Energy Storage in Lead-Acid Batteries: The Faraday Way to Sustainability [and Discussion]

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Energy storage in lead–acid batteries: the Faraday way to sustainability

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Food, warmth, standards of living, transport and future prospects—all depend on society's ability to continue supplying itself with the energy that it has grown to need. This energy is derived mainly from fossil fuels and must be harnessed without harmful disturbance to the ecological and geophysical systems of the biosphere. But—now amplified by a growing population—energy use has become a destructive force: locally, because emissions contaminate air, water and soil; globally, because emissions enhance the greenhouse effect.

Moreover, society must look beyond these environmental concerns to the inevitable decline in the availability of fossil fuels and the need to find substitutes. This paper examines how lead–acid batteries might assist the transition towards a more sustainable balance between energy, the economy and the environment. Particular emphasis is placed on the advances in materials and cell designs that are required for battery performance to meet this challenge.

1. Energy in crisis?

The technological mastery of energy accounts for the rise of civilization. During the early 18th century, the dominant technologies were coal mining, the smelting/casting of iron, and steam-driven rail and marine transport. Through the creation of transportation infrastructures, the provision of materials and the invention of machines to run factories, rapid industrialization was possible. Then, towards the end of the 19th century, came electric power, internal-combustion engines, motor vehicles, aeroplanes and the chemical and metallurgical industries. During this phase, mineral oil emerged as both a fuel and a feedstock for the petrochemicals industry. Now, society has embarked upon a third era of advancement—one that is characterized by a shift to computers, advanced materials, optical electronics and biotechnology. The first two of these transformations were each accompanied by a massive increase in energy consumption. It is not yet certain what impact the present and third phase will have on future global patterns of energy supply and demand.

Almost all of the available energy on planet Earth is derived from the Sun (fossil fuels, biomass, wind and incoming radiation) or from the processes of cosmic evolution that preceded the origin of the Solar System (nuclear power). These energy sources can be grouped into two general categories: capital and income. Once a capital energy resource is spent, it cannot be recovered; that is, it is 'non-renewable'. Coal, mineral oil, natural gas and uranium are capital resources. By contrast, income resources are celestial and, therefore, 'renewable'. They are also relatively pollution-free—a very important consideration.

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The most useful celestial energy source is the electromagnetic energy of the Sun, so-called 'solar energy'. This produces some indirect renewable sources of energy (wind, thermal, wave and hydropower) and can be converted directly into electrical power (photovoltaic conversion). Derivatives of solar energy such as trees (wood) and plants (biomass) are also forms of income, but the stored energy is finite in the rate at which it can be exploited. At present, renewables (including hydropower and biomass) satisfy only 18% of the world's energy needs, and nuclear power 4%; the substantial remainder is met by fossil fuels that are being consumed 100 000 times faster than they are being created.

In industrialized communities, energy demand comes from three major sectors: (i) industry and agriculture; (ii) transport; (iii) domestic and commerce. In many countries, these each account for about one-third of the total energy flow. Cities, industrial facilities and transportation networks cannot function without regular supplies of primary energy. Moreover, the situation is exacerbated by the fact that energy resources are not distributed democratically—some nations have many, others have virtually none. Likewise, the energy requirements of populations vary; they depend upon climate, geography, extent of industrialization and wealth. These inequalities create a potential for conflict as different nations seek to meet their special needs from a finite pool of global resources. Clearly, therefore, the long-term availability and demand of finite, primary sources of energy (coal, oil, natural gas and uranium) and the ability to use them wisely and equitably are major determinants of the limits to the human race's habitation of planet Earth.

2. Planning for the future

The key issues that will shape the future provision and use of energy are population growth, global climate and local/regional environmental impacts.

At the start of the industrial revolution, the population of the world was only a few hundred million. Now it stands at some five billion people, who collectively occupy a billion dwellings, drive 500 million motor vehicles, and expend much effort to produce a wide variety of industrial products to further their well-being. Nevertheless, almost 50% of these people (mainly in the developing countries) still do not have access to commercial energy and, in particular, access to a reliable electricity service. In fact, about one billion people have no supplies of commercial energy in *any* form—they operate entirely on wood fuels and other biomass resources. Moreover, the disparity will intensify. The world population is expected to grow to an estimated eight billion in 2020, and 90% of this growth will take place in the developing nations. Thus, global energy-supply issues will move from the industrialized to the developing countries.

Of equal concern are the destructive effects of energy supply, conversion and usage on the Earth's biosphere. Overall, the energy sector is the single largest source of anthropogenic greenhouse gases, with emissions of carbon dioxide, methane and nitrous oxide. At the local level, energy use in motor vehicles is a major contributor to the degradation of urban-air quality. Exhaust pollutants include carbon monoxide, nitrogen oxides (NO_x), and hydrocarbons. Fuel consumption in large stationary applications, such as power stations, is also a serious source of sulphur oxides (SO_x) and NO_x.

There has been considerable debate over the relative trade-offs between economic growth and the environment, and the consequent outcomes for energy supply and use. In general, two scenarios are advocated for the global energy mix in 2020. The 'consensus' view assumes that consumer habits and lifestyles will not change significantly. Accordingly, impelled by the anticipated growth in population, world energy consumption is expected to double, and the global mix of primary fuels to remain intrinsically the same as today. Therefore, it follows that global emissions of carbon dioxide would also double. Nevertheless, it is argued that 'more of the same' is tolerable and that climate change is neither a serious issue nor a condition to which human beings cannot adapt.

By contrast, the 'sustainable' view assumes concerted international action to alleviate global environmental problems. This would involve radical improvements in efficiency and stabilization of energy demand after 2000. Further, there would be a contraction in coal usage, a surge in natural-gas consumption, and significant exploitation of renewable fuels. In a sustainable world, the balance of new initiatives would shift from producer to consumer, from energy supplier to energy services, and from quantity to quality of energy.

The storage and delivery of electrical energy via rechargeable batteries, and especially via lead–acid systems, can ease the transition to a sustainable world and, thereby, can assist efforts to meet the challenge of providing adequate, safe, economic and equitable supplies of energy. Batteries are electrochemical power sources and the research of Michael Faraday laid the foundation for the science of electrochemistry. Moreover, his genius also led to the electric motor, the transformer and the dynamo—the basic elements of the modern generation of electricity. Thus, the deployment of efficient and benign electrochemical technologies at the cutting edge of energy strategies presents 'The Faraday Way to Sustainability'.

3. Energy storage in batteries—balancing energy supply and demand

While there is no generally accepted system of energy classification, the different energy forms can be divided into six major groups, namely: chemical, electrical, electromagnetic, mechanical, nuclear and thermal energy. All these can be stored, except electromagnetic energy which is purely a transitional form of energy. Unfortunately, primary energy sources are not always of a form that is suitable for the end use. Instead, the sources have to be converted and this involves some wastage of energy. The most important, versatile and controllable of the 'converted' (or 'secondary') energy sources is electricity.

Storage technologies can provide a vital link between the primary source of energy and its actual use. For example, an energy-storage system allows valuable flexibility in the choice of energy source, and in both the size and siting of the power supply. Owing to the number of primary sources and the great variety of energy uses, there is a plurality of technologies for the storage of mechanical, electrical, chemical and thermal energy. The scale of energy-storage systems ranges from minuscule elements on integrated circuits to pumped hydroelectric reservoirs that store the equivalent of gigawatt-hours of electrical energy. Lead–acid batteries are attractive candidates for many energy-storage applications. In particular, this technology promises to have a favourable impact on the energy-intensive areas of electricity generation and road transport.

(*a*) *Central power generation*

Energy storage in lead–acid batteries offers electric utilities a flexible and strategically advantageous means of meeting their energy-management and power-regulation needs. In addition, the technology can help alleviate capacity shortfalls and mitigate air-quality problems.

(i) *Load-levelling and load-following*

The integration of a lead–acid energy-storage system allows supply to satisfy demand more effectively. Less-expensive baseload energy is stored during off-peak times and then supplied when the demand is high. This 'load-levelling' concept is an encouraging alternative to installing extremely costly, continuous-duty plants to balance the power-generation requirements. Battery system specifications include: 5–10 h discharge; high AC-to-AC efficiency (over 70%); long charge/discharge cycle-life (greater than 2000 cycles); small footprint; low operation and maintenance costs.

In load-following applications, the electrical output of the battery storage unit is adjusted to help match system generation with increasing/decreasing system load. Such a strategy can enable the utility to achieve better thermal efficiency, lower maintenance costs, and reduced emissions. The battery must provide rapid response with a discharge that is usually shorter (2 to 3 h) than for load-levelling operations. In both load applications, inadequate cycle-life is the main shortcoming.

(ii) *Demand-side peak-shaving*

Customer-side-of-the-meter storage of electric energy offers the equivalent economic benefits of utility load-levelling to consumers, provided that favourable time-of-day electricity rates are in effect (note, the cost of electrical energy is determined not only by the total amount consumed (kW h) but also by the peak-power demand (kW)). In such 'peak-shaving' applications, the battery is discharged during the customer's peak demand to supply a portion of the customer's load and to reduce the power purchased from the utility. The battery is replenished during off-peak hours when the utility's demand for electricity is lower. Accordingly, there is often no demand charge and lower energy charges. The battery size and discharge time are dependent upon the customer's energy-demand profile. In general, the battery must have a 2–4 h discharge, a deep-discharge capability, and a long cycle-life.

(iii) *Power regulation*

Lead–acid batteries can also improve the reliability and quality of the power supply by regulating short-term voltage fluctuations and harmonic frequencies which, if left unstabilized, could lead to power outages, and by providing reserve energy ('spinning' reserve) to meet power emergencies. To perform such functions, batteries must: provide short-duration power; respond immediately to high rates of discharge; accept charge rapidly. Given present performance, there is a need to develop designs with high charge/discharge rates and more effective active-material utilization at high discharge rates. A long cycle-life is not essential.

(*b*) *Distributed power generation*

Fundamental changes are taking place to the way utilities produce, procure and distribute electric power. The three driving forces of change are cost reduction, customer service and competition. As a consequence, utilities are focusing on energy efficiency, improved environmental performance and alternative energy options.

To meet these challenges, future power-generation needs will be increasingly satisfied by distributed power systems with capacities from 50 MW to as low as 50 kW. Such systems will be embedded in the transmission/distribution network. This trend towards decentralization, with smaller generating units situated close to end-users, offers advantages in terms of protection from major mishaps, decreased costs of transmission/distribution, lower power losses, improved local reliability/quality of supply, greater flexibility in matching capacity additions/retirements with changes in demand, reduced exposure to electric and magnetic fields, and shorter construction times. There are also pressures to include independent generators such as cogenerators, waste-fuel combustors, solar photovoltaic installations, and wind machines. Finally, distributed generation will introduce greater competition into the industry.

Thus, the utility of tomorrow will be a hybrid network of traditional (but improved) central-generation, distributed-generation and energy-efficiency technologies. This less-centralized structure is known as the 'distributed utility concept'. Worldwide, many utilities have begun to implement this concept—they are not building large plants. Concurrently, independent power-producer markets are expanding. These are using small generators, many powered by natural gas and renewable energy technologies. In situations where electricity grids become reliant upon intermittent energy sources such as solar and wind, there will be an increasing requirement for energy-storage facilities. For such dispersed applications, batteries again promise to be a cost-effective option.

(c) *Power generation in remote areas*

Increasing attention is being directed towards the development of stand-alone power supplies that incorporate renewable solar and/or wind technologies (with electricity storage in lead–acid batteries) as more economic, reliable and environmentally acceptable alternatives to traditional diesel sets or diesel–battery hybrid arrangements. The former are particularly useful in remote areas and, accordingly, are commonly termed 'remote-area power supply' (RAPS) systems. It should be noted, however, that stand-alone power supplies can often find application in urban areas as cheaper alternatives to mains connection.

The development of RAPS systems will accelerate the electrification of developing countries. Although power plants in these countries have typically been situated near urban centres to support business and high-density population, the majority of the people live in rural areas. To serve these people would require the installation of extensive distribution systems to deliver very limited amounts of energy. That would make for a very high real cost of electricity. Small diesel sets can satisfy many needs, but they demand a regular supply of fuel, spare parts and skilled maintenance—facilities that are not always available. A more practical approach is the deployment of photovoltaic-based RAPS systems. By contrast, these power sources require no fuel, practically no maintenance, and are technically ideal for low-power, rural applications. It is claimed that 25% of the rural population with no access to electricity could be supplied economically by such technology.

(d) *Electric vehicles*

Throughout the present century, internal-combustion-engined ('motor') vehicles have brought many economic and social benefits. Indeed, the motor car has become a major, if not the supreme, symbol of increasing prosperity throughout the world. But such transportation benefits have created two serious problems. First, the vehicles derive their power from the combustion of dwindling supplies of fossil fuel and, second, the resulting exhaust gases are inflicting serious damage to air quality in both regional and global environments.

The undoubted contribution of road transport to atmospheric pollution has been brought into sharp focus by the introduction of the 1989 California Clean Air Act. This legislation mandates that 2% of all new vehicles offered for sale in California by the major manufacturers shall be zero-emission vehicles (ZEVs) in model years 1998–2000, 5% in 2001–2002 and 10% in 2003 and beyond. The ZEVs must not emit directly any of the regulated pollutants, namely carbon monoxide, nitrogen oxides and non-methane organic gases. In effect, ZEVs have to be electric vehicles powered by batteries and/or fuel cells. The California ZEV legislation was modified in March 1996. This eased the short-term mandates, but maintained the target set for year 2003. Between 1998 and 2000, the seven major automakers (Chrysler, Ford, General Motors, Honda, Toyota, Mazda and Nissan) have now agreed to supply 3750 advanced technology ZEVs with ranges of more than 160 km per charge. Each manufacturer's pro rata share of the ZEVs is based on the manufacturer's share of the California market for passenger cars and light-duty trucks up to 1.7 tonne in curb weight.

To date, the lack of a suitable battery has been the major barrier to the realization of traffic-compatible, electric road vehicles. Consequently, the drawbacks of electric vehicles have remained manifestly obvious: much shorter ranges than petrol-powered counterparts; usually, a markedly inferior on-road performance; frequent recharging (i.e. 'refuelling') that inevitably takes several hours; a short 'engine' life (the batteries have to be replaced at least once during the vehicle's life); a higher initial purchase price (in the absence of manufacturing economies-of-scale). Despite these limitations, a high-performance affordable electric vehicle—recharged rapidly by cleanly generated power and using freely available, safe and recyclable battery materials—is now viewed by an increasing number of countries as a key technology for air-quality management in congested cities.

The first vehicles to replace horse-driven transportation were electrically powered by lead–acid batteries. Today, some 130 years since its invention, this battery is still the preferred choice for many electric vehicles. The battery has many inherent advantages, namely: low-cost abundant materials; proven, though not perfected, basic technologies and manufacturing methods; a substantial track record in electric-vehicle applications; relatively safe operation; an in-place servicing infrastructure; collection infrastructures and recycling technologies for spent batteries. Nevertheless, future transportation needs will require batteries with higher energy/power outputs, longer life, faster recharging, and reduced cost. Fortunately, there is scope for substantial improvements in all these areas through the introduction of new materials, advanced designs, and intelligent charge–discharge management systems. The transformation of the traditional lead–acid workhorse into a high-tech propulsion thoroughbred presents the greatest challenge to battery scientists and technologists. Moreover, success will yield flow-on improvements to the operations of lead–acid batteries in electricity utility energy-storage and other applications.

4. Lead–acid batteries—technical challenges

The lead–acid battery relies on two active materials only—lead and sulphuric acid, both readily available, in plentiful supply and of low cost. Lead is also the basis for the positive and negative grids, intercell connectors, and terminals. The batteries are produced commercially in a broad range of sizes and designs. These are categorized both by the electrode construction and by the electrolyte–separator configuration.

Three designs of positive plates are used, namely, the Planté, the flat pasted and the tubular configurations. All negative plates are constructed as pasted types. Planté plates are made by cycling a high surface-area lead electrode in acid to form a thick corrosion layer of lead dioxide (PbO_2). These designs are used exclusively in standby-power applications where very long life is desired and a high specific energy (see § 4 *a*) is not required.

Pasted plates are produced by machine application of a stiff paste of active materials on to a lead or lead-alloy grid. The latter is made either by casting molten metal, or by slitting and expanding or perforating metal sheet. Lead–antimony alloys have been used since the early 1880s. The antimony strengthens the lead and reduces grid growth but, undesirably, it also accelerates water loss by poisoning the negative plate. Lead–calcium alloys were developed in 1935 to minimize gassing and grid corrosion. These alloys allowed the introduction, in the 1970s, of batteries that require no addition of water (so-called 'maintenance-free' units). The lead paste applied to the grid consists of a mixture of 'leady oxide', sulphuric acid and water, blended together in proprietary proportions. Leady oxide usually comprises 65–85 wt% lead monoxide and 15–35 wt% finely divided lead. The pasted plates are then 'cured' under controlled humidity and temperature. This produces a hardened porous structure composed of lead oxide and basic lead sulphates. Finally, during the 'formation process', the cured plates are converted to a porous structure of PbO_2 by electrochemical oxidation in dilute acid under regulated charging rate and temperature. Pasted negative plates are made in the same manner and have an active material composed of 'sponge' lead.

The tubular positive plate consists of a row of porous vertical tubes made from chemically stable fibres. The tubes contain co-axial lead-alloy 'spines' and are packed with lead oxide powder. The rods are connected together in parallel at the top of the plate. The plates are 'pickled' in acid to convert the majority of the lead oxide to lead sulphate ($PbSO_4$). This extensive sulphation assists the formation process. The tubular design has the advantage of good deep cycle-life, but is less versatile than the pasted plate. Thus, pasted plates are used where low-cost, high specific energy/power, or special grid or plate structures are required.

In the late 1960s, a new type of lead–acid technology emerged to challenge the traditional flooded-electrolyte design of cell. This arose from a strong market demand for batteries that do not require water replenishment. The new technology is based on the 'oxygen-recombination cycle', and uses an electrolyte that is immobilized either by adsorption within a glass-microfibre mat (AGM design) or by forming a gel with silica (gel design). Gas recombination is achieved by arranging for oxygen generated at the positive plate on overcharge to pass via channels in either the glass-microfibre or the gel to the negative plate, where it reacts with excess lead to regenerate water. To assist recombination, the batteries operate with a slight internal overpressure. Since hydrogen generation can never be avoided completely, each cell is fitted with a one-way pressure-relief valve that opens when the internal pressure exceeds tolerable limits. For this reason, the product has become known as the 'valve-regulated lead–acid' (VRLA) battery. The AGM design employs flat positive plates, whereas both flat and tubular types are commonly used in gelled-electrolyte batteries. VRLA batteries are now employed in industrial applications such as uninterruptible power supplies, telecommunications and load-levelling, as well as in portable devices and appliances. The development of VRLA batteries for true motive-power applications is still in its infancy.

Although the lead–acid battery is a mature product and the basic electrochemistry remains the same, significant advancements have been made in recent times. These have included: improved lead alloys and grid-fabrication techniques; more reactive oxides for pastes; more effective plate-curing procedures; improved microporous separators; valve-regulated technology; a better understanding of the properties of the positive and negative electrode systems. Nevertheless, established and emerging markets—especially, electric vehicles—are placing ever greater demands on battery performance. The most pressing need is to develop more energetic, more powerful, long-lived, deep-discharge, inexpensive VRLA batteries that can co-operate and communicate with the electrical circuits that they are powering, and that can be recharged rapidly. The technical challenges are discussed in the following sections.

(*a*) *Increasing specific energy*

Specific energy is the number of W h of electricity that the battery can deliver per kg of its mass for a nominated rate of discharge. For any given battery system, a maximum value for this parameter is easily calculated. Practical specific energies, however, are well below the theoretical maxima. Apart from electrode kinetics and other restrictions that serve to reduce the cell voltage and prevent full utilization of the reactants, there is a need for construction materials that add to the battery weight but are not involved in the energy-producing reaction. These materials are required for current collectors, bus-bars, cell connectors, terminals, separators and the battery container, for instance.

Compared with its competitors, lead–acid has a low specific energy. The reason is twofold: (i) the obvious weight penalty imposed by the high specific density of lead and its compounds; (ii) a particularly low utilization of active material in the positive plate.

(i) *Minimizing inert components*

About 30% of the total battery weight consists of grids and 'top-lead' (bus-bars, cell connectors, posts, terminals) that do not directly provide electrical output. Clearly, it is tempting to minimize such 'dead weight', but this must be done without diminishing energy/power levels, without shortening cycle-life due to complete corrosion of less substantial positive grids or top-lead, or without accelerating failure through the effects of vibration. Weight reduction has been explored via the use of lighter grid materials, thinner grids, and/or novel cell configurations.

Numerous attempts have been made to produce inexpensive, lightweight grids of lead combined with materials of lower density. These composites have included lead-coated aluminium, copper, steel, nickel or titanium, as well as lead-coated graphite, fibreglass, plastics or ceramics. With the possible exception of co-extruded metal–fibreglass grids (see below), none of these alternatives has proved satisfactory in terms of corrosion resistance, mechanical properties, or conductivity.

A complementary approach is to reduce the thickness of traditional designs of grid. This necessitates the development of stronger and more corrosion-resistant alloys, especially lead–calcium-based systems for VRLA batteries. For the latter alloys, tin additions increase the mechanical properties (yield strength, tensile strength, creep resistance, etc.), and also improve the electrochemical characteristics by preventing passivation and permitting recharge of batteries from deeply discharged states. Mechanical properties and corrosion resistance can be enhanced further by incorporating minor amounts of silver. Thin grids are best made from wrought strips formed by rolling cast ingots of the alloys; reduction ratios of up to 10 : 1 are acceptable.

The rolling process endows alloys with superior mechanical properties, and with uniform grain structures that retard both corrosion and grid growth. The optimum alloy composition appears to be: Pb–0.05 to 0.07 wt% Ca–1 to 2 wt% Sn–0.05 wt% Ag. The major problem is the conversion of the rolled material into battery grids. Expanded mesh is employed in some battery designs, but this can introduce weakening of the metal at the nodes. It is more appropriate, therefore, to use either a punch or a rotary cutter for grid fabrication.

A more adventurous approach to weight reduction is to minimize the current pathways between cells through reconfiguration of the vertical, interleaved, plate assembly used in conventional units. Bipolar (see § 4 *b*) and quasi-bipolar designs are promising examples of such imaginative engineering. The term 'quasi-bipolar' describes intercell connections that are not true bipolar connections. In general, the design involves a non-conducting partition (e.g. plastic) between cells, together with various types of connections similar to those used in conventional (monopolar) batteries to join cells in series.

The Dunlop Pulsar battery was the first quasi-bipolar technology to reach commercial production; it was dedicated to automotive applications. By contrast, the Electrosource Horizon battery is being developed for electric-vehicle propulsion (Moore 1994). This valve-regulated, AGM battery comprises several layers of woven, co-extruded, lead–tin/fibreglass wires built up in side-by-side, double-polarity plates ('biplates') that are arranged horizontally and compressed in a cage. The horizontal orientation provides a convenient low profile, and is said to eliminate active-material shedding and intra-plate electrolyte concentration gradients ('acid stratification') that both diminish cycle-life in most lead–acid batteries. The configuration also improves heat distribution and oxygen recombination. By virtue of these features, the Horizon design promises greater specific energy (greater than 45 W h kg^{-1}, $C_3/3$ rate†) and specific power (greater than 300 W kg^{-1}, 80% depth of discharge), as well as longer cycle-life (900 cycles, $\mathrm{C}_2/2$ rate), than conventional counterparts.

(ii) *Improving active-material utilization*

Incomplete utilization of positive active-material is caused by the slow diffusion of acid into the plate interior, and by the continuous decrease in the conductivity of both the positive and negative plates during discharge. These discharge problems become more acute as the discharge rate is increased. In electric-vehicle (high-rate) operations, for example, only about 20–30% of the positive active material in flooded systems can be accessed to provide electrical energy. Obviously, this restricts vehicle range. VRLA technology has raised the utilization level to *ca.* 40%, but further significant improvements must be made to achieve, for example, the target specific energy (50 W h kg^{-1}, $\mathrm{C}_3/3$ rate) set by the Advanced Lead–Acid Battery Consortium (ALABC) for electric vehicles (Cole 1992).

Acid supply can be enhanced by using thinner or more porous electrodes, or by the use of external pumps. To date, both methods have been constrained by adverse effects on cycle-life. The future development of thin, wrought grids is expected to ameliorate this problem. Pumping does not seem a viable option, however, as it increases system complexity and constitutes a parasitic load. A recent, novel approach

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† Accepted practice is to normalize the current (amperes) during discharge to the rated capacity. Thus, the discharge rate is expressed as C_i/X, where i is the hour rate for the rated capacity, and X is a time specification, in hours. For example, the 10 h discharge rate of a 500 Ah cell or battery (rated at the 5 h discharge rate) is expressed as $C_5/10 = 50$ A.

is to induce bulk electrolyte movement, *in situ*, through assisted electro-osmosis. This electrokinetic phenomenon describes the motion of liquid (e.g. battery electrolyte) through a membrane (e.g. porous PbO_2 structure) under the influence of an electric field (e.g. battery discharge). Under such action, there is a separation of electric charge between the solid and liquid phases and this is characterized by the zeta potential. The polarity of the zeta potential determines the direction of induced electrolyte flow, whilst the magnitude controls the flow rate. In battery-strength acid, the discharge product ($PbSO_4$) has a highly positive zeta potential that tends to force acid out of the positive plate. The aim, therefore, is to develop robust electro-osmotic 'promoters' with substantially negative zeta potentials that, when incorporated in the positive active mass, will encourage electrolyte irrigation into the plate during battery discharge. Moreover, the ability of the promoter to keep pace with electrolyte demand is assisted by the fact that the rate of pumping is inversely proportional to electrolyte concentration and directly proportional to the current delivered by the battery. Encouraging results have been obtained by impregnating small battery plates with sulphonated polyvinylidene difluoride (SPVDF), e.g. a 20% capacity increase at the $C_5/5$ rate (Hill *et al.* 1995). Serendipitously, it appears that SPVDF also increases plate cycle-life. Appropriate methods for incorporating the additive to gain optimum results are presently being explored.

The second impediment to positive active-material utilization is the progressive decrease in plate conductivity during discharge. The PbO_2 particles of the active material serve two functions: (i) to participate in the discharge reaction; and (ii) to act as electron pathways from each reaction-site in the active mass to the grid. The non-reacting material provides structure and conductivity to the plate, but does not contribute to the reaction and, clearly, should be minimized. As discharge proceeds, the conductivity decreases with the formation of increasing amounts of $PbSO_4$. In some locations, areas of PbO_2 can become encapsulated by the non-conductive $PbSO_4$ and, thereby, rendered inaccessible to further reaction. This is because the electron pathways, as well as the flow of solution reactants through the pores of the active mass, are both hindered by the $PbSO_4$.

Increasing the porosity of the plate is an obvious approach to reducing the problem of $PbSO_4$ encapsulation (and, incidentally, to improving acid supply). This has encouraged numerous studies of the influence of the plate-processing stages on active-material morphology, and how the growth/distribution of crystals during these stages decreases material availability. The use of low paste densities has been explored, but this tends to reduce cycle-life through weakening of both the mechanical strength and the corrosion resistance of the plates. The incorporation of additives to promote porosity (e.g. carboxymethyl cellulose, carbon black, graphite, glass microspheres) has also been investigated. Except for the glass microspheres, all the materials tested to date undergo oxidative attack and, consequently, any gains in plate performance are not lasting.

The use of an electrically conducting additive is the alternative means to overcoming the insulating effects of $PbSO_4$. If a conductive material can be deployed to connect regions of isolated PbO_2 with their reactive neighbours (and, thus, with the grid), the discharge reaction will proceed at the otherwise inactive locations and the degree of active-material utilization will be increased. Doubtless, a wide range of prospective conductive additives has been examined in-house by battery manufacturers. Published reports, however, are surprisingly few, namely: carbon fibres; barium metaplumbate; titanium suboxides, Ti_nO_{2n-1}; tin-dioxide-coated glass flakes. None of these additives has produced sufficient and enduring improvements to become commercially practical. Nevertheless, the search continues for appropriate materials with high conductivity, good chemical/electrochemical stability, an ability to form a strong network with the PbO_2, and negligible enhancement of gassing rates during battery charging. Materials consisting of particles with a high aspect ratio (i.e. fibrous particles) are likely to be more effective in building up a conductive network than spherical alternatives. Finally, the dosage should be kept to a minimum to prevent any favourable conductivity effects from being suppressed by a concomitant decrease in the amount/pore volume of (potentially) available active material.

(*b*) *Increasing specific power*

Specific power is the maximum number of watts per kilogram that the battery can deliver at a given state-of-charge. Compared with other systems, the lead–acid battery has good specific power ratings, despite its weight disadvantage. Moreover, VRLA technology (especially, AGM designs) has advanced further the high-rate capability. Nevertheless, new applications are placing ever-increasing power demands on batteries. This is particularly true for electric vehicles where it is not only the intrinsic power capabilities of the battery system that are important, but also the performance window in which the battery is operated. Power delivery to an electric-vehicle drivetrain (or, indeed, to any load) decreases rapidly as the required current increases, largely due to resistive effects within the battery. A similar relationship exists with the depth of discharge. Thus, high power demands necessitate batteries with minimal internal resistance down to low depths-of-discharge (at least 80%). The internal resistance can be reduced by: (i) developing thinner plates with high surface areas; (ii) improving current collection with new grid designs; (iii) increasing grid/top-lead conductivity through substitution with lead composites; (iv) developing low-resistance separator materials; (v) ensuring good inter-particle contact within the plate materials through optimizing phase chemistry and architecture, adding binders and dopants, etc; (vi) minimizing current pathways through innovative cell/battery configurations. Clearly, such advances will also assist attempts to increase specific energy and to optimize recharge capabilities (see § 4 *d*), but are generally incompatible with efforts to extend cycle-life.

The difficulty of simultaneously maximizing a battery's energy–power and cycle-life capabilities has given rise to the dual-battery concept for electric vehicles in which the main unit would be optimized for range (specific energy), and a smaller one for acceleration and hill-climbing (specific power). This has rekindled interest in bipolar and quasi-bipolar designs for high-power battery modules.

In a bipolar configuration, each interior plate serves as the positive of a cell on one side, and as the negative of the adjacent cell on the other. The bipolar plates are stacked parallel to each other and the intervening spaces are filled with the electrolyte and separators. This produces a high voltage in a small volume, but a low capacity because each cell has only one set of relatively thin plates. The cell-to-cell current flow is perpendicular through the whole area of each plate, and is transmitted only through its thickness. Thus, resistive losses are much reduced and the current–potential distribution across the plate is uniform. Moreover, the bus-bars and posts that carry the current in monopolar designs are eliminated and this further reduces resistance, as well as weight. The state-of-the-art Arias battery is a 90 V, 24 A h unit that delivers 300 W kg^{-1} and 50 W h kg^{-1} for 3000 cycles at 50% depth of discharge (Arias 1994). The practical realization of the bipolar lead–

acid battery has been delayed by difficulties in maintaining the integrity of both the electrodes themselves and the seals that they must make with the container. Other problems include finding a stable conductive substrate, removing heat from the battery during high-rate charge/discharge and establishing low-cost high-volume methods of manufacture.

Early bipolar designs employed lead sheet as the substrate material. To minimize weight, a thin sheet is desirable but corrosion can render this porous and, thereby, create shorts between cells. Various alternative substrate materials have been examined, namely: carbon, conductive ceramics, transition metal oxides, barium metaplumbate, tin-dioxide-coated glass fibres. None of these has proved entirely satisfactory and the search continues for a material that is electrochemically and chemically stable, has high oxygen and hydrogen overvoltages, has good conductivity, bonds well with the active materials, withstands mechanical stresses imposed by volume changes of the active materials during cycling and is inexpensive.

The Bolder battery is a new approach to the design of high-rate VRLA batteries and is made by the spiral-wrapping of ultra-thin (0.13 mm), lead-alloy foil plates with a glass-microfibre separator (Juergens & Nelson 1995). A key feature is the continuous bonding of the positive plate to a lead plug at one end of the cell, and similar bonding of the negative plate at the other end. The use of opposite-end current collection with continuous contact between the plugs and the electrode foils results in uniform current distribution over the electrode surfaces. Combined with the high plate surface area, this provides a low-resistance path for current flow across the full electrode surfaces. The extremely low internal resistance and good form factor for heat dissipation enables the Bolder technology to accept/deliver current at very high rates. Power levels of 800 and 400 W kg^{-1} can be delivered over 70 and 90% of the discharge lifetime, respectively. Thus, while the specific energy is no better than for other commercial lead–acid designs (typically, 30–40 W h kg^{-1}), the specific power is outstanding. Indeed, the high-rate performance is superior to that of any other known battery system in the advanced stages of development.

(c) *Increasing deep-discharge service life*

The durability of a battery is usually expressed in terms of its cycle-life. In simple terms, this is the number of times that a battery can be recharged to a useful capacity. Measuring battery life purely in terms of charge–discharge cycles is complicated by the fact that the battery is likely to experience differing degrees of discharge between charges, in accordance with the service demands. Moreover, irrespective of the rate of discharge, the cycle-life of a lead–acid battery is markedly dependent upon the depth of discharge.

(i) *Premature capacity loss of positive plates*

In most cases, lead–acid cycle-life is limited by the performance of the positive plate, the capacity of which declines on cycling, especially under deep discharge. This phenomenon has been attributed to one or more of the following degradation mechanisms: (i) electrical isolation of parts of the material due to stress-cracking of the grid corrosion layer, formation of a resistive barrier layer at the grid/active-material interface, grid deterioration/growth, encapsulation by non-conductive $PbSO_4$; (ii) loss of inter-particle contact due to morphological changes; (iii) shedding of material due to grid corrosion and morphological changes; (iv) irreversible plate sulphation due to acid-stratification effects. These phenomena decrease the discharge capability by reducing active-material availability and by introducing large resistance losses. When the collective effects cause a battery to fall significantly short of its design life, the behaviour is termed 'premature capacity loss'.

Two distinct forms of premature capacity loss are now recognized, namely, PCL-1 and PCL-2. Simply stated, the more severe form, PCL-1, is thought to arise from the development of so-called 'barrier layers' (e.g. $PbSO_4$ and/or α-PbO) close to the grid, particularly if the positive-plate potential is driven too low by deep discharge. Batteries constructed of lead–calcium grids (i.e. VRLA batteries) are particularly susceptible to this problem. The phenomenon known as 'passivation' can also cause sudden loss of capacity, but can be distinguished from PCL-1 through the application of simple electrical tests. Following research and technological advances, the problem of very early positive-plate failure, caused either by passivation or PCL-1, has been virtually solved. Remedial strategies include: addition of tin to grid alloys; improved manufacturing techniques; use of phosphoric acid (gelled-electrolyte batteries). The longer-term manifestation of premature capacity loss, PCL-2, applies when positive plates lose capacity at lower rates, but the common and readily identifiable causes of plate failure (e.g. grid corrosion, active-material shedding) are largely absent. PCL-2 is far more subtle in nature and, therefore, considerably more difficult to rectify. It is thought to be active-material related.

(ii) *Unified mechanism of premature capacity loss*

The life of a lead–acid cell can be enhanced greatly by maintaining the plate/separator assembly under a certain degree of compression. This important benefit originates from the effect of the compressive load on the 'apparent density' of the porous positive material. Apparent density is defined as the mass of PbO_2 divided by the total volume occupied by the porous structure (i.e. pore volume is included); it is the complement of porosity. Recently, Hollenkamp *et al.* (1995) proposed that a decrease in apparent density is, in fact, the principal determinant of active-material degradation and, hence, capacity loss during battery service.

The pivotal role of apparent density arises from its direct relationship to active-material conductivity. Two conductivity-related factors conspire to limit the utilization of positive-plate material. First, the transformation of PbO_2 into insulating $PbSO_4$ reduces electrode conductivity during each discharge. Second, positive plates expand with cycling service; this emanates from the volume changes that accompany PbO_2–$PbSO_4$ inter-conversion. Accordingly, the apparent density decreases and the concomitant increasing disruption to the PbO_2 network continuously lowers the amount of active material that can be utilized before plate conductivity limits the discharge. The region close to the current-collector is particularly important. Here, an increase in resistance can effectively prevent discharge of the bulk material. Typically, such a situation is found when severe capacity loss develops within a few cycles (i.e. PCL-1). Virtually all of the $PbSO_4$ is produced near to the corrosion layer, while the bulk positive material exhibits no signs of discharge.

Rapid loss of capacity is promoted by low-density pastes, the use of relatively weak grids and an ineffective level of compression. All of these features contribute to the expansion of the porous material, but if they are attenuated to maintain the apparent density above the minimum acceptable level, the capacity will be preserved for longer periods of service. A progressive decrease in density will still occur, but at a lower rate. The eventual failure is described as PCL-2.

From these observations, Hollenkamp *et al.* (1995) have developed a 'unified mechanism' of capacity loss by which a continuous scale of positive-plate degradation is established, rather than two distinct groups of failure modes (i.e. PCL-1 and PCL-2). Previous interpretations of PCL-2 are in line with the unified mechanism because they focus on changes in the structure and/or function of the porous positive material. By comparison, explanations advanced for rapid capacity loss (PCL-1) have created confusion since they invoke the concept of some form of permanent barrier that electrically isolates the current-collector from the porous material. As intimated above, however, the development of a low apparent density can localize discharge and, hence, can cause the formation of high concentrations of $PbSO_4$ close to the grid. The result of this preferential discharge is indistinguishable from the effects of a 'barrier layer' and, importantly, no separate explanation is required for cases of severe capacity loss.

Basic strategies for maintaining the apparent density above the critical value are widely known, but only at a rudimentary level. New methods and materials are required to guarantee the three-dimensional stability of positive plates throughout service. For VRLA batteries with pasted plates, this demands the development of: (i) new alloys and designs to increase the toughness of grid frames, i.e. to restrict expansion in the plate plane; (ii) improved separators with greater strength and elasticity, i.e. to provide sufficient compression at right angles to the plate.

(iii) *Negative plates*

Negative plates require the presence of additives, known as 'expanders', in order to deliver satisfactory low-temperature and high-rate capabilities. Conventional expanders comprise a mixture of barium sulphate, carbon black and a sulphonate derivative of lignin. These materials act together to prevent the individual lead crystals from growing and combining into a dense structure with low surface area and, therefore, low electrical capacity.

The lignin component is the least stable, and it can cause negative-plate failure via: (i) solubility in the electrolyte (allowing transport to the positive plate and destructive oxidation thereupon); (ii) thermal decomposition; (iii) chemical reaction with the electrolyte. Of these, thermal stability has become the most important criterion for expanders as certain applications (e.g. automotive, RAPS, electric vehicles) require batteries to operate under increasingly aggressive conditions of elevated temperature. This is particularly true when rapid recharging is employed. There is considerable scope, therefore, to evolve new and improved expander materials.

(*d*) *Decreasing recharge time*

Methods for very fast charging of lead–acid batteries have long been sought. With the growing demand for electric vehicles, this need has intensified. Fast charging offers a promising approach towards overcoming the limited driving range of vehicles powered by lead–acid batteries. For practical purposes, this involves shortening charging times from the hitherto usual period of hours to a few minutes; the ALABC, for example, has set a target of 80% capacity return within 15 min. Accordingly, considerable research is now being directed towards the development of procedures and equipment that will achieve this goal without degrading battery performance. Concurrently, cell designs (and, most probably, the cell materials themselves) will have to be modified for minimal resistive/chemical heat generation, as well as effective heat dissipation.

There have been surprisingly few investigations of the possible electrochemical,

chemical and physical effects that fast-charging might exert on battery plates. This fact, together with the recent demonstrations that very fast and efficient recharging of lead–acid batteries is possible, and that pulsed-current techniques can also extend battery life (Lam *et al.* 1995), opens up rapid charging as an exciting new area of research. Apart from optimization of charging algorithms and battery design, there are challenges to find new materials for plates and grids that have good strength, good heat-transfer properties and manageable gassing characteristics.

5. Summing up

Although the lead–acid battery is a mature product, with a long and established record of commercial performance, the search for the most appropriate design and the best materials for a given application continues to engage the enquiring electrochemist and materials scientist alike. The incentive is that present designs offer considerable scope for improvement in terms of greater specific energy and faster recharging, as well as the obvious operational advantages of the neoteric valve-regulated technology.

Ongoing materials research is critical to the advancement of any battery system. For lead–acid, with weight a central issue, the development of lighter, better-conducting designs/materials for grids and top-lead is a priority. Weight reductions, together with active-material utilization enhancement, translate directly into improvements in specific energy. Conducting plastics, metal composites and new processes for creating thinner grids with greater strength and lower corrosion rates will assist efforts to maximize specific power and recharging capabilities. Finally, the incorporation of radically new materials and/or the adoption of new cell-construction techniques and geometries will enhance the structure and containment of the positive active-material and, thereby, will improve cycle-life under the most demanding of service requirements.

The collective task is by no means simple. It will require a multi-disciplinary team of scientists and technologists with expert knowledge of advanced materials in the fields of alloys, plastics, glasses and complex organic chemicals.

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Discussion

N. E. Bagshaw (*Consultant, Stockport, UK*). Lead-perchloric acid and lead-fluoboric acid batteries have, of course, been used successfully as primary reserve batteries in military applications. Apart from the question of stability and safety, one of the major problems from the point of view of secondary batteries is the difficulty in reliably recharging these systems.

The theories of Tony Hollenkamp on premature capacity loss, outlined in the paper, are very interesting. However, one of the factors that needs to be explained is the behaviour of the negative plate. If the positive plate performance is reduced because of the volume difference between PbO_2 and $PbSO_4$, what happens at the negative plate where there is a far greater difference in volume between Pb and $PbSO_4$?

D. A. J. Rand. Negative plates require the presence of certain additives — known as 'expanders' — to prevent the growth and densification of the particles of lead active-material during charge/discharge cycling. Obviously, densification would lower the porosity (and, hence, the active surface area) and cause the plate to lose both capacity and power. Batteries are having to operate under increasingly hotter conditions for which the thermal stability of the lignin component of the expander is inadequate. Accordingly, there is considerable scope to develop new and improved expander materials to prevent negative-plate shrinkage. Recent research has also highlighted the need to enhance negative-plate performance under electric-vehicle duties; these require periods of relatively high specific power, that is, high rates of battery discharge. Under such conditions, discharge uses only a thin surface layer of plate material. Given that the specific surface area ($m^2\ g^{-1}$) of the negative material is always much less than that of the positive material, the surface of the negative will be completely covered by insulating lead sulphate before the positive so that most of the fall in cell voltage (i.e. power) is due to a fall in negative-plate voltage. Thus, for sustainable high levels of power, lead–acid batteries must have negative plates of greater structural integrity (i.e. better expander materials), and for maximum power output batteries must incorporate more and thinner negative plates with high surface areas. The latter requirement presents challenges to existing technology in the areas of grid manufacture, plate processing and cell design.