

The lead/acid battery — a key technology for global energy management

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Abstract

As the nations of the world continue to develop, their industrialization and growing populations will require increasing amounts of energy. Yet, global energy consumption, even at present levels, is already giving rise to concerns over both the security of future supplies and the attendant problems of environmental degradation. Thus, a major objective for the energy industry — in all its sectors — is to develop procedures so that the burgeoning demand for energy can be tolerated without exhaustion of the planet's resources, and without further deterioration of the global ecosystem. A step in the right direction is to place lead/acid batteries — serviceable, efficient and clean technology — at the cutting edge of energy strategies, regardless of the relatively low price of such traditional fuels as coal, mineral oil and natural gas.

Keywords: Electric vehicles; Electricity generation; Energy demand/supply; Environmental problems; Lead/acid batteries; Sustainability

1. Energy for life — setting the scene

1.1. Energy resources

Almost all of the energy that is available on the earth is derived from the sun. Indeed, this source is the driving force behind photosynthesis, a process that converts the sun's radiant energy to chemical energy and, thereby, makes plant life — and, ultimately, all animal life — possible. In addition, photosynthesis is responsible for the formation of fossil fuels. The sun also provides energy that can be captured more directly in the form of solar power, hydro power and wind power. Smaller, or less significant, amounts of energy are derived from both lunar motion (tidal power) and the earth's core (geothermal power). The only other fundamental source of energy is from the fusion or fission of the atoms of certain elements (nuclear power).

Primary energy resources can be grouped into two general categories — capital and income. Once a capital resource is spent, it cannot be recovered; that is, it is 'non-renewable'. Coal, mineral oil, natural gas and uranium are capital resources. Thus, a non-renewable resource is one that has been laid down or formed over geological time. By contrast, income resources are celestial and are continuing or 'renewable'. They are also relatively pollution-free — a very important consideration. The only useful celestial energy sources are the electromagnetic energy of the sun, so-called 'solar energy', and the gravitational energy of the moon, i.e., tidal flows. Derivatives of solar energy such as trees (wood) and plants (biomass) are forms of income but the stored energy

is finite in the rate at which it can be exploited. Solar energy can be converted directly into electrical power (photovoltaic conversion), but also produces some indirect renewable sources of energy. For example, solar heating, combined with the earth's rotation, gives rise to large convection effects in the form of winds in the atmosphere and ocean currents in the seas. The adsorption of solar energy can also set up appreciable thermal gradients in the ocean that have the potential of delivering power. In addition, the evaporation of surface water produces clouds that, when condensed into rain at higher altitudes, provide the source for hydro-electric or water power. Finally, the wind generates ocean waves that can be converted into useful energy.

1.2. Energy demand

The interplay between energy, science and technology has produced three major changes in civilization (Fig. 1). During the early 18th century, the dominant technologies were coal mining, the smelting and casting of iron, and steam-driven rail and marine transport. Through the creation of a transportation infrastructure, 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 both as a fuel and as a feedstock for the petrochemicals industry. Now, as the 20th century draws to a close, the world has embarked on a third era of advancement, one that is characterized by a shift to

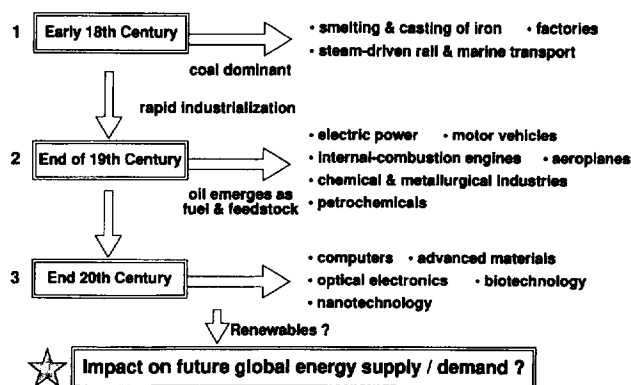


Fig. 1. The development of the industrial revolution — driven by changes in the major source of primary energy.

computers, advanced materials, optical electronics, biotechnology and nanotechnology. The first two of these transformations were each accompanied by a massive increase in the consumption of energy. The impact that the present and third phase will have on future global patterns of energy supply and demand has still to be determined.

In industrialized countries, 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, although the size of domestic demand depends very much on climate. In Australia, for example, domestic demand is relatively small, whereas in Canada it is extremely large because of the more extensive and severe periods of cold weather. It is also possible to identify the demands for particular purposes within these three sectors, namely: (i) low-temperature heat ($< 110\text{ }^{\circ}\text{C}$) for water and space heating in houses and industry; (ii) high-temperature heat ($> 110\text{ }^{\circ}\text{C}$) for industrial processes; (iii) lighting; (iv) power for factories and appliances; (v) mobile transport for public and private use. Primary energy sources are not always of a form that is suitable for these end-uses. Instead, the sources have to be converted once or twice before they become appropriate for their intended use. Unfortunately, each step in a conversion process involves losses, or more correctly, the production of waste energy. The most important, versatile and useful of these 'converted' or 'secondary' energy sources is electricity.

Overwhelmingly, fossil fuels continue to meet the global demand for energy — only about 10% of energy needs are satisfied by other supplies. This situation has persisted despite the fact that coal's share peaked around 1920, when it accounted for more than 70% of all fuel consumed, and that oil usage peaked in the early 1970s at slightly more than 40%. By contrast, the share provided by natural gas is expected to rise. Overall, fossil fuels are being depleted at a rate that is five orders of magnitude faster than the rate at which they are being formed.

Clearly, therefore, the long-term availability and demand of finite, primary sources of energy (i.e., coal, mineral oil, natural gas and uranium) and the ability to use them wisely are critical to the survival of the human race on Planet Earth.

For example, cities, industrial facilities and transportation networks cannot function without regular supplies of primary energy. Moreover, this requirement is exacerbated by the fact that energy resources are not distributed democratically — some nations have many, others have virtually none. Likewise, the energy needs of populations vary; they depend upon climate, geography, extent of industrialization, and wealth. These variations create a potential for conflict as different nations seek to meet their special needs from a finite pool of global resources.

2. Energy for life — securing 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 world population was only a few hundred million. Now it stands at some 5.6 billion people, who collectively occupy around 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, to a reliable source of electricity. In fact, of the two billion people living without electric power, about one billion have no supplies of commercial energy in any form — not even petrol or diesel oil. These people operate entirely on wood fuels and other biomass resources. Moreover, the disparity will intensify. It is generally expected that the world population will grow to an estimated eight billion in 2020, and 90% of this growth will take place in the developing nations (Fig. 2). Thus, over the next few decades, it is clear that global energy-supply issues will move from the industrialized to the developing countries, many of which have serious social, economic and environmental problems.

Of equal concern are the destructive effects of energy supply, conversion and usage on the earth's biosphere. In global terms, the energy sector is the single largest source of anthropogenic greenhouse gases, with emissions of: (i) carbon dioxide from the combustion of coal, oil and natural gas in electricity generation, in transport, and in the direct use of such fuels by industry, commerce and households; (ii) meth-

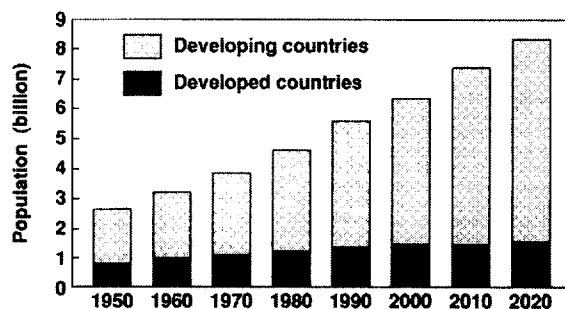


Fig. 2. Population growth 1950–2020. (Source: United Nations).

ane from the production, transport and end-use of natural gas, and from coal mining; (iii) nitrous oxide, which is one of the nitrogen oxides (NO_x) formed during the combustion of fossil fuels. At the local level, energy use in motor vehicles is a major contributor to the degradation of urban-air quality. The exhaust pollutants include carbon monoxide (which displaces oxygen in the blood), NO_x (which combine with water to form corrosive nitric acid) and hydrocarbons (which react with NO_x in the presence of sunlight to form ozone, i.e., photochemical smog, a lung irritant). Energy use in large stationary applications such as power stations is also a serious source of sulfur oxides (SO_x) and NO_x , which are the major precursors to 'acid rain'. Other environmental concerns include: (i) local impacts associated with land use, mining and processing (including dust from coal stockpiles, oil spills, disposal of solid wastes, emissions of volatile organic compounds and trace elements); (ii) electromagnetic fields; (iii) nuclear waste.

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 have been advocated for the global energy mix in 2020. The 'consensus' view assumes that consumer habits and lifestyles will not change significantly. Accordingly, mainly by virtue of the anticipated growth in population, world energy consumption is expected to double, and the global mix of primary fuels to remain substantially the same as today. Therefore, it follows that global emissions of carbon dioxide would also double (Fig. 3). It is argued that 'more of the same' is tolerable and that climate change is either not a serious issue or it is something to which human beings can adapt.

By contrast, the 'sustainable-world' view assumes concerted international action to alleviate global environmental problems. This would involve radical improvements in efficiency and a stabilization of demand after 2000. Further, there would be a contraction in the use of coal, a surge in the consumption of natural gas, and significant exploitation of renewable fuels (Fig. 4). The concept of sustainable devel-

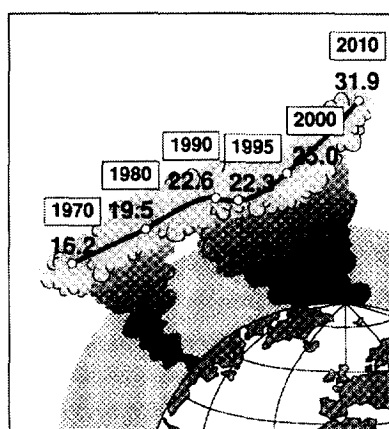


Fig. 3. Global emissions of carbon dioxide (in billion tonnes). Values given for years 2000 and 2010 are IEA forecasts.

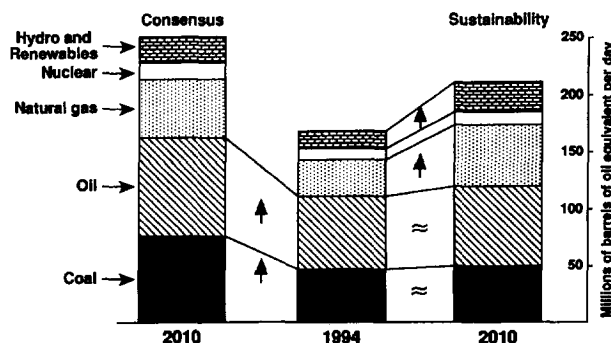


Fig. 4. Consensus and sustainability scenarios for the global energy-mix in year 2010.

opment was first advanced in *Our Common Future*, a report issued in 1987 by the United Nations World Commission on Environment and Development. The ensuing debate, including the 1992 Earth Summit in Rio de Janeiro, has produced an understanding that the concept really means environmentally-sustainable economic development. In a shorthand version, this has come to be called 'sustainability'. In a sustainable world, where economic growth is constrained by the ability of the global community to maintain and improve environmental protection, the balance of new initiatives would shift from producer to consumer, from energy supplier to energy services, and from quantity to quality of energy. This sustainable development is characterized as paths of social, economic and political progress that meet the needs of the present without compromising the ability of future generations to meet their own needs. As will become evident, the conversion and storage of energy via electrochemical systems — in particular, via rechargeable batteries — can ease the transition to a sustainable world and can assist efforts to meet the challenge of providing adequate, safe, economic and equitable energy supplies.

3. Energy storage — balancing supply and demand

While there is no generally accepted method or system of energy classification, the different energy forms can be divided into six major groups or classifications, namely: chemical, electrical, electromagnetic, mechanical, nuclear, and thermal energy. All these types of energy can be stored, except electromagnetic energy which is purely a transitional form of energy. Energy-storage technologies can provide a vital link between the primary source of energy and its actual use. In particular, the inclusion of an energy-storage system allows valuable flexibility in the choice of energy source, and in both the size and the siting of the power supply. Owing to the number of primary energy 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 hydro-

electric reservoirs that store the equivalent of GWh of electrical energy.

As society grows more and more dependent on the ready availability of inexpensive and clean energy, ways of storing it efficiently and controllably have become increasingly important. Rechargeable batteries are attractive candidates for many energy-storage applications. It is considered that these electrochemical technologies will have a favourable impact on areas such as:

1. utility load levelling — to make better use of available plant and fuels, to improve load factors, to reduce pollution in populated urban areas;
2. uninterruptible power supplies (UPS) — to enhance the reliability of supply for critical applications such as hospitals, airports and computing facilities;
3. power supplies for facilities in remote locations — to provide electricity to households, public buildings and services, telecommunications, meteorological stations, and navigational aids;
4. capture and utilization of solar energy in its various manifestations — to relieve the burden on finite resources of fossil fuels and to improve the living environment;
5. electric vehicles — to reduce urban-air pollution and to replace petrol in the long term;
6. industrial mobile power units — to provide better working conditions, especially in confined areas such as warehouses, mines, etc.;
7. portable power — to operate a wide variety of appliances including electric tools, entertainment units, cellular telephones, and laptop computers.

It should be noted that electrical energy can be obtained from two basic types of electrochemical device, namely, batteries and fuel cells. A 'primary' battery is a system in which the electrical energy is obtained directly from the chemical energy of the reagents that are contained within the unit, whereas a 'secondary' battery refers to those systems in which the electrical energy is initially produced elsewhere, stored via chemical transformation of the enclosed reagents, and then delivered on demand. Thus, primary batteries are not capable of being easily recharged electrically and are discharged once and discarded, while secondary batteries can be charged and discharged many times. A fuel cell can be considered to be a primary-type battery, but one in which the reactants are supplied from an external source when power is desired. The internal electrodes and components remain unchanged and the cell can operate continuously as long as reactants are supplied. In concise terms: secondary (or rechargeable) batteries store electricity and require a supply of outside electricity to function; fuel cells make electricity and require a supply of outside fuel. Both batteries and fuel cells are expected to play key roles in future strategies to shift primary-energy demand away from petroleum fuels and towards sources that are more abundant, less expensive, and/or more environmentally benign. The following discussion focuses on the application of rechargeable batteries — especially, the lead/acid system — as a driver for sustainability.

4. A short history of battery development

4.1. Galvani's experiments with frogs' legs

Although archaeological discoveries have indicated that primitive batteries could have been used as early as 2000 BC by Egyptian and Persian craftsmen for the electroplating of metals, the electric battery has its true scientific origins in the late 18th century.

In 1780, Luigi Galvani, a doctor of medicine and a professor of anatomy at the University of Bologna in Italy, commenced a series of studies into the nature of muscle irritability in animal preparations — usually frogs' legs. He found that when a partially dissected frog was placed either directly or indirectly in a circuit of electric discharge to earth, the muscles flexed and caused the legs to twitch as though in a spasm or convulsion.

For his chief supply of electricity, Galvani used the simple electrostatic machines of the day. These were primitive devices that had to be charged by friction; the electricity could be stored in a Leyden jar. In further experiments, Galvani attempted to use electrical disturbances in thunderstorms as a supply of electricity. To conduct the atmospheric electricity to the frogs' legs, Galvani employed large metal objects. For example, he exposed the legs to a storm by hanging them by their nerves from the iron railing in front of his house. The lower end of each suspended member was connected to a grounded wire. With this arrangement, Galvani demonstrated that atmospheric electricity also could act as a stimulus to his frogs — when lightning flashed, the legs twitched under the electrical stress.

In 1786, during the course of these latter experiments, Galvani made the observation that was to lead to the discovery of the electric battery. He noticed that if brass hooks were used to suspend the dissected frogs from the iron railing, twitching would occur on contact of the legs with the iron, even when the skies were clear. Galvani decided that here was a new source of electricity that was independent of friction machines, Leyden jars, or lightning. To explain this phenomenon, Galvani (presumably drawing from his experience in anatomical and physiological matters) proposed that animal tissue itself possessed a vital force, and this he called: 'animal electricity'. Fortunately, his interpretation proved to be incorrect.

4.2. The Volta pile

It fell to Alessandro Volta, a professor of natural philosophy at the University of Pavia, some hundred miles distant from Bologna, to reason correctly that the muscular stimulation observed by Galvani in frogs' legs was not physiological in character (i.e., 'animal electricity') but was of a metallic origin. By 1793, Volta had deduced that the electricity was in fact due to an electrical fluid flowing between two dissimilar metals (e.g., brass and iron) and a moist conductor (e.g., the cell solution in the frog's tissues). The legs acted

merely as detectors of this electricity. Volta termed the phenomenon: ‘metallic electricity’. In fact, Galvani and Volta disagreed strongly over the origin of the electricity, and they and their supporters argued for years. We now know that neither was totally correct!

Volta next proceeded to rank metal pairs according to their ability to create a flow of electricity in a given moist conductor. He found that the effectiveness of such metal pairs was cumulative when they were stacked in a repeating pattern with moist chemicals. This discovery led Volta to the invention, in 1796, of the electrical device that came to be known as the ‘Volta pile’. The details of this device were eventually communicated by Volta to the Royal Society of London in a letter addressed to the Rt. Hon. Sir Joseph Banks, dated 20 March 1800. Volta described how he had constructed a vertical pile from alternating layers of silver, brass or copper discs against tin or zinc discs; the metals in each pair were separated by a pasteboard disc saturated with brine. Tests show that on connecting the outermost plates of the pile with a conducting wire, the device could provide an appreciable source of continuous electrical current. Volta had devised the first primary electrical battery.

The Volta pile functions by means of ‘electrochemical’ reactions. In each metal pair, one disc (e.g., copper) remains inert in that it accepts electrons and supports the generation of hydrogen gas, while the other disc (e.g., zinc) dissolves and releases electrons. The moist conductor in the central disc acts as a supplier of hydrogen and as a host for the dissolved zinc. The electrons move through the connecting wire from the zinc disc towards its copper counterpart. This constitutes the electric current which, ideally, will continue to flow until the moist conductor is exhausted or the zinc is eaten away. The electrical effect can be strengthened by piling up these three-disc units, or cells. From this epochal discovery, batteries — as we know them today — became possible, and for the first time experimenters were provided with a means of generating electricity in considerable and manageable quantities.

Although Volta has been given credit for the invention of the electric battery, he never found the true explanation for its operation. He incorrectly ascribed the current to the actual contact of the two dissimilar metals. Sir Humphry Davy appears to have been the first to recognize that the Volta pile actually consists of a series of ‘cells’ and that the electricity is generated chemically by reaction at each metal/solution interface. The impelling force that allows current to flow was termed an ‘electromotive force (e.m.f.)’. In honour of Volta, it was decided, in 1881, to express this force in units of ‘volts’. Davy was also the first to coin the term ‘electrochemical’: ‘electro’ to signify the electrical charge that metals acquire in contact with other metals or solutions; and ‘chemical’ to take into account the role that subsequent reactions play in producing electricity.

Despite the fact that many distinguished scientists of the day, including Becquerel, Oersted and Ritter, supported the theory of electrochemical action, the contact theory of Volta

was slow to be discarded. It was Davy’s laboratory assistant, Michael Faraday, who identified the mechanism of the processes that take place within electrochemical cells. In the course of his studies, Faraday not only placed the field of electrochemistry upon a quantitative basis, but also invented the electric motor, the transformer and the dynamo — the basic elements of the modern electrical industry.

4.3. Development of secondary batteries

4.3.1. Acid systems

Following Volta’s discovery of the first primary pile, more than half a century of exploratory work passed before Gaston Planté [1] was able to demonstrate, in 1860, the first practical rechargeable battery. This consisted of nine cells that were connected in parallel (Fig. 5). Each cell was constructed by loosely rolling a sandwich made of two long electrodes of lead foil, separated by strips of flannel, and then inserting the coiled assembly into a cylindrical jar, which was subsequently filled with dilute sulfuric acid. The active materials of the electrodes were obtained electrochemically from the lead itself by connecting the cell to a supply of electricity. Passage of current through the lead/acid system resulted in the conversion of the surface of the positive plate into lead dioxide and the surface of the negative plate into spongy metallic lead. Planté found that the level of stored energy depended on the amount of lead dioxide produced — the ‘capacity’ could be increased by larger or repeated charges in the so-called ‘forming’ process.

Unfortunately, the only electrical charging sources available to Planté were primary batteries, and as they delivered only small currents and became exhausted fairly rapidly, lead/acid battery formation was both costly and tedious. Thus, the use of such batteries was at first limited to laboratory experiments. Commercialization was eventually achieved in the 1880s following the practical development by Thomas Edison, and others, of the electromechanical dynamo as a cheap, reliable and practical source of large-scale direct current for battery recharging.

An important and innovative step in the design of lead/acid batteries was the introduction of the pasted plate, first reported by Camille Faure [2] in 1881. This consisted of a lead sheet coated with a lead oxide/sulfuric acid paste that

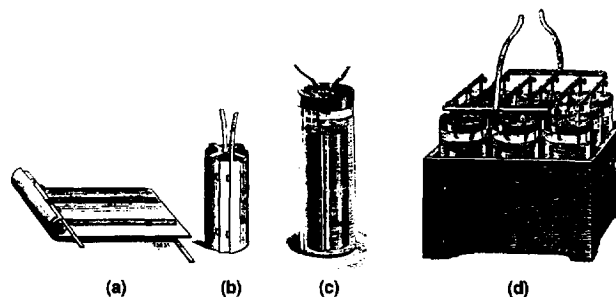


Fig. 5. Lead/acid battery invented by Gaston Planté: (a) electrodes with flannel strips during winding; (b) electrode assembly; (c) complete cell; (d) 9-cell battery.

could be readily formed (by passage of current through the plate) into either of the positive and negative active materials, namely, lead dioxide and spongy lead, respectively. Although the formation process was accelerated, the plates lacked durability because of poor adhesion of the active materials to the lead surfaces. An improved plate was patented by Volckmar, also in 1881; this was perforated with numerous holes that were filled with a paste of lead oxide and sulfuric acid. The design was developed further by Swan and Sellon, who produced a lead grid for holding the paste. In 1881, Sellon [3] took out a patent for a battery in which the grid lead was replaced by an alloy of lead and antimony. This increased considerably the mechanical strength of the plates. Grid-based pasted plates not only reduced the problem of shedding of active material, but also provided higher capacity per unit weight and volume compared with Planté plates.

These developments in plate design, accompanied by improvements in the methods of preparation of active materials, aided the industrial manufacture of lead/acid batteries in the 1880s. Commercial production took place almost simultaneously in countries such as France, UK, USA, and the former USSR. Early applications included: house, factory and train lighting; signal and telephone service; trolley service; electric-vehicle propulsion.

4.3.2. Alkaline systems

The development of alkaline-electrolyte secondary batteries followed closely the introduction of the lead/acid battery. The forerunner of the alkaline systems was the Lalande-Chaperon primary cell, a copper oxide/potassium hydroxide/zinc system patented in 1881 [4]. Since the working voltage of this cell was only 0.85 V, and there were operational problems caused by the high solubilities of both zinc oxide and copper oxide in the alkali electrolyte, many attempts were made to find better active materials. Positive electrodes were fabricated from the hydroxides of manganese, mercury, nickel or silver, and negative electrodes from various geometric forms of cadmium, iron or zinc. Almost all system combinations of these electrode materials were investigated. The two most successful proved to be the nickel/cadmium and nickel/iron cells developed by Waldemar Jungner [5] in Sweden and Thomas Edison [6] in the USA at the turn of the century. These two varieties of alkaline battery were soon in commercial production — Edison nickel/iron cells from 1900, and Jungner nickel/cadmium cells from 1909.

Initially, both systems used flat, perforated pockets of nickel-plated iron sheet to contain the positive and negative active materials. This construction was known as the 'pocket type'. Nickel/cadmium batteries with this electrode configuration are still manufactured in several European countries, the USA, Latin America and Japan. In 1908, Edison introduced an improved version of the nickel/iron system in which the positive material was contained in cylindrical tubes made from perforated nickel-plated steel strip — the 'tubular-type' battery. Batteries of such design were in common usage in

traction applications up to the 1960s, but gradually lost much of their importance; they are still manufactured in Germany and France, whereas the pocket type is produced on a large scale in the CIS.

4.3.3. Advanced systems

Today, over a century later, the above-mentioned batteries — lead/acid, nickel/cadmium and nickel/iron — still constitute the market for large secondary batteries, with the lion's share belonging to lead/acid. Following the so-called 'energy crisis' in the early 1970s and, more recently, the concern over increasing atmospheric pollution from conventional road transport, there has been a great surge of interest in bringing to commercialization other ('alternative') systems of potentially superior performance, especially for electric-vehicle applications.

In the case of traction applications, two important parameters are the energy (Wh) and the power (W) outputs per unit weight, or volume, of the battery (see Section 6.3). The former parameter determines the driving range of the vehicle, the second determines the acceleration and hill-climbing performances. The energy capabilities of the reactants used in conventional lead/acid and nickel/cadmium batteries are very limited compared, respectively, with bromine, oxygen or sulfur positive-plate materials, and with aluminium, hydrogen, sodium or lithium negative-plate materials. Thus, efforts are being made to develop the most favourable combinations of these alternative materials for electric-vehicle propulsion. The more promising systems include: nickel/metal hydride; zinc/air; sodium/nickel chloride; lithium/polymer.

5. Electricity supplies — new value systems

5.1. Central power generation

It is estimated that the demand for electricity — the most versatile and practical form of energy — will increase steadily at between 5 and 7% per year on a world-wide basis. Much of this growth will take place in the developing countries. For example, it is estimated that by 2020 the electricity consumption of the developing countries will increase from less than one-quarter of the world's supply to about half. This will require the installation of some 3000 GW of capacity — an enormous challenge for capital-constrained nations.

In most industrialized countries, electricity is generated mainly by the direct combustion of coal in large, remote, central power plants. Transmission systems are used to deliver electricity to customers on the distribution system. The efficiency of these plants is now approaching 40% — the limit in both technical and economic terms. In the future, however, modification of conventional coal-based power technologies to meet increasingly stringent regulations that relate to emissions of carbon dioxide, SO_x, NO_x, particulates and solid residues will both reduce efficiencies and increase costs. As a consequence, new and alternative technologies

that utilize non-renewable energy sources more effectively and more cleanly are being investigated and implemented. These include fluidized-bed combustors, combined-cycle gas/steam turbines, integrated coal-gasification combined-cycle systems, integrated gasification humid-air turbines, geothermal energy, magnetohydrodynamics, and fuel cells. The major requirements of the advanced technologies are moderate-sized modular construction, higher thermal efficiency, and lower emissions.

Given that the mission of the electric utility industry is to supply sustained power at the lowest possible cost, utilities must have sufficient capacity to meet the highest demand, as well as an adequate reserve to cover equipment failure. (Note, the same applies to industries that provide their own electricity.) The integration of an energy-storage system allows supply to satisfy demand more effectively. In particular, energy-storage technologies offer promising alternatives to installing extremely costly, continuous-duty plants to balance the power-generation requirements: less-expensive baseload energy is stored during off-peak times and then supplied when the demand is high. This is the concept of 'load-levelling'. Such a strategy will enable central power stations to match system generation with changes in demand ('load-following') and, thereby, achieve better thermal efficiency and lower maintenance costs. Load-levelling may also extend the useful life of the plant and mitigate air-quality problems. Customer-side-of-the-meter (CSOM) storage of electric energy offers the equivalent economic benefits 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 energy consumed (kWh) but also by the peak-power demand (kW)). This is the concept of 'peak shaving' in which 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.

Other benefits of energy storage include: (i) improvement in reliability and quality of the power supply by regulating short-term voltage fluctuations (dips, spikes) and harmonic frequencies which, if left unstabilized, could lead to power outages; (ii) provision of reserve energy ('spinning' reserve) to meet power emergencies that arise from failure of generating units and/or transmission lines; (iii) deferral of new transmission lines and transformers — deployment of energy-storage devices at the local substation level will reduce peak day-time transmission as well as enhance local-area reliability and, thereby, will defer capital expenditure on upgrading the transmission system and reduce the possible harmful effects of electric and magnetic fields; (iv) back-up for end-of-line power — in many networks, the ends of the power lines are not connected to each other and, in such situations, energy storage could provide emergency services in the event of transmission-line failure; (v) reduced transmission/distribution losses — if located at the end of the

transmission or distribution line, energy storage will lower the amount of power sent down the line during peak periods and, consequently, will reduce the resistive losses and provide a net energy saving; (vi) assisting the introduction of alternative (renewable) energy supplies — with d.c. energy supplies such as solar and wind, energy-storage devices can act as a buffer to filter out any harmonics associated with d.c. to a.c. conversion.

Electrical energy can be stored chemically (hydrogen, metals), electrically (rechargeable batteries, capacitors, magnetic fields), mechanically (pumped hydro, compressed air, flywheels) or thermally (resistance heating). The use of batteries in load-management operations has been made feasible through the development of high-power, solid-state devices for the interconversion of a.c. and d.c. power. Batteries offer a number of important operating benefits to an electric utility. In particular, batteries respond very rapidly to load changes and thus help to limit the imbalance between local generation and local demand (i.e., load-levelling operations), provide reserve energy to meet power emergencies ('spinning reserve'), accept co-generated and/or third-party power, and enhance system reliability. The short lead-time, convenient siting and modular construction of battery systems will also enable a utility to keep pace with load growth at minimal capital cost.

To date, battery energy-storage facilities have used the traditional lead/acid system. Load-levelling and peak-shaving programmes have been implemented in Europe, Japan and the USA. The largest European battery storage plant came on stream in West Berlin in 1987. The system was based on a low-maintenance lead/acid battery that consisted of 12 strings of 2000 V arranged in parallel. It incorporated a two-converter design to provide 8.5 MW for load-frequency control and 17 MW for instantaneous reserve power. Before the unification of Germany, there was a need for load-frequency control in Berlin as the city was electrically isolated from outside power generation. Japan has operated and tested a 1 MW/8 MWh battery for multi-purpose applications at the Kansai Electric Power Company. In the USA, a 10 MW/40 MWh, load-levelling battery was placed in service in mid-1988 at the Chino substation of the Southern California Edison Company. It is the world's largest battery and contains 8256 cells arranged in eight parallel strings, with a nominal voltage of 2000 V per string. Battery energy-storage systems have been installed for frequency regulation at the Puerto Rico Electric Power Authority (20 MW/14 MWh) and at the Hawaii Electric Light Company (10 MW/15 MWh). CSOM batteries have been evaluated at Vaal Reefs BSP in South Africa (to operate a gold-mine shaft) and at Johnson Controls in the USA (to power a battery manufacturing plant). Depending on utility time-of-day pricing schedules and the customer's daily and weekly load-profile, it appears that CSOM storage plants could save enough in electricity demand charges to provide a payback in three to five years. By virtue of these and other successful demonstrations of the technology, lead/acid batteries are seen to offer utilities a

flexible and strategically advantageous means of meeting their energy-management and power-regulation needs.

5.2. Distributed power generation

Today's utilities are facing four driving forces of change: greater competition; improved customer service; cost reduction; cleaner operation. As a consequence, utilities are focusing on energy efficiency, alternative energy options and improved environmental performance. To meet these challenges, there is a growing opinion that future power-generation needs will increasingly be satisfied by distributed power systems with typical capacities from 50 MW to as low as 50 kW. These systems will be embedded in the transmission and distribution network. (Note, remote-area power supplies, that provide a self-contained alternative to grid connection, are another type of distributed resource and are discussed in Section 5.3.) This trend towards decentralization, with smaller generating units in close proximity to end-users, provides many of the advantages (listed above in Section 5.1) that can be gained from the introduction of energy-storage systems, namely: protection from major mishaps; decreased costs of transmission and distribution; lower power losses; improved local reliability and quality of supply; greater flexibility in matching capacity additions and retirements with changes in demand; reduced concerns over the possible health effects of electric and magnetic fields; shorter construction times. There are also pressures to provide access to electricity networks for independent generators such as co-generators, waste-fuel combustors, solar photovoltaic installations, and wind machines. Finally, distributed generation may be seen to provide a way to introduce competition into the industry.

The availability of electrochemical energy devices (i.e., batteries and fuel cells) with demonstrated attributes of small size, low noise, modular construction, negligible emissions and high efficiency means that generation sources and energy storage can be placed on the distribution system at critical points in the network and nearer to the customer. Furthermore, electrochemical technologies can be installed in incremental capacities that meet more closely the demand at the time. This approach improves the effectiveness of capital by quickly putting a plant into service with little unused capacity. It also permits the rapid adoption of technological advances.

Thus, it appears that the utility of tomorrow will be a hybrid network of traditional (but improved) central-generation, distributed-generation and energy-efficiency technologies (Fig. 6). This less-centralized structure is known as the 'distributed utility concept' and has 'enoughness' (or sustainability) as its operational target, that is, electricity generation must use the least resources with the least environmental impact. Worldwide, many utilities have begun the transformation to the distributed utility of the future — 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. Fuel cells with outputs ranging from 2 to 100

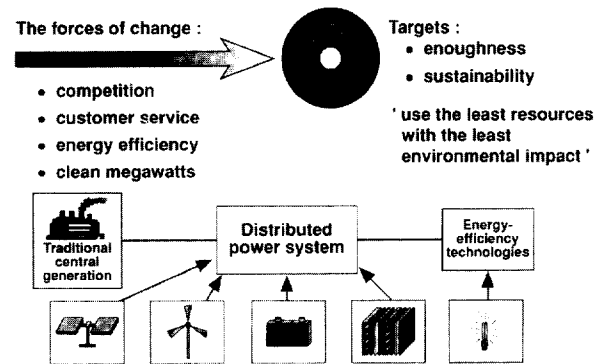


Fig. 6. The distributed utility concept.

MW are considered to be strong competitors for these dispersed-power markets. In other 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, lead/acid batteries again promise to be a cost-effective option since they can be conveniently placed adjacent to power plants and, thereby, will reduce transmission requirements.

5.3. 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 and diesel/battery hybrid arrangements. The former systems show great potential for application in remote areas (e.g., in navigational, telecommunications, village and homestead installations), as well as in space exploration. When intended for terrestrial operations, such a facility is commonly termed a 'remote-area power-supply' (RAPS) system. It must be appreciated, however, that stand-alone power supplies can often find application in urban areas as cost-effective alternatives to mains connection.

The development of RAPS systems is particularly important for progressing the electrification of developing countries. Although power plants in these countries have typically been sited 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 has been claimed that 25% of the rural population with no access to electricity could be economically supplied by such technology.

Renewable energy sources such as solar and wind are stochastic in nature and, therefore, must be coupled with an energy-storage facility to provide a continuous supply of electricity. Rechargeable batteries offer the most appropriate method for storing the electricity derived from such energy sources. The batteries meet the load requirements at night and in times of cloudy/foggy weather (with photovoltaics) or during calm periods (with wind machines). Lead/acid batteries are currently the favoured choice.

For domestic RAPS facilities, battery optimization is particularly hindered by the present limited knowledge of actual service demands. This is not surprising given the fact that the load requirements can vary significantly from site to site (due to differences in occupancy and lifestyle) and that the demand pattern may change once a continuous power supply is installed. Therefore, it is essential to determine representative load profiles for consumers in remote areas in order to assess the suitability of both available and emerging lead/acid technologies, and to use such information to design a battery that is specifically dedicated to RAPS applications.

5.4. Standby-power generation

Historically, rechargeable batteries have been used as back-up power sources to ensure the operation of critical loads during breaks in the primary supply, e.g., mains failure. Standby-power batteries have found service in power stations, telecommunications networks, emergency lighting, lift control, switch gear, signal systems, medical equipment, security devices, etc. More recently, advances in solid-state power electronics have allowed the development of UPS systems. These have extended the use of batteries, particularly in the protection and reliability of computer-based equipment. The latter can be damaged by power interruptions, and data stored either in volatile memory or on disc can be irretrievably lost. In all these applications, the battery is maintained in a fully charged condition by holding it at a controlled potential and is said to be 'on float', or 'floated'.

Lead/acid or nickel/cadmium batteries are used to supply back-up power. Both types have advantages and disadvantages that vary from one application to another. Nickel/cadmium cells for standby service are generally of the pocket-plate type in which the active materials are contained in flat pockets of perforated steel. Cells with this design have good mechanical ruggedness and are not adversely affected by conditions of electrical abuse that would be damaging to lead/acid cells. These features render nickel/cadmium the system of choice for railway service where train lighting, air conditioning, diesel-engine starting, and signalling are all important areas. Nickel/cadmium cells are also more tolerant of low temperatures — they can be frozen without harming performance — while their high-rate capability makes them especially useful for engine starting or closing/tripping circuit-breakers in electric utilities or distribution networks.

The lower cost of lead/acid batteries compared with nickel/cadmium equivalents makes them the more popular

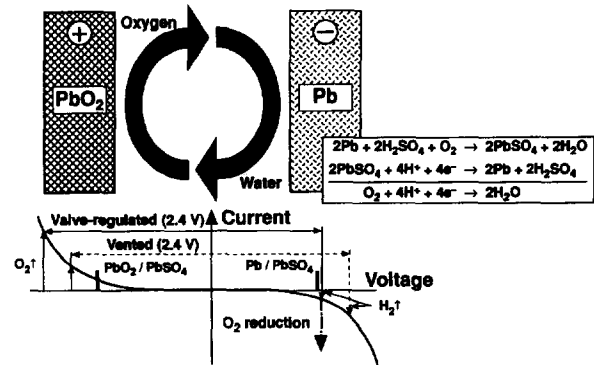


Fig. 7. Principles of gas-recombination technology.

choice for most standby-power duties, and with the advent of maintenance-free designs this competitive position has been enhanced. In these designs, the major maintenance operation of traditional lead/acid batteries, namely, water addition, is eliminated. The technology — commonly known as the 'valve-regulated lead/acid (VRLA) battery' — is based on the 'oxygen-recombination cycle' and uses an immobilized electrolyte (Fig. 7). These features produce a sealed and leakproof unit. Recombination is achieved by arranging for oxygen generated at the positive plate on overcharge to pass via channels 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 the generation of hydrogen can never be avoided completely (Fig. 7), each cell is fitted with a one-way pressure relief valve that opens when the internal pressure exceeds tolerable limits. The electrolyte is immobilized either within a glass-microfibre mat (AGM design) or by gelatinization with silica (gel design).

The continuing trend for power systems to become increasingly complex and integrated into more extensive networks has caused greater emphasis to be placed on overall reliability. Lead/acid batteries will continue to provide the most cost-effective method for satisfying the growing need for standby power. In particular, VRLA batteries will find progressively broader application and win markets from conventional types of lead/acid batteries and nickel/cadmium batteries. The lack of both acid spray and emission of flammable gases, together with the elimination of routine maintenance requirements, permits VRLA batteries to be installed in immediate proximity to electrical/electronic equipment, and in any orientation. For example, VRLA batteries are being widely used by telecommunications authorities in main exchanges, private automatic branch exchange (PABX) systems and remote transmitting stations, as well as for UPS systems, emergency lighting, engine starting, and switch operating.

5.5. Portable power

There is burgeoning demand for batteries to power cordless appliances. Historically, the required power sources have been primary batteries based on the zinc/manganese dioxide

couple. Nowadays, concern over contamination of the environment by the mercury content of used batteries, together with a shift in community attitude from the 'throw-away' society, has resulted in a trend towards rechargeable alternatives.

Nickel/cadmium is the traditional rechargeable battery for consumer applications and improved designs are continuously being introduced to keep pace with market requirements. This system has good performance characteristics and a long service life (500 to 1000 deep-discharge cycles). About one-third of the world's production of cadmium, which is a major by-product of the zinc industry, is used in batteries. As with primary systems, nickel/cadmium batteries are not free from environmental concerns, since the uncontrolled disposal of spent units can result in the release of highly toxic cadmium. To circumvent this problem, legislation has already been introduced in Europe to ensure safe collection and reprocessing.

The use of lead/acid batteries for portable devices has been increased by the recent introduction of the valve-regulated technology, which allows batteries to be sealed and, thereby, to have good safety characteristics (i.e., no acid mist or leakage). VRLA batteries are available in a wide range of sizes and are cheaper than their nickel/cadmium counterparts, but have shorter service lives. The first cells were produced in the USA and comprised two spirally-wound electrodes housed in a cylindrical can. Batteries with this configuration can deliver extremely high levels of power (see discussion of the Bolder battery, Section 7.2). Elsewhere, Japanese manufacturers have produced higher voltage units in flat-pack configurations of multiple sandwich-type cells.

To minimize battery weight, attention has focused on lithium as an electrode reactant. In addition to a much higher energy density, rechargeable lithium batteries have an advantage over their established rivals in that they retain charge for a much longer period. The batteries are also more environmentally acceptable in that they do not contain toxic metals such as cadmium, lead or mercury. The main problem lies in the reactivity of the lithium metal and in the related passivation and instability phenomena at its interface with the electrolyte. Passivation limits the cycleability of the entire battery, while instability can introduce serious safety hazards. One approach to overcoming such difficulties is to replace the lithium by a non-metal compound that is capable of storing and exchanging a large quantity of lithium ions. Thus, the electrochemical reaction at the negative electrode would involve the uptake of lithium ions during charge and their release during discharge, rather than lithium plating and stripping as in conventional systems. If a second, non-metal, lithium-accepting compound is used as the positive electrode, then the entire electrochemical process would consist of the cyclic transfer of lithium ions between the two electrodes. In simple terms, these systems may be considered as concentration cells in which lithium ions 'rock' or 'swing' from one side to the other. Accordingly, such cells have been termed 'rocking-chair batteries' or 'swing batteries'. This concept

has been exploited by Sony Energytec in Japan for the mass-production of the 'lithium-ion rechargeable battery'. Lithiated petroleum coke is used as a novel negative electrode, and LiCoO_2 as the positive. Apart from improved safety characteristics, it is claimed that the cell gives an energy output four times that of nickel/cadmium and an impressive cycle life of 1200 deep-discharge cycles. This development has stimulated work on rechargeable lithium batteries in many countries. Present efforts are directed towards better electrode materials, improved electrical performance, and longer life. Building on expected success in these areas, lithium-based batteries will challenge the supremacy of nickel/cadmium and lead/acid and will make a major impact on tomorrow's markets for portable power.

6. Road electric vehicles — a breath of fresh air

6.1. *The new impetus for electric vehicles*

Throughout the present century, internal-combustion-engined ('motor') vehicles have brought many economic and social benefits. While goods vehicles have oiled the wheels of commerce, private motor cars have given individuals virtually unlimited mobility and, consequently, great freedom in choosing where to live, work and play. Indeed, the motor car has become a major, if not the supreme, symbol of increasing prosperity throughout the world. But such transportation benefits have been achieved not without some cost. First, car production now consumes more resources than any other industry (it uses 20% of the world's steel production, 10% of the aluminium, 35% of the zinc, 50% of the lead, and 60% of all natural rubber); second, the vehicles derive their power from the combustion of dwindling supplies of fossil fuel; third, the resulting exhaust gases are inflicting serious damage to air quality in both regional and global environments.

In terms of regional pollution, the three major harmful emissions from automobiles are carbon monoxide, nitrogen oxides and hydrocarbons. For the industrialized countries of the West and Japan, analysis of the respective total emissions has shown that motor vehicles emit two-thirds of the carbon monoxide, just over one-third of the nitrogen oxides, and nearly half of the hydrocarbons. In developing countries, where environmental controls are lax, inefficient vehicles also contribute significantly to air pollution, even though the traffic population is smaller.

Apart from generating acid rain, photochemical smog and airborne toxins, vehicular emissions also aggravate global environmental problems by the production of large quantities of carbon dioxide. This greenhouse gas is considered to be the main cause of the observed rise in the average global temperature. A world-wide temperature increase of only a few degrees may spell disaster for the planet in the form of rising oceans, and more frequent and severe hurricanes, droughts and floods. At present, road transport is a major

contributor to the carbon dioxide budget. For example, vehicles are responsible for 20, 24 and 28% of all emissions of carbon dioxide in the UK, the USA and Australia, respectively. On average, a car will produce nearly four times its own weight of carbon dioxide every year.

The undoubted contribution of road transport to atmospheric pollution was brought into sharp focus by the adoption of the 1989 California Clean Air Act. This legislation mandated that 2% of all new vehicles offered for sale in California by the major manufacturers should be zero-emission vehicles (ZEVs) in model years 1998–2000, 5% in 2001–2002, and 10% in 2003 and beyond. The ZEVs should not emit directly any of the regulated pollutants, viz., 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 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.

Although battery-powered electric vehicles are clean alternatives for urban conditions, consideration must, of course, be given to the indirect emissions associated with generating the electricity required to run such vehicles. In this respect, a study by the US Department of Energy has suggested [7] that battery-powered electric vehicles should be overwhelmingly less polluting than their petrol-powered counterparts. Following an assumption of the most likely fuel mix for the power plant, the substantial reductions in the emissions of carbon monoxide, nitrogen oxides and volatile organic compounds were calculated to be 99, 86 and 99%, respectively. In a separate analysis [8], it has been estimated that the introduction of 1.5 million ZEVs in the Los Angeles area would lower ozone concentrations by about 4%, i.e., to a level nearly 20% below that projected for the region by 2010. Natural-gas vehicles (NGVs) have been advanced as a better means to alleviate emissions. Counter to this expectation, however, a recent full fuel-cycle analysis has concluded that electric vehicles will emit less than one-half of the total emissions of carbon dioxide and markedly fewer smog precursors than NGVs.

The impact of battery-powered electric vehicles on greenhouse gases — carbon dioxide, nitrous oxide and methane — is less clearcut and is particularly dependent on the source of power. In the worse-case scenario, the use of coal-fired power by electric vehicles is expected [9] to cause a moderate increase in the emissions of all greenhouse gases. If natural gas is used, analysis reveals that the situation will improve to give a moderate decrease in emissions, while the exploitation of non-fossil fuels (i.e., biofuels, hydro power, solar, and/or nuclear) would essentially eliminate all greenhouse gases.

The UK Department of Trade and Industry [10] has conducted an environmental life-cycle analysis for an internal-combustion-engined (ICE) vehicle and compared the data with those for an equivalent vehicle retrofitted with different battery systems (lead/acid, sodium/sulfur, sodium/nickel chloride). The results have shown that greenhouse-gas emissions during vehicle production are insignificant alongside those suffered during lifetime usage (taken as 160 000 km). More importantly, there is little difference in the total impacts (manufacture + usage) from the ICE vehicle and all of the three battery versions. Thus, electric vehicles that are purpose designed and built, and that are not merely ICE conversions, should give battery motive-power an environmental edge. Finally, whatever the future fuel-mix, it should be more easy to control pollutants from the power plant than from the multitudinous, mobile exhaust-pipes of conventional vehicles.

6.2. The battery barrier

The heart of the electric vehicle is the battery. Electrical energy is pumped into the system from a remote source (usually via the mains grid), stored, and then pumped out as motive power. As with the human heart, the battery must be energetic, robust, flexible in operation, and long-lived. This a formidable scientific and technological challenge!

To date, the lack of a commercially available, effective and economical battery system has been the major barrier to the realization of traffic-compatible, electric road vehicles. As a consequence, 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 will 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, cost-effective 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 urban air-quality management in congested cities. The push for a better battery has started!

6.3. What is needed from the battery?

To provide affordable electric vehicles with acceptable performance in mixed traffic, the motive-power batteries must have the following characteristics:

1. high energy per unit mass/volume → for long driving range;
2. high peak power → for good acceleration and hill-climbing;
3. high energy efficiency → for economic use of input electricity;

4. low self-discharge → to minimize energy loss on standing;
5. fast recharge → for rapid refuelling;
6. long cycle (service) life → for low depreciation cost;
7. low cost → to gain customer acceptance;
8. zero (or low) maintenance → so that little routine attention is required;
9. independent of ambient conditions → resistant to extremes and variations in local climate;
10. robust design and operation → tolerant of abuse (both electrical and mechanical);
11. environmentally benign → non-toxic materials;
12. proven safety → safe to use under both normal driving and crash conditions;
13. readily available constituents → made from non-strategic materials.

Among these requirements, the key feature of an electric-vehicle battery is its specific energy, closely followed by specific power, cycle life, recharge time and cost.

(i) *Specific energy*. This is the number of watts-hours of electricity that the battery can deliver per kilogram 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 kinetic 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, separators, connectors, terminals and the battery container, for instance.

(ii) *Specific power*. The specific energy problem is compounded by the fact that this parameter has an inverse relationship with specific power. Specific power is the maximum number of watts per kilogram that the battery can deliver at a given state-of-charge, usually 80% depth-of-discharge (DOD). Three factors dictate the trade-off between specific energy and specific power. First, polarization effects and the inherent internal resistance of the battery cause a current-dependent drop in output voltage, and thus reduce the total available energy. Second, the operating characteristics of some battery systems change at high currents and, thereby, lower the theoretical value of the specific energy. Third, designing a battery to handle high currents requires its current-collectors to be enlarged and this displaces active material, and again lowers the specific energy.

(iii) *Cycle life*. This is the number of times that the battery can be recharged. Ideally, the battery should last as long as the vehicle itself. Ironically, this goal is particularly hard to reach because electric vehicles, by virtue of their greater mechanical simplicity, enjoy a very long life. 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 driver's travel demands. Furthermore, some battery technologies yield a constant-energy throughput,

while others benefit from shallower cycles and last longer under such a regime of service. Still others are more appropriately described in terms of calendar life rather than cycles, particularly those systems that employ highly corrosive reactants.

(iv) *Recharge time*. Conventional recharging of batteries involves periods of several hours. Naturally, this restricts vehicle availability. Accordingly, appropriate methods are being sought for the rapid charging of batteries, especially for lead/acid systems. In particular, considerable research is being directed towards the development of procedures ('algorithms') and equipment that will achieve full recharge from low states-of-charge in a matter of minutes without imparting any adverse effects on battery life.

(v) *Cost*. The eventual factor that determines the commercial success of any new product is, of course, cost. This is especially true of motive-power batteries that may have to be replaced one or more times during the life of a vehicle.

6.4. Setting new performance targets

The first vehicles to replace horse-driven transportation were electrically powered by lead/acid batteries. Today, some 130 years since its discovery, 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 development and applications; relatively safe operation; an established servicing infrastructure; extensive spent-battery collection and recycling infrastructure and technologies. Nevertheless, future transportation needs will require designs with higher energy and 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. It should be recognized, however, that the transformation of the traditional lead/acid workhorse into a high-tech propulsion thoroughbred presents a severe challenge to battery scientists and technologists. Nonetheless, the rewards are worthy of high levels of effort as success will also yield flow-on improvements to the operations of lead/acid batteries in electricity utility energy-storage, remote-area and portable power supplies, and other applications.

7. Lead/acid batteries — technical challenges

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, and a better understanding of the properties and

performance of the positive and negative electrode systems. Nevertheless, established and emerging markets — especially, electric vehicles — are making 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 cooperate and communicate with the electrical circuits that they are powering, and that can be recharged rapidly. The technical challenges are as follows.

7.1. Greater specific energy

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

7.1.1. Minimizing inert components

About 30% of the total battery weight consists of grids and ‘top lead’ (bus bars, cell-connectors, 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 delivery levels, without shortening cycle life due to complete corrosion of less substantial positive grids or top lead, or without causing accelerated failure through the effects of vibration. In general, weight reduction has been explored through 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 and without losses in corrosion resistance, mechanical properties or conductivity. These composites have included lead-coated aluminium, copper, steel, nickel or titanium, as well as metal-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.

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 are found to increase the mechanical properties (yield strength, tensile strength, creep resistance, etc.), and also to improve the electrochemical characteristics by preventing passivation and permitting recharge of batteries from deeply-discharged states. Mechanical properties and corrosion resistance can be increased 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 permissible. The rolling process offers alloys with superior mechanical properties, and with uniform grain structures that reduce both corrosion and grid growth. 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

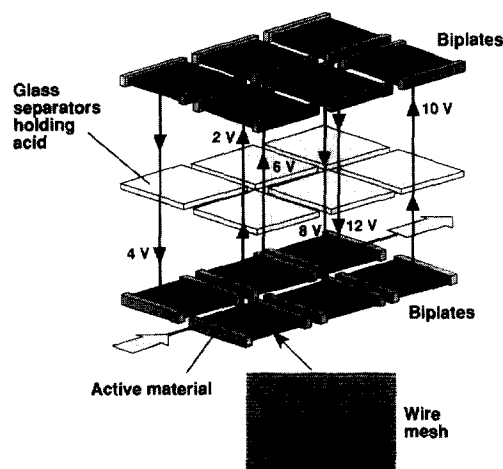


Fig. 8. Quasi-bipolar design of Horizon® lead/acid battery.

metal at the nodes. For this reason, it is more appropriate to use either a punch or a rotary cutter to fabricate the grids.

A more adventurous approach to reducing the lead mass is to minimize the current pathways between cells through reconfiguration of the vertical, interleaved positive/negative plate assembly used in conventional units. Bipolar (see Section 7.2) and quasi-bipolar designs are promising examples of such imaginative engineering. The term ‘quasi-bipolar’ is used to describe intercell connections that are not true bipolar connections. In general, the design involves a non-conducting partition (e.g., plastic) between cells and various types of inter-electrode connections that are 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 [11] for electric-vehicle propulsion (Fig. 8). This valve-regulated battery (AGM design) 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 battery’s horizontal orientation provides a convenient low profile, and is said to eliminate shedding of active material and intra-plate electrolyte concentration gradients (‘acid stratification’) that both contribute to loss of 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 ($> 45 \text{ Wh kg}^{-1}$, $C_3/3$ rate) and greater specific power ($> 300 \text{ W kg}^{-1}$, 80% DOD), as well as longer cycle life (900 cycles, $C_2/2$ rate) than conventional lead/acid batteries.

7.1.2. Improving active-material utilization

Inadequate utilization of positive active material is caused by the slow diffusion of acid into the interior of the plate, 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 to 30% of the positive active material in flooded systems can be accessed to provide electrical energy. Obviously, this limitation restricts vehicle range. VRLA technology has raised the utilization level to ~40%, but further significant improvements must be made to achieve, for example, a practical specific energy of 50 Wh kg⁻¹ (C₃/3 rate) for electric vehicles.

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 the 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.

As mentioned above, the second impediment to the utilization of positive active material is the progressive decrease in plate conductivity during discharge. The lead dioxide (PbO₂) particles of the active material have two functions: (i) to participate in the discharge reaction; (ii) to act as electron pathways from each reaction-site in the porous active mass to the grid; this non-reacting material provides structure and conductivity to the plate, but does not contribute to the reaction and, clearly, should be kept to a minimum level. As discharge of the plate proceeds, the conductivity decreases with the formation of increasing amounts of lead sulfate (PbSO₄). In some locations, areas of PbO₂ can become encapsulated by the non-conductive PbSO₄ so that no further reaction can take place, even if large numbers of PbO₂ crystals and sufficient sulfuric acid solution are present in the inner parts of the PbSO₄ capsules. 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 PbSO₄.

Increasing the porosity of the plate is an obvious approach to reducing the incidence of PbSO₄ encapsulation (and, incidentally, to improving acid supply). This has encouraged numerous studies of the influence of the plate-processing stages on the morphology of the active material, and how the growth and distribution of crystals during these stages result in material unavailability. 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 that either promote porosity (e.g., carboxymethyl cellulose, carbon black, graphite, glass microspheres) or favourably modify crystal size (e.g., silica gel) 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 PbSO₄. If a conductive material can be deployed in such a manner that it connects regions of isolated PbO₂ with their reactive neighbours (and, thus, with the grid), the discharge reaction can 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. The list reported in the literature, however, is surprisingly short, namely: carbon fibres, barium metaplumbate; titanium suboxides, Ti_nO_{2n-1}; tin dioxide-coated glass-flakes [12]. None of these additives has produced sufficient and enduring improvements to become commercially practical. Nevertheless, the search continues for appropriate materials that have good conductivity, high chemical/electrochemical stability, an ability to form a strong network in combination with the PbO₂, and negligible influence on oxygen evolution during battery charging.

7.2. Higher specific power

Compared with other battery systems, the lead/acid battery has good specific power ratings, despite its weight disadvantage. Moreover, VRLA technology (especially AGM designs) have advanced further the high-rate capability. On the other hand, 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 DOD. Thus, conditions of high power demand necessitate a battery with minimal internal resistance down to low DODs (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 introducing innovative cell/battery configurations. Clearly, such developments will also assist attempts to increase specific energy and to optimize recharge capabilities (Section 7.4), 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). During less-demanding driving, the vehicle's energy management system would charge the power battery from the range unit. 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 (Fig. 9). The bipolar plates are stacked parallel to each other with intervening space for the

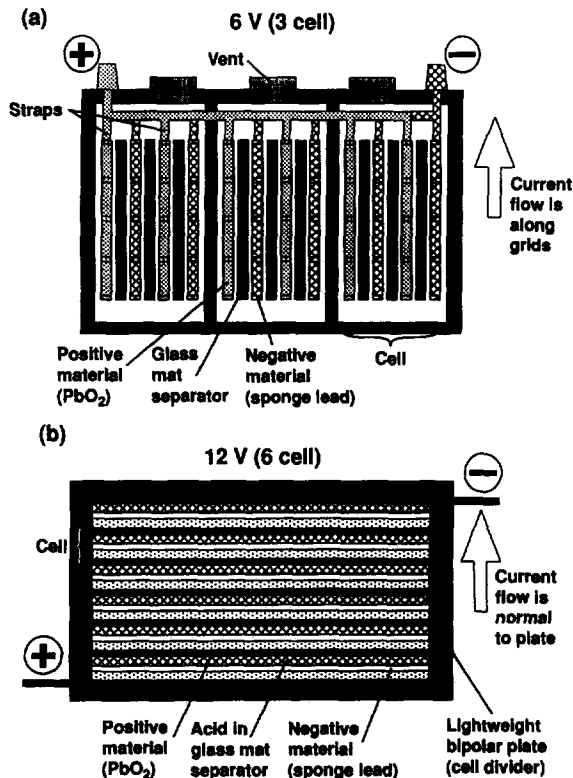


Fig. 9. Designs of valve-regulated lead/acid battery: (a) monopolar; (b) bipolar.

electrolyte and separator. 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 (as opposed to a single conductor in monopolar constructions). Thus, resistive losses are low and current and potential distribution across the plate is uniform. Moreover, the bus bars and posts that are required to carry the current in the monopolar design are eliminated and this further reduces resistance, as well as weight. As an example of the state-of-the-art, the Arias battery is a 90 V, 24 Ah unit that delivers 300 W kg^{-1} and 50 Wh kg^{-1} with a life of 3000 cycles at 50% DOD [13]. 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 interior during high-rate charge/discharge, and establishing low-cost, high-volume methods of manufacture.

The cell developed by Bolder Technologies Corporation [14] is a new approach to the design of high-rate VRLA batteries and is made by the spiral-wrapping of ultra-thin, lead-alloy, foil plates (0.13 mm thick) with a glass-microfibre separator (interestingly, this is a return to Gaston Planté's original design of lead/acid cell, see Fig. 5). 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 col-

lection with continuous contact between the plugs and the electrode foils results in relatively 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 for over 70 and 90% of the discharge life-time, respectively [14]. Thus, while the specific energy is no better than for other commercial lead/acid designs (typically, $30\text{--}40 \text{ Wh kg}^{-1}$), 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.

7.3. Longer deep-discharge service life

7.3.1. Premature capacity loss of positive plates

In most cases, battery cycle life is limited by the performance of the positive plate, the capacity of which declines on cycling, especially under deep-discharge. This loss of capacity 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 and 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 sulfation due to acid-stratification effects. These phenomena decrease the discharge capability both by reducing the amount of material available for reaction and by introducing large resistance losses. When the collective effects cause a battery to fall significantly short of its design life, the behaviour is known as 'premature capacity loss'.

Two distinct forms of premature capacity loss are now recognized [15]; these are termed PCL-1 and PCL-2 (Fig. 10). 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 $\alpha\text{-PbO}$) close to the grid, particularly if the positive-plate potential is driven too low by deep-discharge. Batteries constructed of pure-lead or lead-calcium grids (i.e., VRLA batteries) are particularly susceptible to this problem. It must be noted that the phenomenon known as 'passivation' can also cause sudden loss of capacity. Passivation can, however, be distinguished from PCL-1 through

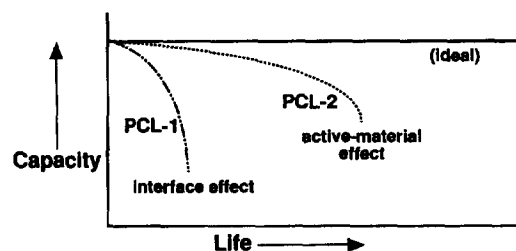


Fig. 10. Typical capacity-cycle plots for PCL-1, PCL-2, and ideal cycling service.

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 the addition of tin to grid alloys, improved manufacturing techniques, and use of phosphoric acid (gelled-electrolyte batteries).

The longer-term form 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.

7.3.2. Unified mechanism of premature capacity loss

The life of a lead/acid cell can be enhanced greatly by maintaining the assembly of plates and separators 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 (i.e., including all pore volume) occupied by the porous structure; it is the complement of porosity. Recently, Hollenkamp et al. [16] have 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 in positive-plate performance is a consequence of its direct relationship to the conductivity of the active material. Two conductivity-related factors conspire to limit the utilization of the 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 is attributed to the volume changes that accompany $\text{PbO}_2/\text{PbSO}_4$ inter-conversion. Accordingly, the apparent density decreases and the concomitant increasing disruption to the PbO_2 network (Fig. 11) 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 the discharge of the remaining bulk of material. Such a situation is typically found when severe capacity loss develops within a few cycles (i.e., PCL-1). Virtually all of the PbSO_4 is produced in the neighbourhood of the corrosion layer while the bulk positive material exhibits no signs of discharge.

Rapid loss of capacity is known to be promoted by low-density pastes, the use of relatively weak grids, and the absence of an effective level of compression. Each of these features contributes to the expansion of the porous material, but if they are attenuated to maintain the apparent density above the minimum acceptable level, then 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.

These observations have led to a ‘unified’ mechanism of capacity loss [16] 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 have focused 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 are based on the concept of some form of permanent barrier that electrically isolates the current-collector from the porous material. As intimated earlier, however, the development of a low apparent density can localize discharge close to the grid and, hence, high concentrations of PbSO_4 will be formed in the region. The result of this localized discharge is indistinguishable from the effects of a ‘barrier layer’ and, therefore, 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

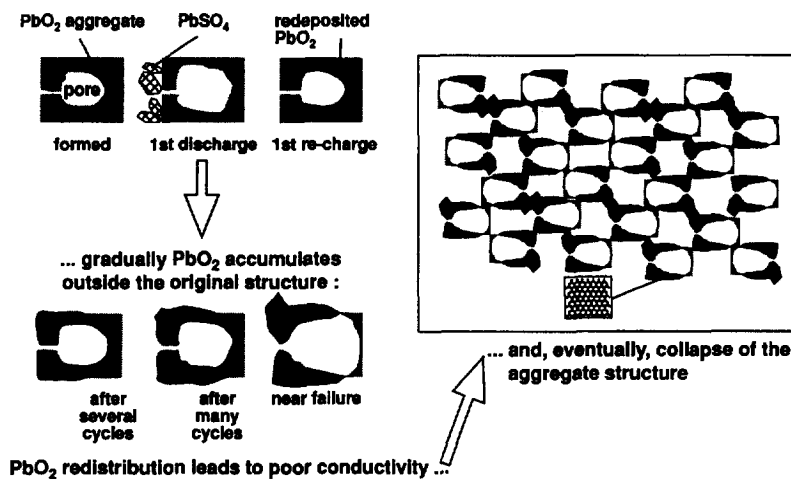


Fig. 11. Two-dimensional representation of changes in positive electrode structure during charge/discharge cycling: redistribution of lead dioxide during cycling leads ultimately to collapse of the aggregate structure [16].

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.

7.3.3. 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 sulfate, carbon black, and a sulfonate 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 failure of the negative plate may occur 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) are requiring 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 develop new and improved expander materials.

7.4. Faster recharge time

Methods for very fast charging of lead/acid batteries have long been sought. With the growing demand for the development of battery-powered electric vehicles, this need has intensified. Fast charging is seen to be a promising approach towards overcoming the limited driving range of vehicles powered by lead/acid batteries. For practical purposes, this involves reducing charging times from the hitherto usual period of hours to merely a few minutes.

Surprisingly little experimental work has been performed on the possible electrochemical, chemical and physical effects that fast-charging might have on battery plates. This fact, together with the recent demonstrations that very fast and efficient recharging of lead/acid batteries is possible [17] and that pulsed-current techniques can in fact extend battery life (Fig. 12), opens up rapid charging as an exciting new area of research. Apart from the optimization of charging parameters and battery design, there are challenges to find plate and grid materials that have good strength, good heat-transfer properties, and manageable gassing characteristics. In addition, the active material must have high porosity.

8. Epilogue or prologue?

In 1859: Raymond Louis Gaston Planté, a French scientist, disclosed the findings of his first experiments on the lead/

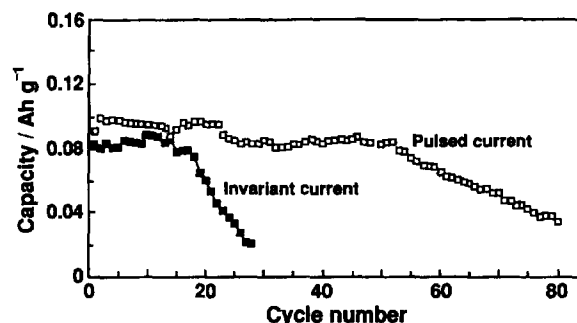


Fig. 12. Demonstration of the beneficial effect of fast (pulsed-current) charging on the cycle life of lead/acid cells [18].

acid system [19] Charles Robert Darwin, a British naturalist, published his seminal study: *On the origin of species by means of natural selection*; Edwin L. Drake, an American railway conductor, sank the first commercial oil well; Svante August Arrhenius, a Swedish chemist and physicist, was born. Remarkably, these four disparate events all relate to the principal energy problems that beset humanity today, and to the importance of electrochemical power sources in providing solutions to these problems.

Gaston Planté's experiments resulted in the discovery of the lead/acid battery — the most practical and widely used of all energy-storage devices.

Charles Darwin argued that most species reproduce in greater numbers than their surroundings can support. Consequently, only those members best adapted to the environment survive. The present custodians of Planet Earth are facing a great challenge — to ensure that all the inhabitants will prosper in an increasingly overcrowded and changing environment. It should be remembered that the physical world ten million years ago was the same as it is today, and its laws were the same. The living world, however, is not the same; for example, ten million years ago there were no human beings. It is evolution that is the real creator of originality and novelty in the universe; it must not be allowed to become the destroyer.

Together with an assistant, Edwin Drake erected an engine-house and derrick on a farm near Titusville, Pennsylvania, and on 27 August 1859, at a depth of 21.2 m, oil began coming to the surface. The well produced eight gallons a day which was hurriedly stored in tubs and whisky barrels. Within less than 24 h, the boom had started. The availability of oil accelerated industrialization and economic growth in many nations — but at the expense of a massive exploitation of the resources. Since 1859, there has been a 44-fold increase in the consumption of oil. Ironically, Edwin Drake profited little from the giant industry that he began; he spent his last years in ill health and near-poverty.

Meanwhile, Svante Arrhenius puzzled over why the temperature of the Earth remained at a stable and habitable level. On average, each square metre of the Earth's surface receives only 240 W of sunlight energy, but emits 340 W back into space. With such a discrepancy, the Earth should gradually cool to about -18°C . Arrhenius recognized [20], however,

that water vapour and certain gases (particularly, carbon dioxide) trap some of the emitted radiation and redirect it back down to earth. Accordingly, the global temperature is around 30 °C warmer than it would be in the absence of these natural gases. The latter are now collectively termed the 'greenhouse gases' because they play the same role as the glass panes in a greenhouse. Thus, Arrhenius provided the scientific foundation for the greenhouse theory of climatic change. If present-day emissions from electricity generation, transport, industry, agriculture and commerce continue unabated, there could occur global warming and, consequently, a concomitant greater change in climate than has happened at any time since the appearance of the human race.

The words of Rose Elizabeth Bird, the first woman to be Chief Justice of California, describe succinctly the cost of progress since 1859. She said: "We have probed the Earth, excavated it, burned it, ripped things from it, buried things in it. That does not fit my definition of a good tenant. If we were here on a month-to-month basis, we would have been evicted long ago."

Sadly, the judgement of Ms Bird is but an echo of the past. In 1897, two years before the death of Gaston Planté, the Russian dramatist Anton Pavlovich Chekhov also turned the spotlight on the environmental damage that can accompany so-called 'progress'. The following lines come from Uncle Vanya, a play that he completed in that year: "Man has been endowed with reason, with the power to create, so that he can add to what he's been given. But up to now he hasn't been a creator, only a destroyer. Forests keep disappearing, rivers dry up, wild life's become extinct, the climate's ruined, and the land grows poorer and uglier every day."

An eventual return to a sustainable economy appears to be inevitable. The vital questions are: How should it be managed? Will it be achieved in time to avoid the stresses that running out of oil and global warming will impose on civilization? Electricity is the key energy vector — it is a uniquely valuable, versatile and controllable form of energy that has become fundamental to the quality of modern life. The means to produce and manage electricity were first given to the world by the electrochemists: Galvani, Volta, Davy and Faraday.

Now, it seems that the future well-being of Planet Earth could again lie in the hands of practitioners of the science of electrochemistry and, in particular, those dedicated to advancing the lead/acid battery — Gaston Planté's great legacy to the techno-industrial world.

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