

## LEAD/ACID — STILL TOP OF THE GALVANIC TRACTION PILE IN 1983

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### Battery requirements for electric vehicles

Present transportation systems in developed countries are almost all based on petroleum fuels. Difficulties in guaranteeing uninterrupted oil supplies, recognition that reserves are indeed finite, and problems in meeting exhaust emission controls have led during the 1973 - 1983 decade to renewed interest in vehicles powered by electrochemical systems. Over this period, electrochemists have searched the Periodic Table for new galvanic combinations of elements, or have re-investigated previously documented systems, in an attempt to develop a secondary battery for electric-vehicle applications that is superior to the existing commercial lead/acid, nickel/cadmium or nickel/iron systems.

As an electric-vehicle power source, an appropriate battery must fulfil many 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 and small size, low materials and manufacturing costs, low maintenance, low self-discharge, good shelf life, rapid and efficient rechargeability, good high- and low-temperature operating characteristics, good temperature control (*e.g.*, no overheating or thermal runaway), safety in operation, crash worthiness, and easy replacement. In view of this wide range of criteria, it is not surprising that the search for a better battery remains the critical area for electric-vehicle research.

### Candidate batteries

Candidate batteries for vehicle propulsion are best classified by the nature of the electrolyte used, *i.e.*, aqueous solution (acid or alkali), molten salt, organic liquid or solid compound. Table 1 lists various systems that have been examined in each of these categories. Such systems are generally referred to as "alternative" or "advanced" batteries.

Aqueous electrolyte batteries include both acidic (*e.g.*, lead/acid, zinc/halogen) and alkaline (*e.g.*, nickel systems, metal/air) batteries. It appears that only  $\text{PbO}_2$  (acid) and  $\text{NiOOH}$  (alkali) positive electrodes are at present satisfactory from the standpoint of performance and durability. However,

TABLE 1

Battery systems considered for electric-vehicle propulsion

Aqueous		Molten-salt	Organic <sup>†</sup>	Solid-state <sup>†</sup>
Acidic	Alkaline			
Pb/PbO <sub>2</sub>	Ni/Zn	Na/S*	Li/TiS <sub>2</sub>	Li/TiS <sub>2</sub> or V <sub>6</sub> O <sub>13</sub>
Zn/Br <sub>2</sub>	Ni/Fe	Li-Al/FeS <sub>2</sub>	Li/V(Fe)S <sub>2</sub>	Ca/BiF <sub>3</sub>
Zn/Cl <sub>2</sub>	Ni/Cd	Na/SbCl <sub>3</sub>	Li/NbSe <sub>3</sub>	
	Ni/H <sub>2</sub>	Li/Cl <sub>2</sub>	Li/Cr <sub>0.5</sub> V <sub>0.5</sub> S <sub>2</sub>	
	Al/air		Li/V <sub>6</sub> O <sub>13</sub>	
	Li/air		Li/polymer <sup>§</sup>	
	Fe/air			
	Zn/air			

\*Na/S, which uses a solid electrolyte, is included here since it operates at high temperatures with molten reactants and products.

<sup>†</sup>Organic-electrolyte and solid-state batteries are still very much in their early stages of development. The systems listed here represent a selection of the various couples that have been the subject of preliminary studies.

<sup>§</sup>Alkali-metal ion conducting polymers include polymeric ethylene oxide and propylene oxide, polyacetylene, poly(*para*-phenylene) and polypyrrole.

nickel electrodes are expensive. Possible negative electrode materials include Pb (acid), Fe (alkali) and Zn (alkali or acid). Cadmium-based systems can be eliminated on cost grounds, and hydrogen electrodes await the development of a lightweight gas storage system. Aluminium alloys and lithium metal are currently being examined as negative electrode materials in mechanically rechargeable metal/air batteries, but these systems have storage, handling, loading, and efficiency problems. These considerations narrow the choice of aqueous-electrolyte batteries to seven systems: three acid (Pb-PbO<sub>2</sub>, Zn/Cl<sub>2</sub> and Zn/Br<sub>2</sub>) and four alkaline (Ni/Zn, Ni/Fe, Fe/air and Zn/air).

Of the two zinc/halogen batteries under investigation, the zinc/chlorine hydrate battery [1] is the less likely to find practical use in traction 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 and there are long-term charge retention and electrode fabrication problems. This battery appears better suited to load-levelling applications. A 472 kW h load-levelling battery, demonstrated in mid-1983 at the Charlotte Substation in Detroit, is presently being installed in the BEST facility in Hillsborough, New Jersey. On the other hand, there are good prospects for the Zn/Br<sub>2</sub> battery [2] as the bromine can be easily and safely stored by complexing with an organic solvent. The electrochemistry of the system is well understood, and the viability of this battery for electric vehicles appears to depend mainly on finding solutions to the engineering and materials problems associated with cell-stack assembly. Exxon intend to deliver a demonstration Zn/Br<sub>2</sub> battery for electric vehicles during 1984.

Metal/air batteries (Fe/air [3], Zn/air [4]) suffer from very low energy efficiencies associated with the fundamental problem of finding a low-cost, high-performance, rechargeable oxygen electrode. System complexity is another unattractive feature here. Fe/air and Zn/air batteries using flat-plate electrodes are not front runners for electric-vehicle applications, although functional batteries have been designed and tested. The mechanically rechargeable concept is more attractive since it avoids range restrictions. Aluminium slurries would be preferable to iron or zinc systems, but this requires the identification of new alloys that have a much lower spontaneous dissolution rate in alkaline solutions. At present, the introduction of the electrode slurry concept is inhibited by the lack of an established infrastructure for distribution and recycling of materials. Other battery systems that can operate on existing electric-grid facilities offer easier solutions in the near term, but slurry metal/air batteries could come to fruition beyond the turn of the century.

The major competitors among nickel-based batteries are Ni/Fe [5] and Ni/Zn [6]. Provided cycle life can be improved, Ni/Zn will be more attractive than Ni/Fe. The latter system suffers from poor power density (particularly at low temperatures), low charge/discharge efficiency, and self-discharge problems. However, the life problems associated with the zinc electrode are proving to be more difficult to overcome than originally anticipated. Thus, Ni/Fe traction batteries appear at this stage to be the nearer to commercialization.

The Na/S [7] system is the favourite in the field of molten-salt batteries and has reached a more advanced developmental stage than its lithium counterpart [8]. The sodium battery is more attractive since it employs cheap and abundant electrode materials, operates at relatively lower temperatures, and less expensive separator, case and insulation materials can be used. Nevertheless, high-temperature operation requires considerable investment in the development of construction materials (insulating seals, containers, separators, current-collectors, etc.) that can withstand the severe operating conditions. Quality control in the production of  $\beta$ -alumina electrolyte tubes is also a serious problem. There has been very little road-testing of the Na/S system and it is not yet certain whether the ceramic materials needed to contain the molten reactants will safely withstand road vibrations. Molten-salt batteries are more likely to be used in the public transport sector, *e.g.*, for supplying off-line power to track-following vehicles such as trams, trolley buses, and railcars.

Both organic-electrolyte and solid-state batteries offer the prospect of high energy density when based on the use of alkali metals, especially lithium. However, it should be noted that lithium is only moderately abundant in the earth's crust and therefore batteries based on this metal may prove expensive. The future of all-solid batteries depends greatly on the success of fundamental research into fast ion-conducting materials. The low conductivity of organic electrolytes has so far limited the use of such cells to low-power applications in electronic equipment. At present, electrically

conducting polymers are attracting considerable interest [9] as alternatives to metal electrodes in organic-electrolyte cells. Such polymers are plentiful, relatively inexpensive, easily moulded into convenient shapes, and can accommodate volume changes of the electrodes by virtue of their elasticity. However, despite the enthusiasm for conductive polymers, practical problems abound. For example, the manufacture of these new polymers is still an inexact process, and their chemical, thermal, and electrochemical stability is uncertain. Thus, organic-electrolyte and solid-state batteries are still at the laboratory experimental cell stage, and although no confident prediction can be made at this time on their application to electric-vehicle propulsion, their commercialization seems a long way off.

### Dénouement — lead/acid unsurpassed

The above considerations indicate that the lead/acid battery, which has been used as the motive-power unit for most of the prototype electric vehicles to date, will continue to be the power source for electric vehicles for some time to come. Each of the candidate alternative batteries has both advantages and shortcomings. Deciding which of these systems, if any, is the most likely to replace lead/acid is not easy — it is clear that, despite the considerable research efforts, the race is still in its early stages and that the competitors will continue to jockey for position as “breakthroughs” are claimed and system advancements achieved. The inherent limitations of each battery system indicate that the future of electric propulsion lies in its application to specialized vehicles, and it is likely that the degree of penetration into the electric-vehicle market of any of the batteries will, in the end, depend greatly on the service a given vehicle has to provide.

### Lead/acid: Present status

#### *Greater cycle life — the prime need*

Although lead/acid has maintained its position as the best state-of-the-art battery for electric-vehicle propulsion, its performance is still inadequate for electric vehicles to be marketable in substantial volume. The principle limitations of this battery are: (i) excessive weight and size, and, hence, low energy storage capability per unit weight or volume, and (ii) short service life. The first of these factors results in limited range, and this problem is further compounded by the fact that many hours are required to re-charge (*i.e.*, “refuel”) the battery. Nevertheless, lead/acid batteries can provide a daily range of up to 100 km, which is adequate to meet most private and city driving needs. Routine delivery van service is an obvious area where lead/acid batteries can compete with petrol-driven vehicles on range performance. The lead/acid battery can also be used in battery/internal-combustion-engine (*i.c.e.*) hybrid concepts to conserve petroleum by improving the

overall i.c.e. efficiency and by partially utilizing the electric grid as a transport fuel.

In the author's opinion, the second problem with lead/acid batteries, *viz.*, short service life, is the area of major concern. Limited cycle life results in expensive electric-vehicle operation, with the battery depreciation cost per km travelled exceeding the cost of electricity for recharging by a considerable margin. This fact is often ignored when comparisons are made between electric and i.c.e. vehicles.

The service life expected for lead/acid batteries in electric-vehicle operations is somewhat of an unknown factor. This is because the value of introducing electric vehicles to conserve liquid transport fuels has only recently been recognized. Consequently, previous battery development has concentrated on other applications, such as starting, lighting, and ignition (SLI) systems for i.c.e. vehicles and traction cells for in-plant electric vehicles. The requirements for an on-the-road electric-vehicle battery present new challenges: it is necessary to combine the high power and energy density properties of SLI batteries with the long cycle life of conventional traction cells. It is difficult to achieve both these performance criteria simultaneously, *i.e.*, in meeting requirements for electric road vehicle traction, manufacturers are forced to trade off economically greater specific energy and power with lower battery life.

Most battery manufacturers have been reluctant to disclose detailed information on the performance of their electric-vehicle batteries, presumably because an optimum between power and energy densities and life has yet to be achieved. Where results have been published, more often than not detailed information on the duty profiles used in the battery or vehicle tests is lacking, and those batteries with reportedly long cycle lives have not been tested under the deep-discharge conditions representative of electric road vehicle service. Thus, in order to make relevant comparisons between the performances of different batteries, international agreement on a standard driving cycle is required, both for field tests and for laboratory simulation studies.

#### *Performance under simulated electric-vehicle service*

Given that poor service life (and, hence, high operating cost) is the major impediment to using lead/acid batteries in traction applications, the research conducted in the author's laboratories aims at optimizing lead/acid batteries by correlating degradation in performance both with changes in physicochemical characteristics (*e.g.*, crystal morphology and structure, phase composition and distribution, grid alloy content and corrosion, active material stability, etc.) and with changes in electric-vehicle design and operating conditions (*e.g.*, temperature, regenerative braking, high-speed pulsed discharge, mode of charge, etc.). It is considered that such an approach will direct both electric-vehicle and battery design along mutually compatible lines.

The CSIRO experimental procedure has been to simulate, in the laboratory, precisely defined duty cycles of on-the-road electric vehicles operating in an urban environment, and to determine the effect of different vehicle parameters on the nature of the processes that limit the capacity and cycle life of the lead/acid battery. In order to identify the principal processes leading to failure, batteries are disassembled at various times and specimens of plate material taken. Attention has been mainly focussed on changes in the characteristics of the positive plate since the cycle life of a lead/acid battery is generally limited by the behaviour of this plate [10].

A battery test facility was designed and constructed [11] to operate batteries for extensive periods of time under simulated electric-vehicle duty profiles. The latter were obtained from road tests using a standard driving schedule. For convenience, laboratory tests are conducted on batteries of lower capacity than those used to power the vehicles, and the current profiles are scaled down accordingly. A larger test unit was also developed in order to examine the performance of commercial batteries and to make comparisons with the lower-capacity "experimental" batteries.

To date, the performance of over 60 experimental batteries and over 15 commercial batteries has been examined under a wide variety of simulated vehicle system conditions. Service lives of over 30 000 and 14 000 km have been obtained with commercial and experimental batteries, respectively.

Studies have further shown that:

(i) service life increases markedly on raising the temperature from 25 to 60 °C [12], but regenerative charging [13] or pulsed discharging [14] exert only minor effects;

(ii) there is an optimum initial  $\alpha$ -PbO<sub>2</sub>: $\beta$ -PbO<sub>2</sub> ratio conducive to good battery performance [13];

(iii) particle size has no marked effect on the electrochemical activity of positive-plate material [12];

(iv) battery performance could be a function of the composition and structure of the cured state of positive plates [14].

Whilst there must remain reservations concerning the detailed relevance of electric-vehicle simulation experiments carried out in conditions which may be far removed from operating practice, it is the author's opinion that such an approach provides a useful datum level on which to base model-system experiments for the intimate study of specific battery characteristics. Indeed, simulation experiments have allowed us to assess the relative importance of various aspects of positive-plate chemistry in determining battery performance and to identify those that warrant more detailed investigation (see R. J. Hill, p. 19 of this issue).

### Closing comments

The only way that electric vehicles can be introduced quickly and effectively into the road transport sector is to demonstrate to potential users that such vehicles are reliable, economic, and traffic-compatible with their petrol-

powered counterparts. In advancing the need for electric vehicles, governmental instrumentalities should remember that industry has not yet evolved acceptable power sources. The key industry is the lead/acid battery industry, since alternative batteries have yet to be proven.

Developing the lead/acid traction battery means reaching an acceptable compromise maximum for energy density, rate of discharge, cycle life, and cost. This will not be easy and may involve taking the whole of the battery manufacturing process by the scruff of the terminals to optimize each of the stages involved in producing a traction battery, *e.g.*, in the manufacture of the components and starting materials (the grid alloys, separators, lead oxides, etc.), in the preparation and application of the active-material pastes, in the curing and formation of the plates, etc.

The failure of alternative batteries to displace lead/acid from the top of the galvanic traction pile, together with the recent successful application of non-electrochemical techniques in investigative studies, foreshadow a renaissance in lead/acid battery research. In particular, valuable new information on the chemical and electrochemical processes that take place during manufacture and operation of the battery is being obtained from the use of X-ray [12, 15], neutron [16 - 19] and electron diffraction [20, 21] techniques, and scanning electron probe microscopy [22]. It is anticipated that the united efforts of electrochemists, solid-state chemists, and physicists will provide technologists with the necessary information to establish the lead/acid battery as an effective power source for electric-vehicle propulsion.

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