems with the system are high self-discharge due to hydrogen mobility, high materials and manufacturing costs, and the weight and volume penalties imposed by the hydrogen storage system (high pressure vessel [19, 20] or reversible metal hydride [21 - 23]). However, a vehicle concept involving storage of hydrogen in a high-strength tubular system constituting the car chassis has been proposed [24]. If hydrogen becomes the fuel of the future (*i.e.*, we have a "Hydrogen Economy" [25]), then internal combustion engines, batteries, and fuel cells operating on hydrogen will play an important part in the transport sector. At least one major car manufacturer, Daimler Benz AG, is building and testing hydrogen-powered vehicles [26].
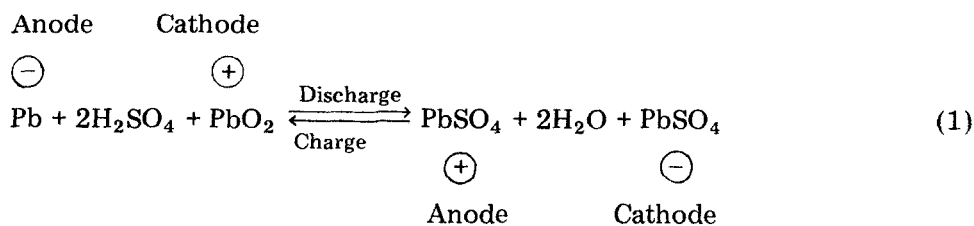
Of the halogen systems, Zn–Br_2 has received the least attention. Major problems include the storage and handling of bromine and a high self-discharge rate. The Zn–Br_2 battery loses nearly 50% of its charge in 2 days, whereas the corresponding Zn–Cl_2 system has an average self-discharge rate of only 5% per day. Research on organic complexes (for Br_2 storage) and

high-density polymer membranes (for semi-permeable separators) is currently being pursued in different laboratories, *e.g.*, Eco-Control Ltd [27], Exxon Enterprises, G.E.C. [28], and Gould Inc. in the United States. The Exxon battery uses bipolar carbon particle electrodes and operates at normal temperatures with a reported energy density of 77 W h/kg and a projected cost of \$30/kW h. A $Zn-Br_2$ prototype battery for electric vehicles was built by Magneti Marelli Battery Laboratories in Italy and gave an energy density of 60 W h/kg (5-hour rate), a power density of 73 W/kg and a cycle life of more than 200 cycles [29].

The most promising metal–air batteries are the zinc and iron systems. The major development of air electrodes has come as a result of fuel cell research in the last two decades. Lead–air batteries show poor cycle life and only moderate energy density [30], and Cd-based systems have low efficiency and can be eliminated, again on economic grounds. A Li–air battery operating in water-based solution is being developed at the Palo Alto Laboratories of the Lockheed Missiles and Space Company. This is a new version of the Company's patented lithium–water power cell [31], and is considered to be a suitable power source for a lightweight automobile [32]. A 67 kW h battery is expected to have an energy density of 384 W h/kg and a power density of 171 W/kg. The battery is recharged mechanically by replacing the lithium anodes.

3.1.1 Lead–acid battery

As mentioned previously, the lead–acid battery has been the popular choice of power source for electric vehicles designed and tested to date. The cell reaction is shown in eqn. (1). The main drawbacks of this system include (a) low energy density, (b) slow recharging time, (c) the need for careful maintenance. During discharge the cathode is positive and the anode negative, and the reverse is the case during charging.

Anode   Cathode

$\ominus$ $\oplus$

$$Pb + 2H_2SO_4 + PbO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O + PbSO_4 \qquad (1)$$

$\oplus$ $\ominus$

Anode   Cathode

When discussing the energy density of lead–acid batteries, or, indeed, any battery, it is important to remember that the amount of energy available depends on how quickly it is extracted, *i.e.*, the energy density decreases as the power density is increased. In other words, it is necessary to define the rate at which the energy is delivered. This is particularly important in the case of the lead–acid system, which shows a marked rate dependency. This is mainly due to the formation of $PbSO_4$ during discharge (reaction (1)), which blocks the electrode pores and reduces diffusion of acid to the interior

of the electrode. Many authors neglect to provide details of the discharge rate when quoting the energy densities of batteries, or at best provide figures in the 5 - 20 hour discharge range. These figures will be different from those achievable at the 1 - 2-hour rate — rates suggested [33, 34] as characterizing electric vehicle operation.

The theoretical energy density of the lead–acid battery is 171 W h/kg (Table 3) and is considerably greater than that available from current proto- type and commercial systems. Conventional automotive lead–acid batteries have energy densities of around 22, 29 and 34 W h/kg at the 1-, 2- and 5-hour rates, respectively. This suggests great room for improvement, and battery manufacturers around the world are currently trying to improve their products to compete with the new breed of advanced batteries (*v.i.*). Improvements are being sought in battery weight, use and retention of active materials, maintenance and rechargeability.

About half the weight of a lead–acid battery is accounted for by inert materials, *e.g.*, supports (grid metal), water, separators, connectors, terminals, and cell containers. Attempts to reduce the weight of support materials have involved the use of low-density grid materials such as lead-coated aluminium, magnesium, and titanium (expanded, rolled or punched), and metal-coated plastics. The introduction of carbon fibres into positive electrode grids has resulted [35] not only in a reduction in weight, but also in prolonged cycle life and increased power capability of lead–acid cells. The main factors affecting the choice of alternative grid materials are: (1) good adherence of the active material to the grid, (2) good corrosion resistance, (3) good electri- cal conductivity, (4) good mechanical properties (*e.g.*, castability, creep strength, etc.), (5) low cost. The recent introduction and development of rotational moulding techniques have allowed the manufacture of thin-walled, high-strength, heat-sealed polypropylene containers of reduced weight. Highly durable plastic separators have also been developed which improve the per- formance and life of the battery. Further weight savings may come from the use of aluminium for terminals and intercell connectors. This practice has been adopted by Chloride Ltd in their new, high-energy density, motive- power battery (HP13) — the use of aluminium and of plastic packaging resulted in a 15% saving in battery weight. Research and development is also being carried out on bipolar electrode structures (*v.i.*) which offer a reduction in the weight of internal connectors.

The remainder of the battery weight (about half) consists of the active materials. However, less than half of these actually take part in the cell reaction during discharge at the rates required in electric vehicle applications. This is mainly due to active material becoming inaccessible through blocking of the pores of the electrode by the reaction product, $PbSO_4$, formed during discharge. Recently, computer programs have been developed to ensure uniform, optimum utilization of active materials and grid metal. Improved grid designs have led to more effective current collection. Other attempts to increase the utilization of active materials by reducing plate thickness or increasing the porosity of the active mass have generally caused a decrease in

TABLE 3

Candidate electric vehicle batteries

Battery System	Electrolyte	Temp. (°C)	O.C.P. (V)	Energy density (theoretical) (W h/kg)	Current performance			
					Energy density (W h/kg)	Power (peak) (W/kg)	Cycle life	Depth of discharge (%)
Lead–acid	H_2SO_4	20 - 30	2.05	171	22*	50	700+	90
Lead–acid (Improved)	H_2SO_4	20 - 30	2.05	171	30*	50 - 100	500+	60
Ni–Zn	KOH	20 - 30	1.706	321	66**	150+	400+***	65
Ni–Zn (Vibrocel)	KOH	20 - 30	1.706	321	45 - 65**	–	1 200+	–
Ni–Fe	KOH	20 - 30	1.370	267	55**, 82.5†	50 - 100	1 500+	90
Fe–air	KOH	~40	1.280	764	81†	30 - 40	200+	65
Zn–air	KOH (stagnant)	50 - 60	1.645	1 084	131.5†	–	200 - 300	–
Zn–air	KOH (flowing)	50 - 60	1.645	1 084	109†	26	200 - 300	–
Zn–air	KOH (slurry)	50 - 55	1.645	1 084	110††	80††	500 - 600	90
Zn–Cl$_2$.6H$_2$O	$ZnCl_2$	50	2.12	465	110 - 157†††	88 - 132†††	400+	–
Na–S	β-Al$_2$O$_3$	300 - 375	1.76 - 2.08	664	180†††	220†††	300+	60
Li/Al–FeS$_2$	LiCl–KCl (eutectic)	400 - 450	1.5	625	70***,***	50***	250+	50
Li/Al–FeS	LiCl–KCl (eutectic)	400 - 450	1.6	869	40 - 60***	–	600+	50
Li–TiS$_2$	?	90 - 110	1.87 - 2.5	480	132	132	120+	–

*At 1-hour rate. †At 5-hour rate.
**At 2-hour rate. ††Projected figures.
***Cell only. †††At 4-hour rate.

Cycle life depends on a number of factors, including depth of discharge, rate of charge and discharge, temperature, and amount of over-charge. This information is rarely provided in full but lifetimes given here are for batteries and cells operating under deep discharge cycles required in electric vehicle applications.

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cycle life through earlier failure due to grid corrosion and accelerated "shedding" of active material. In meeting the requirements for electric vehicle traction there is a trade-off between shorter battery life and greater specific energy, and this has to be kept within the range of economic viability.

The performance of a lead–acid battery is generally limited by the behaviour of the positive plate, the capacity of which gradually falls on charge/discharge cycling as a result of (a) shedding of active material (PbO_2), and (b) gradual inactivation of PbO_2 [36]. Shedding of active material from the positive plate is a principal cause of deterioration within a cycled lead–acid cell, and is associated with the depth and rate of discharge, specific gravity of the acid, composition of the supporting metal grid, and perhaps, other, unknown factors. Research into shedding has centred largely upon the particle morphology changes that occur during preparation, formation, and utilization of the positive active material. Two polymorphic forms of PbO_2 have been found in the initial active material of positive plates, α-PbO_2 and β-PbO_2 [37 - 40], the presence of α-PbO_2 depending on plate construction and method of formation [41].

The morphological structure of any solid material can have a strong influence on the chemical and physical properties of the material. Different authors have shown [36, 42 - 50] that there is a relation between mechanical strength and morphology of the crystals in battery plates. In the case of the lead–acid battery, the preferred structure for the active material is one that combines the properties of high electrical capacity with good mechanical strength. In other words, the morphology of the material must be such that it is porous enough to allow maximum reaction with electrolyte (*i.e.*, a high degree of utilization), but at the same time is robust enough to withstand stresses caused by volume changes that accompany the chemical reactions during charging and discharging of the battery. Studies of plate morphology have excited a great deal of interest and have been shown [36, 43 - 49, 51 - 73] to be useful in relatihg properties of the active material to the method of manufacture, performance, and ultimate failure of the system. Early studies [43 - 47, 51 - 59] involved optical microscopic examination of polished specimens, but these have now been complemented by electron microscopic studies [48, 49, 60 - 67] of replicas of the surface, and more recently by analysis using scanning electron microscopy (s.e.m.) [36, 68 - 77]. S.e.m. has become a popular and powerful tool in battery research and has advantages over the other two microscopic techniques in that it provides great depth of field and does not require the preparation of flat, polished specimens.

As a result of the many studies using optical, electron, and scanning electron microscopy, the literature contains much discussion on the complex structural changes that take place in the positive active material of lead–acid battery plates during charge/discharge cycling. Such discussion has, in many cases, promoted theories to account for the low utilization of active material in the positive plates and their ultimate failure on cycling. For example, a recent study by Simon *et al.* [36] reports that after formation, PbO_2 has a

uniform, closely-packed structure which is transformed during cycling into a "coralloid structure" characterized by large voids and a dense network of PbO_2. The development of this coralloid structure was found to be independent of the methods used for curing and forming the plates. At the end of discharge, particles of unreacted PbO_2 were found to be embedded in the lead sulphate crystals. These were considered to be an inactive form of PbO_2 (evidence of inactive and active forms of PbO_2 had been obtained previously from n.m.r. [77] and d.t.a. [78] investigations) and to be responsible for the emergence of the well-defined PbO_2 coralloid structure on repetitive charge/discharge cycling. It was further suggested that loss of life and capacity were probably due to an increase in the amount of inactive material during cycling — an effect attributed to a change in microstructure and also to the amount of hydrogen or hydroxyl species in the lead dioxide lattice [77]. The coralloid structure was observed to break up towards the end of cycle life.

Physical retention of active materials by supporting flat plate materials with plastic or glass-fibre envelopes, or by using tubular electrodes clad with fabric gauntlets, is being re-investigated by several battery manufacturers. The tubular plate structure was developed at the beginning of this century and, in addition to improving active material retention, offers the advantage of a lighter grid construction and, hence, an increased energy density. The HP13 battery of Chloride Ltd, for instance, consists of 13 plates, each of 22 tubes enclosed in a fabric gauntlet, and has an energy density of 37.5 W h/kg (5-hour rate) and a lifetime ~1 000 cycles. However, the increased cycle life of clad-type batteries compared with the pasted flat plate type must be balanced against their higher manufacturing costs.

Corrosion of the grid structure supporting the active material is the other main cause of plate failure in cycled lead–acid batteries. Generally, lead–antimony alloys (>4 wt.% Sb) have been used for grids owing to their good mechanical properties and good castability (i.e., ease of fabrication); also, they improve paste adhesion [48, 50, 63, 67]. Further, there is evidence that the presence of antimony retards positive grid growth and corrosion [39]. Apart from leading to eventual mechanical failure, anodic corrosion of the grid also contributes to the self-discharge of the negative electrodes. During battery charge, antimony dissolves from the positive plate, diffuses through the electrolyte and deposits on the negative plate. This results in a reduction of the hydrogen overpotential of the negative plate, and leads to hydrogen evolution with concurrent oxidation of the spongy lead during battery charge and on open-circuit stand. Chemical reduction of lead peroxide by the lead metal in the positive grid (or by hydrogen peroxide produced in the electrolyte during charging) also contributes to the self-discharge of lead–acid batteries, which, in total, amounts to about 20 - 30% of the nominal capacity per month. With recent improvements in plate casting, handling, and pasting equipment, the strength required for adequate grid handling has decreased considerably, and alloys of lower antimony content can be used. Thus, attempts to minimize, or overcome, the detrimental

effects of antimony have involved the use of low-antimony- (<4 wt.%) or antimony-free (*e.g.*, Pb–Ca–Sn [79], Pb–Sr [80]) alloys. The rate of corrosion of Pb–Sb alloys is reduced on decreasing the antimony content [81], and it is possible to produce low-antimony grids of sufficient mechanical strength through the addition of minor amounts of alloying elements, *e.g.*, As, Ag, Co, Cu, Se, Sn or Te. Lead–calcium alloys have been shown [82, 83] to corrode more slowly than Pb–Sb alloys and at a rate comparable with that of pure lead. The mechanical strength of pure lead grids is insufficient to ensure dimensional stability during use. Paste softening is another problem with pure lead grids, but the active material can be hardened by the addition of phosphoric acid to the electrolyte; unfortunately there is a slight capacity decrease. Small amounts of phosphoric acid have been shown [84] to increase the formation of α-PbO_2 and lead to an improvement in battery cycle life [85, 86]. Different alloys show large differences in physical and electro-chemical characteristics of the corrosion layer, and present lead–acid battery research is concerned with relating deep-cycle life to the behaviour of the corrosion film formed between the grid metal and the positive active material.

The major maintenance operation of a lead–acid cell is the addition of water to make up that lost by electrolysis and self-discharge reactions. Although many traction batteries are now fitted with automatic, or semi-automatic, topping-up devices [87], with the more popular operating on floats or an air-lock system, there is great interest in the development of maintenance-free systems. These batteries are based on the use of grids cast from lead–calcium alloys with some tin added to improve castability. These alloys produce less gas and have lower self-discharge rates (about one-fourth) than the conventional Pb–Sb grid battery [88]. Lead–calcium grids also have better electrical conductivity than those made from Pb–Sb alloys. How-ever, although Pb–Ca maintenance-free batteries are now extensively mar-keted as both standby and automotive starter batteries, particularly in the U.S.A., they have not yet been proved to be satisfactory for vehicle propulsion. Apart from drossing problems in producing grids of the required alloy com-position (0.03 - 0.075 wt.% Ca), the main drawback in the use of Pb–Ca grids is the poor adherence of the active material to the grid under deep-discharge cycling conditions. Poor cycle life has been attributed to changes in the morphology of the PbO_2 active material [48], and to the irreversible formation of a continuous corrosion layer of lead sulphate between the grid and the active material which inhibits current flow and enhances shedding of active material [85]. However, more recent studies using electron probe microanalysis have shown that this barrier layer is, in fact, discontinuous [89, 90] and is almost completely reconverted to PbO_2 during charging [89]. Research on the metallurgy and electrochemical behaviour of the Pb–Ca system is being pursued in several laboratories, and General Motors Corpora-tion were reported to have developed recently a lead–acid battery with Pb–Ca–Sn alloy grids, said to be capable of deep discharge and suitable for electric vehicle propulsion.

There has been much speculation about the extent to which the energy density of the lead–acid system can be improved without serious effects on

battery life. Part of the problem is that there has been surprisingly little published information on the behaviour of lead–acid batteries operating under duty cycles normal for electric traction. In particular, detailed information is lacking on the relation between battery capacity and rate of discharge over a variable load profile involving high-rate discharge interrupted by (a) regenerative charging pulses during braking, and (b) intervals at open circuit corresponding to temporary halts of the vehicle at traffic signals, and in road congestion, etc. Another important area where information is needed is the effect of high-speed, pulse discharge on battery capacity, since many electric vehicles are fitted with solid-state switches (transistor or SCR) for stepless speed control, *i.e.*, "chopper control". These electronic devices are turned on and off at a fairly high frequency and have the effect of chopping the constant voltage of the battery into a series of rectangular voltage pulses at the armature terminals of the motor.
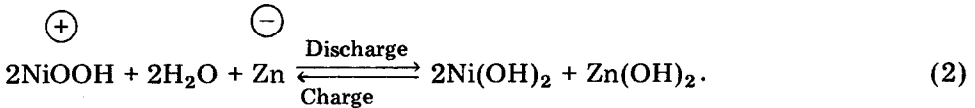
To date, one of the best performances obtained from a vehicle-tested, lead–acid battery appears to have been achieved by a mat-structured battery developed in Japan [16]. This has an energy density of over 50 W h/kg at the 5-hour rate and 32 W h/kg at the 2-hour rate, and a cycle life (60% depth of discharge) of over 500 cycles. This is remarkable in the light of popular opinion that a 50 W h/kg battery (5-hour rate) of adequate durability will not be available commercially within the next five years. In this respect, Lucas Industries expect to market in the near future a lightweight lead–acid battery with a capacity of 48 W h/kg at the 5-hour rate and a service life of 400 - 500 cycles. The Taiwan Yuasa Battery Company has developed [91] a battery with an energy density of 48 W h/kg (5-hour rate), but cycle life is only 150 deep cycles. General feeling is that eventually a battery with an energy density of ~60 W h/kg at the 5-hour rate, and an acceptable lifetime and cost, will become available. This system is referred to as the "improved", or "advanced", lead–acid battery. Recently, the U.S.A. Department of Energy awarded a four-year, $3.3 million contract to ESB Ray-O-Vac for the development of improved and advanced lead–acid batteries by April 1980 and August 1981, respectively. These two prototypes must be able to deliver 96 - 105 and 145 - 153 km of variable-speed local driving per charge and have service lives of 800 and 1 000 cycles, respectively. Meanwhile, Varta are developing a low-maintenance traction battery capable of storing at least 50 W h/kg, and Globe-Union are producing a battery with an energy density of 35 - 37 W h/kg at the 3-hour rate.

Lead–acid batteries are also being developed with the high rate discharge capabilities required for some propulsion purposes, *e.g.*, acceleration, ascending gradients. A high power density lead–acid battery using bipolar electrodes is being investigated [92] by Westinghouse Electric Corporation in the United States. The bipolar electrode consists of a flat sheet with positive active material pasted on one side and a negative active material on the other side. In order to cool the battery at high rates, the electrolyte is circulated through the system. A 12-cell battery has been constructed that exhibits a peak power capability of over 440 W/kg and a specific energy density of

27.5 W h/kg at the 2-hour rate. The Tyco bipolar battery is expected [93] to provide 220 W/kg and an energy density of 21.4 W h/kg. The prevention of electrolyte leakage between cells is the main problem with bipolar configurations. This involves the use of a corrosion-resistant substrate through which electrolyte cannot penetrate, and the formation of a reliable and lasting bond between the individual conducting substrates and the wall of the battery container.

3.1.2 Nickel–zinc battery

In this battery, zinc is used as the anode and the cell electrolyte is typically 30 - 35% KOH. The cell reaction is:

$$\underset{(+)}{2NiOOH} + 2H_2O + \underset{(-)}{Zn} \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} 2Ni(OH)_2 + Zn(OH)_2. \tag{2}$$

The theoretical energy density of the system is 321 W h/kg. Batteries have been built with energy densities at the 2-hour rate of 66, 44.4 and 40.1 W h/kg by Yardney Electric Corporation, Deutsche Automobilgesellschaft (D.A.U.G.) and A.G.A. Innovation Centre (Sweden), respectively. Gould, in the United States, have produced cells capable of 66 W h/kg energy and 132 W/kg power and with a projected, mass-produced cost of \$75/kW h. A battery with an energy density of 88 W h/kg is currently being developed by the Energy Research Corporation (E.R.C.) in the U.S.A. Cells at G.C.E. (Marcoussis, France) have given energy densities in the range 60 - 70 W h/kg and lifetimes of over 400 cycles. A 6 V (4-cell) monoblock battery has been developed by Furukawa Electric Industry Co. Ltd. in Japan and has an energy density of 73 W h/kg and a life expectancy of 500 cycles.

Several prototype systems have been field-tested in electric vehicles. The D.A.U.G. battery (164 A h/92 V: 2-hour discharge) failed after about 100 charge/discharge cycles in vehicle service. A range of 235 km at 64 km/h was obtained during testing of nickel–zinc batteries in the Copper Electric Town Car. In the U.S.S.R., batteries with an energy density of 44 W h/kg and a 300-cycle operational life have been used to power electric vans. The Yardney nickel–zinc battery is currently being evaluated by Fiat for electric vehicle applications. The A.G.A. battery is being made ready for use in a vehicle, and General Motors Corporation are developing a battery aimed at giving a 2-passenger electric car a top speed of 80 km/h and a range of around 160 km. A nickel–zinc battery designed for electric vehicle propulsion by Eagle-Picher has achieved 300 cycles at 65% depth of discharge.

The main problem with the nickel–zinc battery is its short cycle life. Other problems include nickel electrode cost, mass production problems, hydrogen liberation at the negative electrode, separator stability, and temperature control. Poor cycle life is caused by the high solubility of the reaction products at the zinc electrodes. Redeposition of zinc during charging results in the growth of dendrites (which penetrate the separators of the

battery and cause an internal short circuit) and the redistribution of active material (the so-called "shape change"). Shape change is brought about by preferential dissolution of active material from the electrode edges during discharge, followed by redeposition in a more compact form at the electrode centre during charging. This results in a reduction of active electrode area and a corresponding loss in energy storage capability. The rate of capacity loss increases with charge/discharge cycling and with the rate and depth of discharge [94, 95]. Shape change has also been associated [96] with non-uniform current distribution in the zinc electrode, and with osmotic pumping. A zinc electrode structure has been developed [98] at E.R.C. which permits uniform redeposition of dissolved zincate, and lifetimes of over 500 deep discharge cycles at the 5-hour rate have been obtained in 40 A h cells. The D.A.U.G. cell discussed above uses auxiliary electrodes and excess electrolyte in an attempt to overcome the zinc problem. New, mercury-free zinc composite electrodes have also been developed to control the deposition of zinc during charging [97]. The solubility of zinc has been reduced by introducing additives to either the electrode material, *e.g.*, $Ca(OH)_2$ [99], or the electrolyte, *e.g.*, K_3BO_3 [100], or by the use of zinc-impregnated polyvinyl alcohol membranes [101]. A number of different electrode additives have also been used to decrease the hydrogen evolution rate at the zinc electrode. Some of these additives have been claimed to help retard zinc dendrite growth.

Attempts have also been made to suppress the growth of zinc dendrites during charging. The most promising of these involves internal agitation of the electrode or electrolyte. An operational life of about 300 deep discharge cycles has been obtained from a cell built by Atomics International [102] which uses a rotating shutter between each pair of electrodes. The shutter stirs the electrolyte and provides for pulsed charging as it rotates. Improvement in cycle life has been obtained at the expense of energy density, which is quite low for the system (44 W h/kg). In the new "Vibrocel" zinc battery developed [103] by A.G.A.-Tudor (now E.S.B. Ray-O-Vac), the zinc electrode is vibrated along its plane during the charging process. The vibration creates microturbulences in the liquid layer next to the zinc electrode and macroturbulences in the bulk of the electrolyte. The combination of these effects leads to the deposition during charging of adherent, compact zinc layers with no shape change or dendritic growth. A prototype battery has been operating for more than 1 200 cycles in a test involving a 2-hour discharge, but the energy density is generally lower (45 - 65 W h/kg) than that of a stationary plate type. The weight of the vibrator mechanism is about 5% of the total battery weight. A second-generation battery is now being built for powering a converted Volkswagen transporter. In another attempt [104] to overcome dendrite problems, zinc dendrites formed during charge are dissolved by contact with an auxiliary electrode (placed between the positive and negative plates of the battery) at which hydrogen is evolved.

Nickel is the most expensive item in nickel–zinc batteries (over 30% of the total cost), and so efforts are being directed towards producing less costly positive electrodes without sacrificing the lifetime and performance of

the conventional nickel electrode. This electrode uses a sintered porous nickel plaque to serve as both a current-collector and a support for the active NiOOH which is deposited within the pores of the matrix by electrochemical means. About 60% of the total nickel content is used in this structure, and thus attempts are being made to replace unessential nickel by alternative, less expensive, support materials, *e.g.*, graphite, or by the development of pressed-plate versions. Non-sintered, high energy electrodes have been developed [98] by blending nickel hydroxide, graphite, cobalt hydroxide and a polymeric binder, and rolling or pressing the active material onto pure nickel or nickel-clad screens. Using this technology, the nickel cost is reduced by a factor of about three compared with the conventional sintered electrodes. Further, the addition of cobalt has been found to improve both the capacity and life of the active material. Tests in nickel—hydrogen cells showed that after 800 cycles the loss in capacity of these electrodes was about 20%. Lightweight, non-sintered electrodes have also been developed by General Motors and have led to significant cost savings through the use of a graphite—organic binder matrix as the current-collecting and support medium for the active material. Problems encountered with non-sintered electrodes include: (a) reduced cycle life due to graphite oxidation and severe swelling of the active mass during cycling; (b) inferior performance at high discharge rates. Efforts in other laboratories to reduce nickel costs include the use of nickel or nickel-plated fibrous materials or nickel powder with improved shape and surface structure. Recently, a process for recovery of active materials from spent batteries has been proposed [105] and this could result in further cost savings.
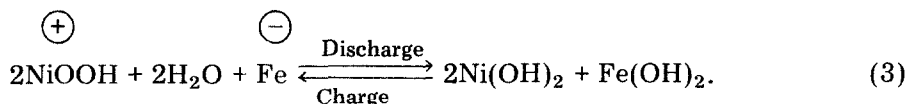
Improvements have also been made in the durability of separators. Conventional separator systems employ cellulosic materials and oxidation of these during cell operation gives rise to CO_2 evolution, which leads to carbonation of the electrolyte and a resultant lowering of the cell voltage and loss of positive electrode capacity. Alternative separator materials which are immune to oxidative attack, either by the electrolyte or by oxygen evolved from the nickel positive during charge, have been investigated, *e.g.*, graft copolymers [106, 107]. More encouraging results have been obtained with the so-called "inorganic—organic" separators developed by the N.A.S.A.– Lewis Research Centre and by E.R.C. [98]. The N.A.S.A. material consists of asbestos impregnated with polypropylene oxide and coated with a slurry, whereas the E.R.C. composite was made by rolling a mixture of plastic and ceric oxyhydroxide. Small pore-sized inorganic materials have also been investigated as separator materials in attempts to reduce cell shorting problems caused by zinc dendrite growth through separator films. However, microporous separators are difficult to prepare and therefore are more expensive than conventional types.

Other research on the nickel—zinc system is concerned with determining an optimum method for charging cells and terminating charging, and with problems of electrolyte management and oxygen transport (for sealed systems). A solution to the latter problem has been to provide excess negative

active material for reaction with oxygen that is released from the positive plates during the final stages of battery recharge.

3.1.3 Nickel–iron battery

This is an alkaline storage battery using KOH as electrolyte. The cell reaction is:

$$\overset{\textstyle\oplus}{}\qquad\overset{\textstyle\ominus}{}$$
$$2NiOOH + 2H_2O + Fe \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} 2Ni(OH)_2 + Fe(OH)_2. \tag{3}$$

The theoretical energy density of the system is 267 W h/kg. Batteries have been developed and tested in vehicles in Japan by Matsushita Electrical Industrial Company (82.5 W h/kg at the 5-hour rate, 82 W/kg peak), in Germany by Varta (50 W h/kg, 5-hour rate), in the U.S.A. by Westinghouse (44 - 55 W h/kg, 2-hour rate [108]), and in the U.S.S.R. (26 W h/kg). The Swedish National Development Company has produced a battery with an energy density of 60 W h/kg at the 5-hour rate [109], and Eagle-Picher in the United States is also developing a battery. The performance of the Matsushita battery is particularly impressive; electric cars fitted with this battery have run for over 200 km with a single battery charge [16] and durability tests conducted in the laboratory reveal that the battery can with-stand between 1 500 and 2 000 cycles.
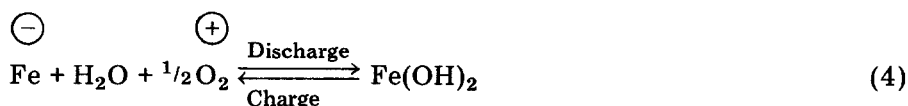
The major objection to nickel–iron batteries for electric vehicle applica-tion has been their mediocre energy density. However, recent developments with the Japanese and Swedish systems are fast placing this battery on a par with the nickel–zinc system. The low energy density is partly due to the weight of inactive electrode support materials and partly due to the poor utilization of the iron active material. The battery does, however, suffer from a poor peaking capability, particularly at low temperatures. Other shortcomings of the nickel–iron battery are low cell voltage (necessitating more cells for a given battery voltage) and the low hydrogen overvoltage of the iron electrode which results in substantial self-discharge (about 2% loss in capacity per day at 25 °C) and low cell efficiency (about 60%). The latter problems are unfortunate since batteries using iron electrode materials are very appealing given the large global supplies of iron ore.

Improvements in the positive electrode have followed those advances made in nickel oxide electrode technology for nickel–zinc batteries, e.g., the development of nickel fibre electrodes of high surface area at a lower cost. Fibrous supporting structures have been used as current collectors in the iron electrode of the Westinghouse battery. Lower gas evolution and self-discharge rates have been obtained in the Varta battery by use of a special iron powder [110]. The Matsushita battery uses sintered compacts for both types of electrodes. The self-discharge of iron electrodes can be reduced by suitable additives to the electrode and the electrolyte, e.g., elemental sulphur [111].

Other research on nickel–iron systems is concerned with the problem of hydrogen gassing during charge, electrolyte maintenance, and thermal control. Westinghouse has reduced problems of heat and gas removal, and maintenance of a uniform concentration of electrolyte, by circulating cooled electrolyte from an external reservoir during charge. However, the addition of such auxiliary systems introduces parasitic power losses in the operation of blowers, pumps, etc.

3.1.4 Metal–air batteries

These batteries produce electrical energy due to the electrochemical reaction between oxygen present in the air and a metal negative electrode, *e.g.*, Fe, Zn, etc., in an alkaline electrolyte (highly concentrated NaOH or KOH). The products of the reaction are either metal hydroxide or oxide, depending on the metal used:

$$\ominus \qquad \oplus \atop Fe + H_2O + {}^1\!/_2 O_2 \; \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \; Fe(OH)_2 \qquad (4)$$

$$\ominus \qquad \oplus \atop Zn + {}^1\!/_2 O_2 \; \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \; ZnO. \qquad (5)$$

Although the use of atmospheric oxygen has the advantage of removing the need for a storage facility which would add to the weight and complexity of the battery, scrubbers are required to avoid detrimental effects from carbon dioxide present in the air. Reaction of carbon dioxide with the alkaline electrolyte produces carbonates which lower the ionic conductivity of the electrolyte and cause blockage of electrode active material. The air cathode determines both the performance and operational life of metal–air batteries. The poor high-rate capability results mainly from polarization losses in the air electrode. In practical electrodes, potentials of the order of 1.0 - 1.1 V are obtained, whereas the theoretical potential for air at 1 atm and 25 °C is 1.219 V. These losses may be reduced by developing better oxygen electrocatalysts and better diffusion conditions.

Much effort has been directed to the development of a rechargeable, low-cost, high-rate oxygen electrode. In particular, cheaper alternatives to the expensive noble metal electrocatalysts are being sought. Conventional carbon- and silver-bearing electrodes for oxygen reduction in alkaline media were found to exhibit poor cycle lifetimes when operating at the high positive potentials necessary for battery recharging. In fact, even noble metals such as platinum, palladium, rhodium, and gold show significant dissolution at these potentials [112]. The use of auxiliary electrodes for evolving oxygen during charging increases the volume, weight, and complexity of the battery.

A rechargeable electrode has been developed [113] in Sweden that has a lifetime of around 1 000 cycles. This consists of a pressed nickel powder structure of two layers — a fine-pore hydrophilic layer with good current

conducting properties on the electrolyte side and a hydrophobic layer containing silver catalyst on the air side. The electrode is designed to operate at 40 °C, but has a stability to temperatures up to 60 °C which occur during peak power. Three-layer oxygen electrodes have been developed by Siemens A.G. in Germany. The problems of carbonate formation, poor oxygen electrode efficiency, and limited cycle life are common to all batteries and fuel cells using air cathodes in alkaline electrolyte.

The iron–air system has a theoretical open-circuit voltage at 25 °C (for air at 1 atm) of 1.265 V and a theoretical energy density of 755 W h/kg. In practice, the realized open-circuit voltage is about 1.1 V. Batteries have been built and tested in electric vehicles in Japan and Sweden. The Matsushita battery was reported [16] to have an energy density of 81 W h/kg at the 5-hour rate and a cycle life of over 200 cycles at 60% depth of discharge. The battery was combined with a lead–acid battery to power a lightweight electric passenger car. The vehicle achieved ranges of up to 260 km between battery charges. A 15 kW h battery was built by the Swedish National Development Company and used to power a mine vehicle [114]. More recently, a 30 kW h battery has been built and tested in an electric van [115]. The battery contains 8 modules, each consisting of 190 air and 95 iron electrodes, and has achieved an energy density of 80 W h/kg at the 5-hour rate and a lifetime of more than 200 cycles. A double cathode enveloping a central anode is an optimum configuration when gas electrodes are employed in a power source system. Other research into the iron–air system is being undertaken in Germany (Siemens A.G.) [116] and the United States (Westinghouse).

The iron–air battery suffers from high self-discharge of the iron electrode (about 2% of the capacity per day at 25 °C), poor charge efficiency (about 40%, or less), low utilization of active materials (about one-fourth of theoretical capacity), limited power capability (30 - 40 W/kg maximum), a low cell voltage (*i.e.*, more cells required for a given battery voltage), and thermal problems.

Much effort has been directed towards determining the mechanism and reaction products formed during the anodic discharge process of a charged iron electrode. Discharge proceeds in two steps, and recent studies [117] by the Swedish group have shown that at temperatures below 60 °C, $Fe(OH)_2$ is formed during the first stage, and a product sludge, consisting mainly of hydrated FeOOH, during the second. The iron electrode has a potential more negative than that required for hydrogen evolution in alkaline solution and a low hydrogen overvoltage. The latter results in poor charge efficiency due to hydrogen evolution competing with $Fe(OH)_2$-reduction during the charging process. Overdischarge is undesirable since a passivation phenomena occurs and the recharge reaction goes over to hydrogen evolution before full capacity is regained. The solubility of $Fe(OH)_2$ is very low and the charge reaction is essentially a solid-state reaction, so that the secondary iron electrode does not suffer the dendrite formation problems that are found in its zinc counterpart (*v.s.*).

Self-discharge of the iron electrode occurs by a mixed-potential mechanism in which the anodic process is corrosion of iron to $Fe(OH)_2$, and the cathodic process, evolution of hydrogen. Some success has been obtained in decreasing the corrosion rate by the introduction of additives to the active material, *e.g.*, sulphur, or to the electrolyte, *e.g.*, Li^+, K_2S, hydrazine sulphate. Since the discharge process is accompanied by considerable expansion of the active material, attempts have been made to control the structure and porosity of iron electrodes during manufacture. These efforts have resulted [114, 115] in the development of a sintered electrode with a much improved capacity.

Consideration has also been given to designing an efficient, low-cost, simple auxiliary system for iron–air batteries. Auxiliary equipment is required for: (a) circulating electrolyte and air, (b) cooling, (c) water makeup, and (d) carbon dioxide removal from the air. Bulky, complex auxiliary systems can seriously reduce the effective energy density of the battery. The auxiliary system of the 30 kW h Swedish battery [115] comprises about 20% of the weight of the whole battery and consumes about 5% of the battery energy, but volume penalties are still a problem.

The theoretical open-circuit potential of the zinc–air system is 1.645 V, and, on this basis, the energy density is 1 084 W h/kg (or 1 347 W h/kg if zinc is considered to be the only consumable reactant, the battery having an inexhaustible supply of outside oxygen).

Primary systems have been in operation for many years and now have demonstrated energy densities of up to 311 W h/kg. Recently, the main interest in the zinc–air system has centred on the development of an electrically rechargeable type suitable as a power source for electric vehicles. As with the iron–air system, the zinc–air couple has a poor overall charge–discharge efficiency due to the polarization losses associated with the air electrode. The main difficulty in developing a secondary system lies in the instability of the zinc electrode. The zinc oxide formed during discharge dissolves in the electrolyte to give zincate ions, and redeposition of zinc during charging leads to the problems of electrode shape change and dendritic growth discussed above for nickel–zinc batteries. Attempts [118] to produce even zinc deposits by the high speed circulation of electrolyte have not resulted in any significant improvement in cell lifetime or performance. The use of fluidized bed electrodes has also proved [119] unsuccessful. Batteries using conventional zinc plates in either stationary or circulating electrolyte have been used in hybrid electric vehicles in Japan and have achieved energy densities of up to 131.5 W h/kg (5-hour rate) with lifetimes of 200 - 300 cycles.

By far the most promising battery is that using a circulating system of zinc powder suspended in the electrolyte. This system has been developed principally by C.G.E. in France [120], although other aspects of the system have been developed by Lucas in the U.K. [121], the Sony Corporation in Japan [122], the Battelle Memorial Institute in Geneva [123], and Citroën in France [124]. In the C.G.E. battery, the electrolytic zinc powder–electro-
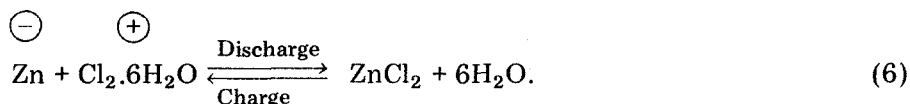
lyte (12N KOH) slurry is pumped through tubular air cells (consisting of Teflon-bonded active carbon material) during discharge. After discharge, more than 90% of the zinc has reacted to zincate dissolved in the KOH electrolyte. Individual cells have shown service lives of up to 1 000 3-hour cycles at a discharge current of 80 mA/cm^2 and at a temperature around 55 °C, whereas modules, or blocks of cells (normally 12 series-connected tubes), have consistently shown 500 - 600 cycles (1 800 h) lifetime to failure. Automobile propulsion batteries are expected to provide an energy density of 110 W h/kg and a peak power density of 80 W/kg. This performance will provide a 1-tonne vehicle with a 140 - 180 km range. The lifetime of the system will be limited by degradation of the air-electrode.

The C.G.E. battery system was initially designed to operate as a straight fuel cell with mechanical recharge by exchanging the electrolyte for new zinc–electrolyte slurry and then regenerating the spent slurry externally in an electrolysis unit. However, recent cost analysis has shown that because the electric vehicle market is still small, installation of a rapid-refuelling service-station system will be uneconomic. Therefore, a prototype system for on-board electrolysis has been developed [125]. The charge unit consists of tubular cells, each equipped with a series of magnesium points along the tube axis. Zinc is deposited in dendritic form at these points and can be removed in particulate form by reversing the electrolytic flow. A unit has operated successfully for 1 800 hours continuously. Use of a built-in charger reduces the effective energy density of the system to $\sim$90 W h/kg and introduces volume penalties, but lowers the overall cost of recharging the battery.

Apart from dendritic shorting and shape-change capacity loss, other problems with the zinc electrode include passivation and self-discharge through direct reaction with oxygen. Attempts to prevent zinc passivation during charging have included wrapping the electrodes in electrolyte-soaked polyamide felts [126], and self-discharge has been lessened [126] by encapsulating the electrode in an acrylic acid-grafted polyethylene separator to reduce oxygen transport.

3.1.5 Zinc–chlorine battery

This battery attempts to overcome the replating problem of zinc by using an acid electrolyte. The reaction is:

$$\ominus \quad \oplus$$
$$\text{Zn} + \text{Cl}_2.6\text{H}_2\text{O} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{ZnCl}_2 + 6\text{H}_2\text{O}. \tag{6}$$

The system has an open-circuit potential of 2.12 V and a theoretical energy density of 465 W h/kg. Batteries have been developed [127] principally by Energy Development Associates (E.D.A.), and in 1972 a prototype primary version was installed in a Vega automobile and propelled the car 240 km on a single charge at an average speed of 80 km/h around a Detroit test track.

The unique feature of the E.D.A. battery is the storage of chlorine as solid chlorine hydrate by refrigeration below 9.6 °C. The system is a flow

type using circulating $ZnCl_2$ electrolyte. During charge, zinc is deposited as a non-porous layer on the negative plates of the battery (apparently without the dendrite problems encountered in alkaline media) and chlorine gas is generated at the positive plates. The circulating electrolyte replenishes the zinc chloride and carries away the chlorine, which is cooled and stored externally as chlorine hydrate. When the hydrate store is full, the battery is considered to be fully charged. On discharge, the flowing electrolyte removes the reaction product, aqueous zinc chloride, and supplies chlorine to the chlorine electrode. In order to maintain an adequate supply of chlorine, warm electrolyte is passed into the hydrate store at a rate proportional to the current being drawn from the battery. The overall efficiency of the system is 65%, the voltage efficiency and power density of the system being determined by the performance of the chlorine electrode. The capacity is relatively independent of the rate of discharge. Bipolar electrodes consisting of a fine-grained graphite plate (zinc electrode) bonded to a porous graphite plate (chlorine electrode) have been shown to be satisfactory for automotive type applications.

   Exact performance data have rarely been released, but energy densities up to 150 W h/kg (4-hour rate) and peak power densities around 120 W/kg have been obtained from a 50 kW h battery which fits into a volume of $0.28 \ m^3$; three such batteries have been built as prototypes for load-levelling applications. E.D.A. is currently working on the development of a complete battery package, the performance target for which is a system capable of propelling a 4-passenger urban-type vehicle for 240 - 320 km, on a single charge, at 80 km/h with a top speed of 120 km/h, and having a battery life of 160 000 km. The prototype system is expected to be ready in August 1979, and the U.S. Department of Energy has awarded a $2.1 million contract to aid the development of the project.

   There are difficulties with the zinc−chlorine hydrate battery in that the system is complex, and complicated plumbing is required to maintain continuous and safe operation, especially under the vibration and acceleration conditions of electric vehicle applications. The auxiliary equipment for refrigerating, heating and storing the chlorine places severe weight and volume penalties on the system as well as reducing overall energy efficiency through parasitic power losses. Also, the self-discharge rate is likely to be high due to the access of chlorine to the zinc electrode by diffusion through the electrolyte. The system does, however, have commercial possibilities since both zinc and chlorine are relatively inexpensive, abundant, and lightweight raw materials.

3.2 Molten-salt batteries

   These batteries are still in an early stage of development. For traction purposes, they offer both a high energy density through the selection of suitable reactant pairs, and a high power density through the use of a molten-salt electrolyte of low electrical resistance. High temperature operation also alleviates heat rejection problems. Of the several electrode pairs so far in-

vestigated, the sodium–sulphur and lithium–sulphur systems are the most technologically developed. The lithium–chlorine system has received much less attention, presumably because this system is even more difficult to handle than either the sodium–sulphur or the lithium–sulphur systems. Apart from material and seal degradation problems associated with working at high temperatures, other operational difficulties encountered with molten-salt batteries include: immobilization of the constituents, structural and volume changes on cycling, self-discharge, container corrosion, and provision of adequate insulation for high temperature maintenance. Further, since lithium is extremely reactive with oxygen, nitrogen, water, etc., manufacture of batteries using this metal must be carried out in inert-atmosphere dry boxes. Oxygen has also to be excluded during the assembly of sodium–sulphur cells.

3.2.1 Sodium–sulphur battery

The sodium–sulphur cell uses a liquid sodium negative electrode, a liquid sulphur positive electrode and a solid ceramic electrolyte* (β-alumina doped with small amounts of sodium oxide [128], composition $Na_2O.5Al_2O_3$ to $Na_2O.11Al_2O_3$), which can selectively conduct sodium ions. Since the electrolyte is not an electronic conductor, it also functions as a separator for the electrode materials. The cell reaction can be written as:

$$\overset{\ominus}{} \quad \overset{\oplus}{}$$
$$x \text{ Na} + y \text{ S} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Na_x S_y. \qquad (7)$$

On discharge, elemental sodium is oxidized at the sodium/β-alumina interface and sodium ions migrate through the solid electrolyte into the cathode compartment which is filled with electronically-conducting graphite felt impregnated with sulphur. For the first 60% of discharge, sulphur is converted to sodium pentasulphide (Na_2S_5), which is immiscible with sulphur. The open-circuit voltage of the cell is 2.08 V throughout this stage. Further discharge results in the transformation of Na_2S_5 to a single-phase polysulphide with a composition between Na_2S_3 and $Na_2S_{2.7}$ at 360 °C. The open-circuit voltage falls continuously to 1.76 V and then remains constant as solid Na_2S_2 begins to separate out in the melt. In order to keep all the phases liquid throughout the compositional range, the sodium–sulphur cell is operated between 300 and 375 °C. A wicking system has been developed in the U.K. to keep the ceramic electrolyte covered with sodium at all times. The final reaction product, Na_2S_3, corresponds to 100% discharge. During charge, the reactions are reversed. However, problems are encountered at a charge state exceeding Na_2S_5, since a two-phase region is encountered and sulphur, which is an electronic insulator, separates out and isolates the current collector from the polysulphide melt and also corrodes the container. Recently, a patent has been issued [129] which claims that imidazole reduces the operating tem-

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*Sodium–sulphur, which uses a solid electrolyte, is included here in the molten-salt battery group, since it operates at high temperatures with molten reactants and products.

perature of Na–S cells without any significant deleterious effects on the operating characteristics.

The theoretical energy density of the system is 664 W h/kg, taking 1.76 V as the open-circuit potential and Na_2S_3 as the final reaction product. The pioneer work on the battery was done by Ford Motor Co. in the U.S.A. [130] and further research is being carried out in England (Chloride Silent Power Ltd. — a joint venture company between the Chloride Group and the U.K. Electricity Council, British Rail, and the Atomic Energy Research Establishment [131]), France (Compagnie Générale d'Electricité [132]), Germany (Brown, Boveri and Cie A.G. [133], Battelle Institute), Japan (Yuasa Battery Co. [134]), South Africa (Council for Scientific and Industrial Research), and United States (Dow Chemical Co. [135], E.S.B.*, General Electric [136] and T.R.W.). A sodium–sulphur battery (50 kW h, 63 W h/kg) was tested in a Bedford van by the U.K. Electricity Council in 1972. The vehicle reached a maximum speed of 56 km/h and a range of 128 km. The Yuasa battery has been used to power a lightweight van, and has been developed to give an energy density of more than 180 W h/kg (4-hour rate) and a life of more than 300 cycles (60% discharge depth) [16].

Most cell designs employ tubular geometry, the cell consisting of a hollow, close-ended cylinder of ceramic electrolyte sealed into a cylindrical metallic can (iron-, nickel- or cobalt- based alloys). The wall thickness of the electrolyte tube is typically 1 mm. Hermetic seals are required between the ceramic tube and the insulating separator (usually an α-alumina collar) and between the separator and the metal can. These seals must be stable in the presence of molten sulphur and sodium and must also have an expansion coefficient which is matched to that of the electrolyte and cell body. Seal leakage and degradation greatly limit the operational lifetime of sodium–sulphur cells, and much effort is being directed towards developing new materials and methods for making more robust seals to satisfy the necessary electrical, chemical, mechanical, and thermal requirements. Current practice is to use a glass seal to join the electrolyte tube to the alumina separator. Lifetimes of up to one year have been obtained with this type of seal. A mechanical seal in which the alumina collar is clamped in compression with a deformable metal gasket (*e.g.*, aluminium, Inconel), and not a bonded seal, is generally preferred for fixing the alumina separator to the cell body.

Another factor limiting the lifetime of sodium–sulphur cells is corrosion of the container material by the polysulphide melt. In an attempt to reduce corrosion problems, British research groups in recent tests have exchanged [131] the normal position of the reactants so that sulphur is now contained in the central tube and sodium in the container. A central graphite rod was used as the current collector for the sulphur electrode. With this cell arrange-

*The sodium cell of E.S.B. employs a mixture of aluminium trichloride, sodium chloride, and antimony trichloride instead of sulphur. An energy density of 110 W h/kg has been obtained, but cell life is low despite the fact that the cell operates at only 180 - 220 °C.

ment, the cover of the upper end of the electrolyte tube is the only part which is exposed to corrosive sulphur species, and the stainless steel case used in previous cells can be replaced by mild steel at substantial cost savings. It has also been shown [137] that the central sulphur design is more suitable for motive power applications by providing a better balance between energy and power capabilities. An argument against the design can be made on the grounds of safety — it would seem more desirable to have the sodium in the inner part of the cell.

Considerable effort is being directed towards manufacturing high-purity electrolyte tubes with high conductivity (5 Ω^{-1} cm^{-1}), high fracture strength (30 000 - 40 000 p.s.i., 207 - 275 MPa), and resistance to sodium degradation. Most batteries under development use β-alumina as the electrolyte. This consists of closely packed spinel blocks of alumina which are separated by oxygen bridges, the spacing between layers allowing sodium ions to migrate through them under the influence of an electric field. The alumina, obtained from the Bayer process, consists of a mixture of β- ($Na_2O.11Al_2O_3$) and β''- ($Na_2O.5Al_2O_3$) alumina, and has an ionic resistivity in the range 2 - 12 Ω at 300 °C. The resistivity is a function of dopant concentration, pressing and sintering conditions, and composition. Very pure material is required for long cell life.

Tubes are made either by isostatically pressing the powder, or by electrophoretic deposition from a suspension in an organic medium on to an electrically charged mandrel. The green deposits are then removed from the mandrel and sintered. Careful control is required at this stage as sintering strongly affects the physical properties of the tubes. In order to reduce the possibility of electrolyte deterioration during cell operation, the grain size of the β-alumina should be kept uniform and small. Tubes made from large-grain alumina break down after a few cycles and become electronic conductors due to the penetration of metallic sodium as dendritic needles. Sodium penetration has also been shown to be dependent on the chemical composition of the electrolyte and the current density. Attempts are also being made to discover three-dimensional sodium ionic conductors (β-alumina is only a two-dimensional conductor), and in this respect the electrical properties of the material "Nazirpsio" ($Na_3Zr_2PSi_2O_{12}$) have been closely examined at the Massachusetts Institute of Technology. The material competes directly with β-alumina at the operating temperature of the sodium–sulphur battery. It is formed more easily than β-alumina with sintering temperatures ~1 200 °C, is not affected by exposure to moisture, and has a conductivity at 300 °C comparable with, or better than, β-alumina.

The Dow cell uses a special borate glass as the sodium-ion conducting electrolyte. Sodium is contained in borate glass capillaries 80 μm in diameter with walls approximately 10 μm thick, which are bundled together in thousands and intermeshed with aluminium foil current collectors. Thin-walled fibres must be used since the resistance of the glass is much higher than that of β-alumina. The Dow cells have a relatively low current density (a few mA per cm^2 of glass fibre) and operate at a lower temperature (200 °C) than the

β-alumina cells. Cells containing 1 000 fibres (0.55 A h capacity) have operated for over 550 deep-discharge cycles at 12 mA/cm^2 of fibre. Conceptual designs of this battery show that 220 W h/kg and 220 W/kg can be obtained and a 60 kW h prototype battery is expected to be available for an electric vehicle by 1980.

Another problem with sodium—sulphur batteries is loss in capacity after extended periods of charge/discharge cycling. This is associated with build-up of corrosion products [136], and with the wetting properties of the sulphur electrode. Because elemental sulphur is an electronic insulator, graphite felts are added to provide a large electrode area. Sulphur wets carbon surfaces more effectively than sodium polysulphides [138] and during recharge will tend to spread over the carbon fibres in the electrode to form a continuous insulating film. This results in an increase in cell resistance and the failure of the cell to reach a fully-charged state. Increases in recharge-ability have been achieved by changing the shape and surface chemistry of the felt, e.g., Al$_2$O$_3$ coating, and the composition of the melt [133]. Good performances (85% capacity after $\sim$500 cycles) were obtained from the British central sulphur cell which is less prone to attack by corrosion and, hence, does not suffer from the effects of excessive accumulation of corrosion products during cycling.

The sodium—sulphur battery is considered attractive for electric vehicles because of its high energy density (about 3 - 4 times greater than the lead—acid battery) and potentially low cost. However, the major drawback for use in private vehicles is the need to maintain the battery at an elevated temperature, and for this reason, the most likely application of sodium—sulphur batteries will be in public transport and fleet operations which can support an efficient maintenance service.

3.2.2 Lithium—sulphur battery

A research and development program on rechargeable lithium—sulphur batteries was commenced at Argonne National Laboratory in the United States in 1968 [139]. In initial studies, the system consisted of liquid lithium and sulphur electrodes and an electrolyte of molten LiCl—KCl eutectic at an operating temperature between 380 and 450 °C. The cell reaction is:

$$\overset{\ominus}{}\overset{\oplus}{} \qquad 2Li + S \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2S. \tag{8}$$
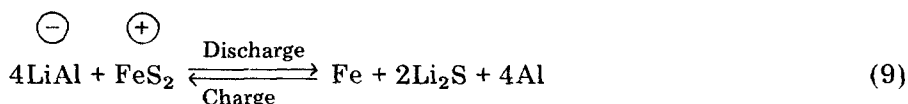
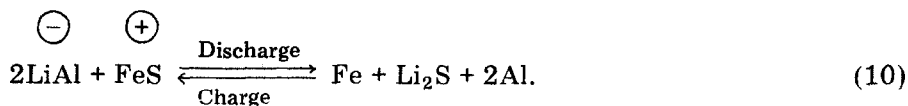The open-circuit potential at 400 °C is 2.20 V and the theoretical energy density, 2 567 W h/kg.

The development of such cells is beset with many practical difficulties. Problems encountered with the negative electrode include: (a) attack of ceramic insulators, current feed-throughs and separators by the highly-corrosive liquid lithium, (b) difficulties in retaining lithium in porous metal current collectors during extended cycling, (c) self-discharge caused by

lithium dissolving in the molten LiCl–KCl electrolyte, and (d) the tendency of lithium to react with KCl in the electrolyte to form potassium vapour (Li + KCl → K + LiCl). These problems were eliminated, or greatly reduced, by the use of a solid lithium–aluminium alloy as the negative electrode. The lithium–aluminium electrode consists of a porous bed of alloy particles (~48 at.% Li)* in molten LiCl–KCl contained within a porous aluminium current collector.

Problems were also found with the positive electrode, the main difficulty being the loss of sulphur through vaporization and through the formation of polysulphides that are soluble in the molten-salt electrode. Work at the Atomics International Division of Rockwell International and at Argonne has shown that the use of iron sulphide (FeS) or iron disulphide (FeS_2) as the active material in the positive electrode greatly decreased sulphur losses during cell operation. Electrode construction was similar to that of the lithium–aluminium negative electrode and consisted of a porous bed of the particulate material saturated with LiCl–KCl electrolyte and held within a current-collector matrix. The cell reactions are:

$$\ominus \qquad \oplus$$
$$4LiAl + FeS_2 \; \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} \; Fe + 2Li_2S + 4Al \qquad\qquad (9)$$

and

$$\ominus \qquad \oplus$$
$$2LiAl + FeS \; \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} \; Fe + Li_2S + 2Al. \qquad\qquad (10)$$

The use of lithium–aluminium alloys and iron sulphide electrodes has resulted in the development of practical cells delivering energy densities ~70 W h/kg at the 2-hour rate and peak power densities around 50 W/kg, and having a lifetime of 200 - 250 cycles. Argonne's long-term target energy density is 175 - 185 W h/kg at the 4-hour rate and the target power density is greater than 100 W/kg at 50% discharge. These cells have a lower theoretical specific energy (625 W h/kg) than lithium–sulphur cells, but are considered to be still capable of meeting performance requirements for electric vehicle propulsion. The FeS electrode is less corrosive than FeS_2, but the Li–Al/FeS system has a lower open-circuit potential (1.35 V, cf. 1.65 V for Li–Al/FeS_2 systems), lower specific power and a lower theoretical specific energy (458 W h/kg). Batteries using FeS electrodes are, therefore, more suitable for stationary energy storage.

Considerable effort has been devoted [140, 141] to identifying the electrochemical reactions that occur during charging and discharging of FeS_2 and FeS electrodes. For FeS_2 electrodes, it has been found that charging and

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*at.% = atomic weight per cent.

discharging results in the formation of intermediate phases, $Li_4Fe_2S_5$ and Li_2FeS_2, and that overcharging gives $FeCl_2$ (complexed with KCl in the electrolyte) and elemental sulphur. For FeS electrodes, Li_2FeS_2 and $LiK_6Fe_{24}S_{26}Cl$ occur as intermediate phases, and overcharging results in the formation of complexed-$FeCl_2$, elemental sulphur, and probably FeS_2. Maximum charge cut-offs of 2.2 and 1.65 V are recommended for cells with FeS_2 and FeS electrodes, respectively. Since cells having slightly differing coulombic efficiencies and capacities become mismatched after several cycles, a charge equalization device has been developed at Argonne which allows battery cells to be charged in series, with safety, to the cut-off voltage.

Other problems encountered with FeS and FeS_2 positive electrodes include: (a) low utilization of active material, and (b) excessive swelling during charge/discharge cycling. The high polarization of FeS electrodes caused by interaction of FeS with potassium in the LiCl–KCl electrolyte during discharge (v.s.) can be reduced by the addition of Cu_2S, with consequent higher utilization of the theoretical capacity. The use of electrolytes containing only lithium ions also improves electrode performance, but increases the cost of the cell constituents. The addition of CoS_2 to FeS_2 was found to increase the power characteristics of cells and to improve current collection within the electrode [142]. However, the additives do not eliminate the problem of volume expansion during cycling and, consequently, methods have been developed [143] for assembling Li–Al/FeS and Li–Al/FeS_2 cells in the maximum volume (uncharged) state, i.e., the negative electrodes consist of porous aluminium plaque and the positive electrodes contain Li_2S and iron powder. This procedure led to a marked improvement both in cell performance and lifetime and, in addition, assembly operations are simplified since the high-purity, inert atmosphere necessary when handling Li–Al alloys is no longer required.

Much of the work now in progress at Argonne and contracted industrial firms (e.g., Gould Inc., Atomics International, Eagle-Picher Instruments Inc., Catalyst Research Corporation) is concerned [144] with evaluating electrode designs and materials for the fabrication of various cell and battery components. The materials must be inexpensive and resistant to corrosive attack. Stainless steels, nickel, and mild steel have proved suitable materials for cell housings and current collectors for the negative electrodes. However, finding an effective, low-cost separator and a positive electrode current collector has proved more difficult. The separator material must not only provide electronic insulation between the electrodes, but also must support the molten-salt electrolyte and allow the passage of lithium ions. Cells currently in operation at Argonne have successfully used boron nitride (BN) cloth as a separator material in tests lasting up to 8 000 hours. However, alternative separator materials, e.g., Y_2O_3, MgO [145], are being investigated, as BN cloth is expensive ($\sim$\$500/ft^3), relatively thick ($\sim$2 mm) and has a structure which is too coarse for effective particle retention. A number of current-collector materials are available for FeS electrodes, but the choice is very limited for FeS_2 electrodes. Present FeS_2 cells have molybdenum current collectors, but

there are fabrication, cost, and weight problems when using this metal. Promising results are being obtained from carbon-bonded FeS_2 positive electrodes which are both inexpensive and relatively easy to manufacture. The carbon lattice acts as both a current collector and a support for the active material. The porosity of the lattice structure can be accurately controlled by the addition of a volatile, pore-forming material, $e.g.$, $(NH_4)_2CO_3$, during the fabrication process.

A wide variety of shapes and sizes has been used in cell designs. First designs favoured a cylindrical cell containing upper and lower lithium–aluminium electrodes and a central FeS_2 electrode; with this arrangement both sides of the positive electrode are used. These cells gave a maximum specific energy density of 155 W h/kg and a lifetime of 248 cycles. Under typical driving profile loads, an energy density of 61.4 W h/kg and a power density of 50.4 W/kg was obtained [146]. Cells of similar design containing FeS positive electrodes have operated [147] for 121 cycles with a maximum specific energy of 82 W h/kg and typical values in the range 40 - 60 W h/kg*. The energy efficiencies of these cells were generally in the range 70 - 80%.

Recently, rectangular cells have been developed [148] which are considered more suitable for installation in a practical battery. These are of similar design to the cylindrical cells, with a central iron sulphide positive electrode sandwiched between two lithium–aluminium negative electrodes. Both FeS and FeS_2 are being used as positive electrode materials, and by March 1977 the best cells under test had reached lifetimes of 585 (Li–Al/FeS) and 225 (Li–Al/FeS$_2$) cycles over periods of 8 000 and 3 200 hours, respectively. The common cause of failure in other cells was found to be a short circuit. In some tests, cells have withstood thermal cycling (20 - 400 °C) without any observable ill effects.

Two- or three-cell batteries have been built and tested for both the Li–Al/FeS and Li–Al/FeS$_2$ systems. Lifetimes of over 300 cycles have been shown by each battery system, and coulombic efficiencies of 95 - 100%, and energy efficiencies of 80 - 85% have been obtained [149]. Argonne plan to test a prototype Li–Al/FeS$_2$ battery in a van late in 1979. The battery is being built by Eagle-Picher and consists of 120 rectangular cells in a parallel/series combination to give about 40 kW h capacity and 100 W h/kg energy density at the 5-hour rate. The cells are housed in a vacuum insulation jacket and temperature control is maintained by ambient-air cooling with resistance heaters for start-up. The battery case measures 28 cm × 97 cm × 1.52 m and encloses both the heating and cooling coils. The battery will store about two and one-half times as much energy as an equivalent-weight conventional lead–acid battery, and is expected to give the van a range of more than 160 km at speeds around 72 km/h. Battery cycle life will be about 200 cycles.

The lithium–sulphur system is also being investigated by General Motors Corporation [150 - 152] in the U.S.A., in Germany by the Battelle Institute,

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*The weight of thermal insulation necessary for high temperature operation was not included in the energy density figures reported and, therefore, direct comparison with other systems (Table 3) should be made with caution.

in South Africa as a joint research project between C.S.I.R. and the Anglo American Corporation, and in the U.K. by the Admiralty Materials Laboratory. The General Motors cell design is similar to that of Argonne and consists of two negative electrodes enclosing a central positive electrode. A two-layer separator of zirconia cloth and boron nitride cloth was used and tests have been conducted on two systems: (55 at.%) Li−Al/FeS$_2$ and (80 at.%) Li−Si/FeS$_2$. Li−Si/FeS$_2$ cells showed better maximum specific energy (130 cf. 115.5 W h/kg), and better sustained power density (52.8 cf. 25.2 W/kg) than Li−Al/FeS$_2$ cells. This was attributed to the lighter weight of Li−Si Alloy electrodes and to better packaging which reduced the weight of excess electrolyte. It was reported that a Li−Al/FeS$_2$ cell was operating satisfactorily after more than 700 deep charge/discharge cycles during a 14-month period. The durability of the Li−Si/FeS$_2$ system was unknown, since a failure in the cycling device had destroyed the cell after 77 cycles of stable operation.
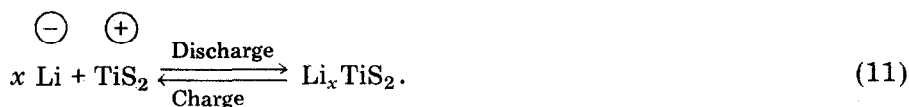
3.3 Organic electrolyte batteries

These systems are based on the use of lithium as the high energy negative electrode. Since lithium is unstable in contact with water, electrolytes used consist of aprotic organic solvents (e.g., propylene carbonate, dimethyl-sulphoxide, dimethylformamide, etc.) containing dissolved lithium salts, e.g., LiClO$_4$, LiBF$_4$, LiPF$_6$, LiAsF$_6$, LiCl, LiBr, LiAlCl$_4$, etc.. However, the low conductivity of these electrolytes (at least an order of magnitude lower than aqueous solutions) has so far limited the use of such lithium cells to low-power applications in electronic equipment. A wide variety of materials has been considered as candidates for the positive electrode, but most investigations have met with little success. Among the materials tested have been metal halides, e.g., AgCl, CuCl$_2$, NiCl$_2$, gases, e.g., Br$_2$, CO$_2$, H$_2$S, NH$_3$, SO$_2$, oxides, e.g., Bi$_2$O$_3$, CrO$_3$, MnO$_2$, and MoO$_3$, and organic compounds (quinones, hydroquinones). Typical problems to be faced with these systems include: low cycling efficiency and discharge rates; positive electrode stability and utilization; formation of lithium dendrites and lithium-shape change; self-discharge; electrolyte conductivity, purity, and stability; separator durability; temperature control; high manufacturing costs.

Recently, there has been much interest in a new type of rechargeable lithium−organic electrolyte system that uses lamellar transition metal dichalcogenides as positive electrode materials [153]. The sulphides, selenides, and tellurides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum have been tested as cathode-active materials and the most promising system appears to be the Li−TiS$_2$ couple [154].

3.3.1 Lithium−titanium disulphide battery

The electrochemical discharge reaction of this system proceeds via the insertion of lithium ions between adjacent sulphur layers in the dichalcogenide, i.e.,

$$\overset{\ominus \quad \oplus}{x \text{ Li} + \text{TiS}_2} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} \text{Li}_x \text{TiS}_2. \tag{11}$$

This type of reaction is commonly called an intercalation reaction; it does not require any bonds in the positive electrode to be broken and occurs with no change in the host matrix except for a slight expansion perpendicular to the basal planes [155]. The charge/discharge process shows good reversibility and operates at room temperature. At complete discharge, the compound LiTiS$_2$ is formed. The open-circuit voltage ranges from ~2.5 V for fully-charged TiS$_2$ to 1.87 V for completely-discharged TiS$_2$. Based on an average voltage of 2.15 V, the theoretical energy density of the Li–TiS$_2$ couple is about 480 W h/kg. Titanium disulphide is the most suitable cathode material as it is the lightest of all the dichalcogenides, is relatively inexpensive, and allows rapid diffusion of lithium. High values of the diffusion coefficient for lithium permit current densities up to 10 mA/cm^2 to be maintained at room temperature [156]. The Na–TiS$_2$ couple is less promising since the limiting formula of the alkali-intercalated lattice is Na$_{0.8}$TiS$_2$. Titanium disulphide has recently been successfully employed as a reversible cathode in the high temperature cell Li–Al/KCl–LiCl/TiS$_2$ [157]. A disadvantage of using compounds such as TiS$_2$ is that they must be manufactured synthetically to exact stoichiometries, and production in large quantities could pose severe technical problems.

Research and development of the Li–TiS$_2$ system has been pioneered by the Exxon Research and Engineering Company in the United States [156]. In 1975, Li–TiS$_2$ cells with pure lithium anodes and lithium perchlorate–propylene carbonate electrolyte were cycled [158] at greater than 60% material utilization for more than 250 high-rate cycles at current densities up to 7.5 mA/cm^2. These encouraging results, together with the advantages of operating at near normal temperature, e.g., no need for insulation, reduced corrosion, etc., have encouraged Exxon to develop a Li–TiS$_2$ battery for electric vehicle propulsion. No details have been announced of the electrolyte used in the battery, but it definitely does not contain lithium perchlorate [159], and has reduced problems of lithium dendrite formation and shape change on cell cycling. An energy density of 132 W h/kg and a peak power density of 132 W/kg are claimed together with an energy efficiency of about 80% after 120 cycles. In February 1978, it was announced that Exxon was moving into pilot plant production of Li–TiS$_2$ batteries which will be capable of powering a car for about 160 km.

More recently, Bell Telephone Laboratories in the United States have developed an experimental, rechargeable lithium–vanadium–iron disulphide system using a lithium perchlorate–propylene carbonate electrolyte. This system offers advantages in good rechargeability, high-voltage potential, light weight, small volume, long shelf life and an energy density about five to eight times that of a lead–acid battery. To date, the Bell system has been

subjected to 50 charge/discharge cycles without detectable change in the structure of the cell materials. An alternative intercalation battery system based on the use of molybdenum disulphide as cathode has been tested and evaluated at the University of British Columbia [160]. The performance characteristics of this system have been found to be very similar to those of the Exxon TiS_2 battery.

3.4 Solid-state batteries

The main interest in developing all-solid batteries lies in the hope that such systems will avoid many of the problems encountered when using batteries with liquid constituents, *e.g.*, corrosion, electrode and electrolyte containment, structural changes on cycling, seal failure, need for careful maintenance, etc. Considerable effort is being expended on developing better solid electrode and electrolyte materials. These materials must be relatively inexpensive, easy to fabricate, have good mechanical strength, high chemical stability, give a good geometrical match at interfaces, and exhibit high ionic conductivity, preferably at normal or relatively low temperatures. Materials for electrolytes must also have low electronic conductivity. A mixed-conductor is suitable for electrode applications since it serves as the interface between the battery (in which current is carried by ions) and the external, electronically·conducting circuit. Such materials are commonly referred to as "solid solution electrodes", a term introduced by Steele [161].

The research effort in the area of fast ion conduction has increased quite dramatically over the last few years [162], and much attention has been devoted to developing alkali ion conductors as electrolyte and electrode materials. This has arisen partly from the immediate potential of β-alumina compounds as solid electrolytes in molten-salt batteries and also from attempts to develop all-solid batteries, especially systems using lithium anodes, as these provide the possibility of high cell voltages and very high energy densities. However, at present, there is no lithium conductor available with an ambient ionic conductivity comparable with that of sodium β-alumina except lithium β-alumina single crystals [163].

Electrolyte materials examined so far can be classified as: (a) those which have an open framework structure of ions within which the alkali ions can reside and move, (b) those with an excess of available sites over the number of mobile ions actually present. In the first class of materials, compounds with the type formula $Li_{16-2x}D_x(TO_4)_4$ (D = Mg^{2+}, Zn^{2+} or Ca^{2+}; T = Si^{4+} or Ge^{4+}) have been examined [164] and in the second class, compounds such as $LiAlSiO_4$ [165], Li_4SiO_4 and Li_5AlO_4 [165 - 168] have been investigated as lithium superionic conductors. The effect of dopants on the ionic conductivities of these materials is also being examined — a comparison of the ionic conductivities of various solid lithium electrolytes can be found in ref. 169. A material comparable with sodium β-alumina (co-ionic Li^+–Na^+ β-alumina) is currently being examined [170] by General Electric as an electrolyte for use in solid-state lithium batteries, and encouraging results are also being obtained from studies on Li_3N [171].

Materials considered for solid solution electrodes for alkali ions have included: (a) graphite and fluorographite, (b) transition metal dichalcogenides (v.s.), (c) molybdenum, tungsten, and vanadium bronzes, (d) potassium β-ferrite (for review see ref. 161). A major problem with solid-state battery systems is the maintenance of good contact at the electrode/electrolyte interface, especially when lattice expansion effects take place during charge/discharge cycling of a battery. For example, intercalation of lithium in TiS_2 electrodes results in a lattice expansion of ~8%, whereas only ~1% can be tolerated for good conduction [172]. Another problem is high internal resistance, and in this respect much work is being directed towards developing thin cells with high electrode area.

Despite all recent research efforts, very few materials with immediate technological applications have emerged, and solid-state batteries so far examined have proved unsuitable for electric vehicle applications, being expensive to manufacture and producing too low discharge currents. A promising system is the $Ca-NiF_2$ battery developed at the Battelle Institute in Germany. This uses a NaF- or YF_3-doped CaF_2 electrolyte and operates at 400 - 500 °C. The theoretical energy density of the system is 1 091 W h/kg and the open-circuit potential 2.82 V. Encouraging results have also been obtained [173] from a prototype 72 kW h solid-state $Li-Si/LiI(Al_2O_3)/TiS_2$, Sb_2S_3, Bi system. This battery operates at 300 ± 10 °C, exhibits good reversibility and has a projected energy density of 200 W h/kg and a cost of \$35/kW h. Despite such developments, it is clear that much more research is required into fast ionic conduction in the solid state, thin film technology, and structural changes during battery cycling before all-solid concepts become practical for vehicle traction applications.

4. Comparison of batteries

An electric car industry will be fashioned by the interplay of fuel shortages, pollution controls, electricity demands, costs, technology, and legislation. The future of the electric vehicle as a viable transportation alternative to the internal combustion vehicle depends upon the development and commercial availability of a battery which can meet a number of requirements, among the most important being: high energy density (for long range), high power density (for good acceleration and hill-climbing performance), long life (for low vehicle operating costs), great simplicity, low materials and manufacturing costs, safety in operation, and crash worthiness. Other requirements include: low maintenance, low self-discharge, easy, efficient, and rapid rechargeability, good high- and low temperature characteristics, good shelf-life, small size, and easy replacement. With these requirements in mind, the advanced batteries discussed above may be categorized principally into near- (0 - 8 years) and long- (>8 years) term prospects for traction applications (Table 4).

TABLE 4

Evaluation of electric vehicle batteries

Battery	Problems	Initial cost ($/kW h)	Projected cost ($/kW h)	Efficiency (%)	Near-term prospects (0 - 8 years)	Long-term prospects (>8 years)
Lead–acid (Improved)	Low energy density, grid corrosion, slow recharge, electrolyte maintenance, cost.	~90	50	60 - 65	excellent	fair
Nickel–zinc	Short life, Zn solubility, separator stability, Ni cost, electrolyte maintenance, oxygen transport, thermal control.	180	55	60 - 65	good	good
Nickel–iron	Low power capability, Ni cost, low efficiency, electrolyte maintenance, thermal control.	100 - 150	65 - 70	<60	good	good
Iron–air	Low efficiency, low power capability, short life, system complexity, electrolyte maintenance, thermal control.	100	60	<40	poor	poor
Zinc–air	Short life, weight, low efficiency, system complexity, manufacturing cost.	53	35	~40	fair	good
Zinc–chlorine hydrate	Size, system complexity, safety, life, electrolyte maintenance.	100	30 - 35	65	poor	poor
Sodium–sulphur	Short life (seals, corrosion), electrolyte stability, size, safety, thermal management, manufacturing process.	50	35	85	fair	good
Lithium–sulphur	Short life, positive electrode performance, separator, thermal management, charge control, manufacturing process, safety.	60	35 - 40	70 - 80	poor	good
Lithium–titanium disulphide	Short life (?), low power capability, poor reversibility, electrolyte conductivity; requires more research.	?	40 - 50	80 - 90	poor	fair

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Three battery systems offer prospects of near-term applications: advanced lead–acid, nickel–iron and nickel–zinc. In the United States, it is expected that these systems will be used in the first batch of demonstration electric vehicles delivered under the Electric and Hybrid Vehicle, Research, Development and Demonstration Program (Public Law 94-413), and required to be on the road by December, 1978. The Program is being organized by the Department of Energy, and, at present, there are ten D.o.E. sponsored contracts with industry working on these three battery systems. Advanced lead–acid and nickel–iron batteries have already been used as propulsion batteries in the Japanese Electric Vehicle Program over the period 1971 - 1976 [16]. The lead–acid battery has been used as the motive-power unit for most of the prototype electric vehicles now in commercial use, and is likely to serve in this capacity until the end of the decade. Nickel–iron batteries are extremely rugged and capable of running well in excess of 1 500 charging cycles. On the other hand, conventional nickel–zinc batteries have the disadvantage of a short cycle life (<400 cycles) due to dendrite formation on the zinc anode. However, given further improvements in life by the suppression of dendrite growth, e.g., with a vibrating electrode, and by developing more stable separators, the nickel–zinc system will be more attractive for traction applications than the corresponding nickel–iron system. The latter has a poor high-rate capability and charge/discharge efficiency, and is subject to self-discharge problems. Nickel–zinc batteries have demonstrated energy densities much higher than those of lead–acid, and could power present-day vehicles two-and-a-half times further; ranges of 90 - 190 km are expected in city traffic use. It has been estimated [174] that vehicles with this range could meet the transportation needs of over 75% of current second-car owners in the United States. A recent cost analysis of these three near-term battery systems has shown [175] that lead–acid offers the lowest initial cost, nickel–iron the lowest cost per km and nickel–zinc the greatest range but highest cost per km.

Batteries with long-term prospects for traction application include the iron–air, zinc–air, zinc–chlorine hydrate, sodium–sulphur, lithium–sulphur and lithium–titanium disulphide systems. Although metal/air batteries appear attractive because of their high energy densities and low material cost, the systems suffer from a very low efficiency of the charge/discharge process (Table 4), which is associated with the fundamental problem of finding a high-performance, rechargeable oxygen electrode of low cost. Air electrodes are not capable of operating at the high current densities required for traction applications, and thus metal/air batteries all suffer the common problem of low specific power (<50 W/kg). System complexity is another unattractive feature; bulky auxiliary equipment required for electrolyte circulation, water maintenance, CO_2 removal, etc., severely limits the usefulness of metal/air batteries as power sources for small electric vehicles. The iron–air system has a lower cell voltage than zinc–air and, hence, more cells are required for a given battery voltage. The most sophisticated metal/air battery so far developed is the C.G.E. circulating zinc–air system which avoids the problems of

dendritic growth on recycling that have beset previous secondary alkaline zinc batteries. The present performance is better than most other aqueous electrolyte batteries (Table 3), but the system has yet to be tested in a proto-type electric vehicle. A detailed cost analysis has shown that the initial investment cost per kW h will be low ($53) for high-volume production (6 600 batteries of 20 kW peak power per annum), and consequently the success of this zinc–air battery is subject to the development of a thriving electric vehicle market.

The zinc–chlorine hydrate battery is unlikely to find practical use in electric vehicle applications. The battery is complex, requires a large auxiliary refrigeration/storage system and stringent safety precautions. All these factors seriously add to the weight and cost of the system. In addition, the cycling ability of this system has yet to be proven. This battery appears better suited to load-levelling applications. In fact, E.D.A. has just been awarded a $3.8 mil-lion contract by E.P.R.I. to design, develop, fabricate, and test a 10 MW h zinc–chlorine hydrate system as a means of levelling utility power loads.

Molten-salt batteries are viewed with great optimism — particularly in the case of the sodium–sulphur system. The main advantages of these systems are that they are the only batteries now under development that are capable of providing the high energy densities (>150 W h/kg) and specific power required by electric cars for private travel (Table 2), and that are capable of being 60% recharged in two hours. Added advantages are that the batteries have high volumetric energy densities and are potentially cheaper than the lead–acid system since they are based on cheap and abundant electrode materials, although there may be some initial problems with world lithium supplies since present usage of this metal is relatively low compared with other metals. There has been very little road-testing of high-temperature batteries and it has yet to be established whether the ceramic materials needed to contain the molten chemicals will withstand road vibrations. Much concern has been expressed over the dangers of an explosive reaction between molten alkali metals and sulphur in an accident, but advocates of high-temperature batteries have pointed out that the specific energy of these systems is considerably less (some 65 times) than that of the gasoline used in i.c.e. vehicles. Sodium batteries are more attractive for automotive use than lithium batteries since they operate at lower temperatures, and therefore less expensive case materials and insulation can be used. Sodium batteries have reached a more advanced developmental stage than their lithium counterparts, and the Chloride Group in Britain expect their sodium–sulphur battery to become commercially available in about five years [176], whereas Argonne believe that lithium–sulphur battery production will commence in the mid-1980s. It is likely that high-temperature batteries will be used mainly for public transport vehicles, particularly for track-following vehicles collecting wayside power, e.g., trams, trolley buses and railcars. It has been estimated that a sodium–sulphur battery weighing just over 1.5 tonne applied to a conventional electric railcar would give, away from the electrified line, a 145 km range at up to 120 km/h.

All-solid and organic electrolyte–lithium batteries are still at the laboratory experimental cell stage. At present, no confident prediction can be made on their suitability for electric vehicle propulsion. These systems are expected to have energy densities lower than that of the higher temperature lithium–sulphur battery, but place less stringent mechanical requirements on cell materials and remove the need for thermal insulation. The future of these systems depends greatly on the level of support for fundamental research into fast ion-conducting materials. However, commercialization of these systems for traction purposes seems a long way off. Lithium is only moderately abundant in the earth's crust and therefore batteries based on this metal may prove expensive.

The degree of penetration into the electric vehicle market of any one of the advanced battery systems discussed here will depend greatly on the job the vehicle has to perform. Electrics will find increasing use in city public transport, and as delivery and service vehicles operating in a regular fashion, but it is unlikely that the electric car will ever replace the petrol-powered family car. This is a vehicle which is generally used on impulse and is required to perform widely different daily tasks. This is particularly true in countries such as Australia and the U.S.A., where great distances outside the cities and the sparsely populated countryside require vehicles to have a good range and speedy refuelling capability. Present electric vehicles do not fulfil these requirements; they have an energy store equivalent to ~1 gallon of petrol, and this takes several hours to refill. In the private transport sector, the electric car is more likely to take the place of the second family car, provided that there is a sufficient market for such vehicles to be produced at a cost competitive with their i.c.e. counterparts. In the U.S.A., the second car market is estimated at 25% and this represents a substantial number of vehicles with prospects of appreciable petroleum savings if replaced by electric transport. For this type of application, simply-built batteries with energy densities in the region of 50 - 100 W h/kg for a 2-hour discharge period and peak power densities of more than 70 W/kg will be required (Table 2). The battery that would best meet these requirements is the nickel–zinc system. If cycle life can be increased by a factor of 3 - 5, then the nickel–zinc system will take the major share of the market for electric vehicle batteries.

References

1 The Japan Times, Monday July 5, 1976.
2 Electr. Rev. Int. London, 200 (1977) 41.
3 Electr. Vehicle News, 6 (1977) 28.
4 Stanford Res. Inst., Patterns of Energy Consumption in the U.S.A., Office of Science and Technology, Executive Office of the President, Washington, D.C. 20506, January 1972.
5 J. P. K. Peeler (CSIRO Div. Mineral Eng.), personal communication.
6 National Energy Advisory Committee, Proposals for an Australian Conservation of Energy Program, submitted to Minister for National Resources, September 1977 (Australian Govt. White Paper).

7 Energy for Transport — Long Term Possibilities, U.K. Dept. of Energy, Energy Paper No. 25, April 1978.
8 A. M. Munro, Int. Conf. Electric Vehicle Development, PPL Conf. Publ. No. 14, Peter Peregrinus, London, 1977, p. 64.
9 E. V. Focus, 1, No. 9, June 15, 1978, p. 6.
10 C. R. Barker, Electr. Vehicles Q., June, 1978, p. 24.
11 J. Johnson, Commer. Motor, 18 Feb., 1977.
12 P. Chapman, G. Charlesworth and M. Baker, Future Transport Fuels, TRRL Suppl. Rep. 251, Transport and Road Research Lab., Crowthorne, England, 1976.
13 U.S. Dept. of Energy, State-of-the-Art Assessment of Electric and Hybrid Vehicles, U.S. Dept. of Commerce, HCP/M1011-11, January, 1978.
14 J. H. B. George, L. J. Stratton and R. G. Acton, Prospects for Electric Vehicles, Arthur D. Little, Rep. to U.S. Dept. H.E.W., N.A.P.A.C., Arlington, Va., May, 1968.
15 J. L. Hartmann, E. J. Cairns and E. H. Hietbrink, Gen. Mot. Corp., Res. Lab., Res. Publ. 2 654, February 22, 1978.
16 Research and Development of Electric Vehicles in Japan (Agency of Industrial Science and Technology, the Ministry of International Trade and Industry, the Society of Automotive Engineers of Japan, Inc., 1977).
17 S. Gross, Energy Convers., 15 (1976) 95.
18 J. Giner and J. D. Dunlop, J. Electrochem. Soc., 122 (1975) 4.
19 M. Klein, Proc. 10th Intersoc. Energy Conv. Eng. Conf., Newark, 1975, p. 803.
20 L. E. Miller, Proc. 10th Intersoc. Energy Conv. Eng. Conf., Newark, 1975, p. 807.
21 J. J. Reilly, K. C. Hoffman, G. Strickland and R. H. Wiswall, Proc. 26th Power Sources Symp., Atlantic City, April and May, 1974, p. 11.
22 F. A. Lewis, M. C. Witherspoon and A. Obermann, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 361.
23 N. S. Lidorenko, G. F. Muchnik, D. E. Bogatin, N. M. Kagan and Z. R. Karichev, Elektrokhimiya, 10 (1975) 808.
24 A. J. Appleby, in (a) J. O'M. Bockris, D. A. J. Rand and B. J. Welch (eds.), Trends in Electrochemistry, Plenum, New York, 1977, p. 71; (b) H. Bloom and F. Gutmann (eds.), Electrochemistry — The Past Thirty and the Next Thirty Years, Plenum, New York, 1977, p. 683.
25 J. O'M. Bockris, Energy: the Solar — Hydrogen Alternative, Australia and New Zealand Book Co., Sydney, 1975, Ch. 2.
26 D. Clutterbuck, New Sci., 18 August 1977, p. 414.
27 M. Walsh, F. Walsh and D. Crouse, Proc. 10th Intersoc. Energy Conv. Eng. Conf., Newark, 1975, p. 1 141.
28 F. G. Will and H. S. Spacil, in J. D. E. McIntyre, S. Srinivasan and F. G. Will (eds.), Proc. Symp. Electrode Materials and Processes for Energy Conversion and Storage, Electrochem. Soc., Proc. Vol. 77-6, Princeton, 1977, p. 713.
29 G. Clerici, M. de Rossi and M. Marchetto, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 167.
30 H. Christopher and P. Moran, ILZRO Project No. LE-156, Int. Lead–Zinc Res. Organization, Inc., Final Rep., June, 1971.
31 H. J. Halberstadt, E. L. Littauer and E. S. Schaller, Proc. 10th Intersoc. Energy. Conv. Eng. Conf., Newark, 1975, p. 1 120.
32 E. L. Littauer (Lockheed Missiles and Space Company, Inc.), personal communication.
33 A. R. Landgrebe, K. Klunder and N. P. Yao, Proc. 27th Power Sources Symp., Atlantic City, June 1976, p. 23.
34 F. J. Port, Electr. Vehicle News, 5 (1976) 6.
35 J. L. Weininger and C. R. Morelock, J. Electrochem. Soc., 122 (1975) 1 161.
36 A. C. Simon, S. M. Caulder and J. T. Stemmle, J. Electrochem. Soc., 122 (1975) 461.
37 A. I. Zaslavskii, Y. D. Kondrashov and S. S. Talkachev, Dokl. Akad. Nauk SSSR, 75 (1950) 559.
38 R. Bode and E. Voss, Z. Elektrochem., 60 (1956) 1 053.

39 P. Ruetschi and B. D. Cahan, J. Electrochem. Soc., 104 (1957) 406.

40 J. Burbank, J. Electrochem. Soc., 104 (1957) 693.

41 S. M. Caulder, P. D'Antonio and A. C. Simon, ILZRO Project LE-255, Int. Lead–Zinc Res. Organization, Inc., Prog. Rep. No. 5, Jan. 1 - Dec. 31, 1977.

42 H. B. Mark, Jr., J. Electrochem. Soc., 109 (1962) 634.

43 A. C. Simon and E. L. Jones, J. Electrochem. Soc., 109 (1962) 760.

44 A. C. Simon, in D. H. Collins (ed.), Batteries 2, Pergamon Press, Oxford, 1965, p. 63.

45 J. R. Pierson, J. Electrochem. Technol., 5 (1967) 323.

46 A. C. Simon, C. P. Wales and S. M. Caulder, J. Electrochem. Soc., 117 (1970) 1 339.

47 A. C. Simon and S. M. Caulder, J. Electrochem. Soc., 118 (1971) 659.

48 J. Burbank, J. Electrochem. Soc., 111 (1964) 765, 1 112.

49 J. Burbank, J. Electrochem. Soc., 113 (1966) 10.

50 E. J. Ritchie and J. Burbank, J. Electrochem. Soc., 117 (1970) 299.

51 I. I. Koval and H. I. Barilenko, Trudy Chetvertogo Soveshch. Elektrokhim., Moscow, 1956, p. 748 (published 1959).

52 A. C. Simon, Electrochem. Technol., 1 (1963) 82.

53 N. E. Bagshaw and K. P. Wilson, Electrochim. Acta, 10 (1965) 867.

54 J. Armstrong, I. Dugdale and W. J. McCusker, in D. H. Collins (ed.), Power Sources 1966, Pergamon Press, Oxford, 1967, p. 163.

55 A. C. Simon, in D. H. Collins (ed.), Power Sources 2, Pergamon Press, Oxford, 1970, p. 33.

56 J. R. Pierson, in D. H. Collins (ed.), Power Sources 2, Pergamon Press, Oxford, 1970, p. 103.

57 A. C. Simon, S. M. Caulder and E. J. Ritchie, J. Electrochem. Soc., 117 (1970) 1 264.

58 J. R. Pierson, P. Gurlusky, A. C. Simon and S. M. Caulder, J. Electrochem. Soc., 117 (1970) 1 463.

59 A. C. Simon, S. M. Caulder, P. J. Gurlusky and J. R. Pierson, J. Electrochem. Soc., 121 (1974) 463.

60 J. Burbank, J. Electrochem. Soc., 104 (1957) 693.

61 J. Burbank, in D. H. Collins (ed.), Batteries, Pergamon Press, New York, 1963, p. 43.

62 J. Burbank, in D. H. Collins (ed.), Power Sources 1966, Pergamon Press, Oxford, 1967, p. 147.

63 J. Burbank and E. J. Ritchie, J. Electrochem. Soc., 116 (1969) 125.

64 J. Burbank, J. Electrochem. Soc., 117 (1970) 299.

65 W. O. Butler, C. J. Venuto and D. W. Wisler, J. Electrochem. Soc., 117 (1970) 1 339.

66 J. Burbank, J. Electrochem. Soc., 118 (1971) 525.

67 J. Burbank, in D. H. Collins (ed.), Power Sources 3, Oriel Press, Newcastle upon Tyne, 1971, p. 13.

68 T. J. Hughel and R. H. Hammar, in D. H. Collins (ed.), Power Sources 3, Oriel Press, Newcastle upon Tyne, 1971, p. 35.

69 J. L. Weininger, J. Electrochem. Soc., 121 (1974) 1 454.

70 J. L. Weininger and F. W. Secor, J. Electrochem. Soc., 121 (1974) 1 541.

71 J. L. Weininger and C. R. Morelock, J. Electrochem. Soc., 122 (1975) 1 161.

72 A. C. Simon and S. M. Caulder, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 109.

73 S. Hattori, M. Yamaura, M. Kohno, Y. Ohtani, M. Yamane and H. Nakashima, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 167.

74 D. Pavlov and G. Papazov, J. Appl. Electrochem., 6 (1976) 339.

75 P. Reinhardt, M. Vogt and K. Wiesener, J. Power Sources, 1 (1976/77) 127.

76 P. Casson, N. A. Hampson, K. Peters and P. Whyatt, J. Appl. Electrochem., 7 (1977) 257, 93 (1978) 1.

77 S. M. Caulder, J. S. Murday and A. C. Simon, J. Electrochem. Soc., 120 (1973) 1 515.

78 S. M. Caulder and A. C. Simon, J. Electrochem. Soc., 121 (1974) 1 546.

79 M. V. Rose and J. A. Young, Proc. 5th Int. Conf. Lead, Met. Bull. (London), 1974, p. 37.

80 N. E. Bagshaw, J. Power Sources, 2 (1977/78) 337.
81 D. Berndt and S. C. Nijhawan, J. Power Sources, 1 (1976/77) 3.
82 H. E. Haring and U. B. Thomas, Trans. Electrochem. Soc., 68 (1935) 293.
83 A. H. Taylor, F. Goebel and J. Giner, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1972, p. 561.
84 W. Visscher, J. Power Sources, 1 (1976/77) 257.
85 S. Tudor, A. Wiestuch and S. H. Davang, J. Electrochem. Technol., 3 (1965) 90; 4 (1966) 406; 5 (1967) 21.
86 J. P. Carr and N. A. Hampson, Chem. Rev., 72 (1972) 69.
87 E. V. Focus, 1, No. 6, May 1, 1978, p. 3.
88 T. Sabatino, Lead and Zinc into the 80's, Lead and Zinc Development Association, London, 1978, p. 5.
89 S. Hattori, M. Yamaura, M. Kohno, M. Yamane, H. Nakashima and J. Yamashita, ILZRO Project No. LE-253, Int. Lead Zinc Res. Organization, Inc., Rep. for period March - November, 1977.
90 J. L. Weininger and E. G. Siwek, J. Electrochem. Soc., 123 (1976) 602.
91 K. W. Mao and G. J. Hwang, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 357.
92 D. W. Kassekert, A. O. Isenberg and J. T. Brown, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 411.
93 A. H. Taylor, F. Goebel and J. Giner, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 541.
94 K. W. Choi, D. N. Bennion and J. Newman, J. Electrochem. Soc., 123 (1976) 1 616, 1 628.
95 S. -P. Poa and C. H. Wu, J. Appl. Electrochem., 8 (1978) 427.
96 J. McBreen, J. Electrochem. Soc., 119 (1972) 1 620.
97 R. A. Grown, Ext. Abs. No. 32, Electrochem. Soc., Proc. Vol. 77-2, Atlanta, 1977, p. 88.
98 A. Charkey, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 452.
99 F. A. Schneider and Z. Dominiczak, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 115.
100 G. Kucera, H. G. Plust and C. Schneider, SAE-Paper 750147, Automot. Eng. Congr., Detroit, U.S.A., 1975.
101 J. Appleby (C.G.E., Marcoussis, Fr.), personal communication.
102 S. Sudar and W. Thomson, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 424.
103 O. v. Krusenstierna, in·D. H. Collins (ed.), Power Sources 6, Academic Press, London, 1977, p. 303.
104 G. Benczúr-Ürmössy, K. von Benda and F. Haschka, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 303.
105 M. Klein and M. Helms, Ext. Abs. No. 34, Electrochem. Soc., Proc. Vol. 77-2, Atlanta, 1977, p. 92.
106 P. J. Fydelor, A. Messenger, G. Partridge, J. A. Bant and D. Johnson, in D. H. Collins (ed.), Power Sources 3, Oriel Press, Newcastle upon Tyne, 1971, p. 327.
107 L. B. Adams, P. J. Fydelor, G. Partridge and R. H. West, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 141.
108 J. Birge, J. T. Brown, W. Feduska, C. C. Hardman, W. Pollack, R. Rosey and J. Seidel, in D. H. Collins (ed.), Power Sources 6, Academic Press, London, 1977, p. 111.
109 L. Öjefors (Swedish National Development Co.), personal communication.
110 G. Krämer, A. Oliapuram and K. Salamon, Chem. Ing. Techn., 49 (1977) 322.
111 P. R. Vassie and A. C. C. Tseung, Electrochim. Acta, 21 (1976) 299.
112 D. A. J. Rand and R. Woods, J. Electroanal. Chem., 35 (1972) 209.
113 L. Öjefors (Swedish National Development Co.), personal communication.
114 O. Lindstrom, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, p. 283.

115 L. Öjefors and L. Carlsson, J. Power Sources, 2 (1977/78) 287.
116 H. Cnobloch, D. Gröppel, D. Kühl, W. Nippe and G. Siemsen, in D. H. Collins (ed.), Power Sources 5, Academic Press, New York, 1975, p. 261.
117 L. Öjefors, J. Electrochem. Soc., 123 (1976) 1 691.
118 D. S. Adams, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 347.
119 M. I. Gillibrand, J. Gray and J. F. Gudger, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 297.
120 (a) A. J. Appleby, J. P. Pompon and M. Jacquier, Proc. 10th Intersoc. Energy Conv. Eng. Conf., Newark, 1975, p. 811;
(b) A. J. Appleby and M. Jacquier, J. Power Sources, 1 (1976/77) 17.
121 D. S. Adams, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973, p. 347.
122 H. Baba, U.S. Pat. 3,555,032 and 3,560,262.
123 Battelle Memorial Institute, French Pat. 2,096,046.
124 D. Doniat, K. Beccu and A. Porta (Automobiles Citroën, S.A.), German Pat. 2,125,576.
125 A. J. Appleby, J. Jacquelin and J. P. Pompon, SAE paper No. 770 381, 1977.
126 O. C. Wagner, Ex. Abs. No. 16, Electrochem. Soc., Proc. Vol. 73-2, Boston, 1973, p. 44.
127 P. C. Symons, Proc. Electric Vehicle Symp., Washington, D.C., 1974.
128 G. J. May, J. Power Sources, 3 (1978) 1.
129 J. Broadhead, U.S. Pat. 4,054,728.
130 S. A. Weiner, Research on electrodes and electrolyte for Ford sodium–sulphur battery, Ann. Rep. Nat. Sci. Found. (1975), Contract NSF C-805.
131 R. M. Dell, J. L. Sudworth and I. Wynn Jones, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 503.
132 J. Fally, C. Lasne, Y. Lazennec and P. Margotin, J. Electrochem. Soc., 120 (1973) 1 292.
133 R. Bauer, W. Haar, H. Kleinschmager, G. Weddigen and W. Fischer, J. Power Sources, 1 (1976/77) 109.
134 S. Hattori, M. Yamaura, S. Kimura and S. Iwabuchi, SAE paper No. 770 281, March 1977.
135 C. A. Levine, R. G. Heitz and W. E. Brown, Proc. 7th Intersoc. Energy Conv. Eng. Conf., San Diego, 1971, p. 50.
136 M. W. Breiter, in J. O'M. Bockris, D. A. J. Rand and B. J. Welch (eds.), Trends in Electrochemistry, Plenum, New York, 1977, p. 127.
137 I. Wynn Jones, Electrochim. Acta, 22 (1977) 681.
138 B. Cleaver (Southampton University), personal communication.
139 E. C. Gray, W. W. Schertz, F. J. Martino and K. E. Anderson, Proc. 9th Intersoc. Energy Conv. Eng. Conf., San Francisco, 1974, p. 862.
140 Z. Tomczuk, R. K. Steunenberg and R. E. Hollins, Proc. Symp. and Workshop on Adv. Battery Research and Design, ERDA-ECS Rep. ANL-76-8, Argonne National Laboratory, March 1976.
141 Z. Tomczuk, A. E. Martin and R. K. Steunenberg, Ext. Abs. No. 47, Electrochem. Soc., Proc. Vol. 76-2, Las Vegas, 1976, p. 131.
142 E. C. Gray, D. R. Vissers, N. -P. Yao, F. J. Martino, T. D. Kaun and Z. Tomczuk, in D. H. Collins (ed.), Power Sources 6, Academic Press, London, 1977, p. 735.
143 H. Shimotake, W. J. Walsh, E. S. Carr and L. G. Bartholme, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 471.
144 E. C. Gray, T. D. Kaun and F. J. Martino, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 477.
145 J. E. Battles, J. A. Smaga and K. M. Myles, Met. Trans. A., 9A (1978) 183.
146 W. W. Shertz, A. A. Chilenskas and V. M. Kolba, Proc. 10th Intersoc. Energy Conv. Eng. Conf., Newark, 1975, p. 634.

147 R. K. Steunenberg (Argonne National Laboratory), personal communication.
148 W. J. Walsh and H. Shimotake, in D. H. Collins (ed.), Power Sources 6, Academic Press, London, 1977, p. 725.
149 R. K. Steunenberg (Argonne National Laboratory), personal communication.
150 J. S. Dunning, T. G. Bradley and E. J. Zeitner, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 491.
151 R. A. Sharma and R. N. Seeforth, J. Electrochem. Soc., 123 (1976) 1 763.
152 F. Hirschfeld, Mech. Eng., June 1977, p. 30.
153 D. W. Murphy and F. A. Trumbore, J. Cryst. Growth, 39 (1977) 185.
154 M. S. Whittingham, in J. D. E. McIntyre, S. Srinivasan and F. G. Will (eds.), Proc. Symp. Electrode Materials and Processes for Energy Conversion and Storage, Electrochem. Soc., Proc. Vol. 77-6, Princeton, 1977, p. 784.
155 M. S. Whittingham, J. Electrochem. Soc., 123 (1976) 315.
156 M. S. Whittingham, Science, 192 (1976) 1 126.
157 D. Inman and Y. E. M. Mariker, Symp. on Molten Electrolytes and High Temperature Batteries, Brighton, September 22 - 23, 1977, Abs. 2.
158 L. H. Gaines, R. W. Francis, G. H. Newman and B. H. L. Rao, Proc. 11th Intersoc. Energy Conv. Eng. Conf., State Line, 1976, p. 418.
159 M. S. Whittingham (Exxon), personal communication.
160 Canadian Pat. Appl. 282,696, filed 14th July 1977.
161 B. C. H. Steele, in J. O'M. Bockris, D. A. J. Rand and B. J. Welch (eds.), Trends in Electrochemistry, Plenum, New York, 1977, p. 145.
162 W. Van Gool (ed.), Fast Ion Transport in Solids, North Holland, Amsterdam, 1973.
163 G. C. Farrington and W. L. Roth, in G. D. Mahan and W. L. Roth (eds.), Superionic Conductors, Plenum, New York, 1976, p. 418.
164 H. Y. -P. Hong, Ext. Abs. No. 317, Electrochem. Soc., Proc. Vol. 77-1, Philadelphia, 1977, p. 811.
165 U. v. Alpen, E. Schonherr, H. Schulz and G. H. Talat, Electrochim. Acta, 22 (1977) 805.
166 I. D. Raistrick, Y. -W. Hu, C. Ho and R. A. Huggins, Ext. Abs. No. 318, Electrochem. Soc., Proc. Vol. 77-1, Philadelphia, 1977, p. 813.
167 R. A. Huggins, Electrochim. Acta, 22 (1977) 773.
168 R. D. Shannon, B. E. Taylor, A. D. English and T. Berzins, Electrochim. Acta, 22 (1977) 783.
169 W. Weppner and R. A. Huggins, J. Electrochem. Soc., 124 (1977) 35.
170 G. C. Farrington and W. A. Roth, Electrochim. Acta, 22 (1977) 767.
171 U. v. Alpen, A. Rabenau and G. H. Talat, Appl. Phys. Lett., 30 (1977) 621.
172 B. C. H. Steele (Imperial College, London), personal communication.
173 C. C. Liang, A. V. Joshi and N. E. Hamilton, J. Appl. Electrochem., 8 (1978) 445.
174 E. V. Focus, 1, No. 8, June 1, 1978, p. 2.
175 E. S. Carr, W. C. Harsch, Jr., L. R. Erisman and D. Judd, Fourth Int. Electric Vehicle Symp., Düsseldorf, 1976, paper 2.
176 The Australian Financial Review, Mon. Sept. 12, 1977, p. 12.