LEAD-ACID BATTERY STORAGE

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ABSTRACT: Lead-acid batteries are a prime form of chemical storage that we regard as holding most promise for large-scale energy storage applications. This paper includes a few pertinent comments on these rechargeable systems in their present stages of research and development.

Keywords: Lead-acid batteries, Battery storage, Flat-plate batteries, Tubular-plate batteries, Valve-regulated batteries**.**

RESUMO:. As baterias de chumbo-ácido são uma das melhores formas de armazenamento químico e que encaramos como uma das mais promissoras para aplicações de armazenamento de energia em larga escala. O presente artigo inclui alguns comentários pertinentes sobre estes sistemas recarregáveis, na sua actual fase de investigação e desenvolvimento.

Palavras chave: Baterias de chumbo-ácido; Armazenamento em baterias, Baterias de placa plana; Baterias de placa tubular, Baterias reguladas por válvula.

1. GENERAL REMARKS

Of the many possible ways of storing electrical energy, the only ones that are truly practical and widely used today are pumped hydro on the medium-to-large scale and battery storage on the small-to-medium scale. Other possibilities (compressed air, flywheels, electromagnetic and electro-static energy storage, hydrogen) are still at the development stage and, as yet, only have limited application in special situations.

Batteries are of two basic types: "primary" batteries that are discharged once and then discarded and "secondary" batteries that are recharged many times [1]. Here, we are concerned only with the latter type. Another useful distinction is between "consumer" batteries as purchased by individuals, and "industrial" batteries as used in industry and commerce. Most consumer rechargeable batteries are small, single-cell devices (with the notable exception of the automotive battery), whereas industrial batteries tend to be much larger, multi-cell modules [2].

The manufacture of batteries is a growing industry. The reasons for this are quite clear. There is a huge increase in the sales of portable electronic devices (mobile telephones, laptop and notebook computers, camcorders, etc.) that require battery power, and also mains-connected devices that use batteries for memory backup. Industry and commerce are facing a strong growth in the demand for stationary batteries to provide instantaneous power in the event of mains failure [3].

In the transport sector, electric traction is proving more popular in environmentally sensitive areas and major automobile manufacturers are working towards battery electric and hybrid electric vehicles [4]. And finally, the urgent need to harness renewable energy sources (solar, wind, etc.), as part of an overall strategy to ensure global energy sustainability, will require many more batteries to store the generated electricity and to smooth out fluctuations in power supply and demand [5].

In a battery, the processes taking place in the so-called "active materials" of the electrodes are quite complex, although usually they can be represented, to a first approximation, by simple electrochemical equations. During discharge, the equations define a reduction process with uptake of electrons at the positive electrode, and an oxidation process with release of electrons at the negative electrode. The electrons pass from the negative electrode to the positive electrode via the external circuit. Recharging a secondary battery is simply a reversal of the processes that occur during discharge [6].

Rechargeable batteries come in many different sizes - from the small consumer cells used in toys and hand tools, to the huge banks of large cells or modules employed in some standby-power applications (e.g. telephone exchanges) and in submarine propulsion. The batteries are also based on different chemistries, some of which are classical and well established while others are of more recent origin and employ novel electrode materials and/or electrolytes. For all types, however, there are on-going development programmes to improve performance and quality, as well as to reduce the cost of manufacture. For example, the classical lead-acid battery, as used in almost all internal-combustion-engined vehicles, is now improved in performance, is lighter in weight, lasts longer, and (in relative terms) is cheaper than it was some 50 years ago [7].

The minimum cycle-life required from a secondary battery depends on the application, but is often many hundreds of cycles. For instance, a traction battery for an electric vehicle should have a life of at least 1000 cycles, whereas a battery in a low-earth orbit satellite, recharged by solar electricity, is expected to last for more than 20,000 cycles. In chemical terms, this translates into electrode reactions that are fully reversible throughout cycling. Even a 1% irreversibility per cycle (e.g. due to a side-reaction) soon compounds into a significant loss of capacity. Restricting irreversibility to a very low level can be difficult, particularly when the electrode reactions involve solid-phase transformations and there is the possibility of other chemical or physical processes that could lead to battery deterioration and failure. For the different battery chemistries, these processes variously include:

- densification of the active materials with loss of porosity and, hence, reduced availability for electrochemical reaction;
- expansion and shedding of active material from the electrode plates;
- progressive formation of inactive phases, which electrically isolate regions of the active material;
- growth of metallic needles at the negative electrode, which give rise to internal short-circuits;
- gassing of electrode plates on overcharge, which can cause disruptive effects;
- corrosion of current-collectors, which results in increased internal resistance;
- separator dry-out through overheating.

Such degradation processes may result in precipitous battery failure, e.g. through an internal short-circuit, or in progressive loss of capacity and performance. Generally, the degenerative stages are interactive and accumulative so that when the performance starts to decline, it soon accelerates and the battery becomes unusable. Despite this catalogue of problems, some remarkable successes have been achieved in designing batteries of several different chemistries to have long cycle-life (> 1,000 cycles) [8-12].

Cycle-life is not, however, the only important criterion when selecting a battery for a particular application. Other generally desirable features are:

- a stable voltage plateau over a good depth-of-discharge (DoD);

- high specific energy (Wh kg^{-1}) and high energy density (Wh dm^{-3});
- high peak-power output per unit mass (W kg^{-1}) and volume (W dm^{-3});
- high energy efficiency (Wh output:Wh input);
- a wide operating temperature range;
- good charge retention on open-circuit stand;
- ability to accept fast recharge;
- ability to withstand overcharge and overdischarge;
- reliable in operation;
- maintenance-free;
- rugged and resistant to abuse;
- safe both in use and under accident conditions;
- made of readily available an inexpensive materials that are environmentally benign;
- efficient recovery of materials at end of service life.

Overall, this is a formidable set of specifications, even before going into technical detail, and explains why the development of new rechargeable batteries has proved to be so difficult. The relative importance of the different criteria will depend upon the intended application. For instance, energy efficiency is especially important for solar photo-voltaic applications, whereas the ability to accept fast recharge is not a prime consideration. For use in hybrid electric vehicles, fast recharge is a factor even more important than energy efficiency. One of the complications is that a battery is a multi-variant system with many complex interactions between the variables. Thus, the energy recovered from a battery varies with the discharge rate employed and the ambient temperature; the peak-power output depends on the state-of-charge (SoC) of the battery; and the life is a function of the DoD to which the battery is subjected in each cycle. Batteries with different chemistries vary widely in their performance parameters, but so also do different designs of battery with the same chemistry. Accordingly, it is difficult to make precise comparisons between the various types of batteries. Moreover, the problem is compounded by the fact that the numerical values also depend on the conditions under which the battery is operated. Thus, although comparisons between batteries have often been made, it should be recognised that, at best, they are only semi-quantitative.

With these general remarks in mind, this paper focuses on lead-acid batteries that hold most promise for the storage of energy [13].
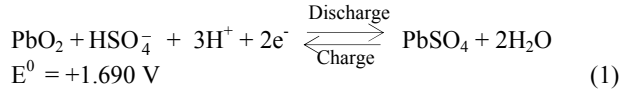
2. CHARACTERISTICS OF LEAD-ACID BATTERIES

By far, the most common type of storage battery is the ubiquitous lead-acid battery, which was invented by Planté in 1859 and greatly improved by Faure in 1881. Over 90% of the world market for medium-to-large rechargeable batteries is still met by lead-acid; most of the rest is satisfied by nickel-cadmium. For small-sized batteries, traditional nickel-cadmium cells are being rapidly replaced by nickel-metal-hydride and lithium-ion cells on account of their superior performance.
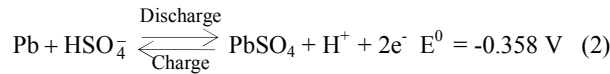
Since its invention, the lead-acid battery has undergone many developments, most of which have involved

modifications to the materials or design, rather than to the underlying chemistry. The electrode reactions of the cell are unusual in that the electrolyte (sulfuric acid) is also one of the reactants, as seen in the following equations for discharge and charge.
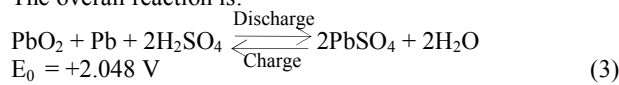
At the positive electrode:

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4 + 2H_2O$$
$$E^0 = +1.690 \text{ V} \tag{1}$$

At the negative electrode:

$$Pb + HSO_4^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4 + H^+ + 2e^- \quad E^0 = -0.358 \text{ V} \tag{2}$$

where E^0 is the standard electrode potential for each electrode reaction, i.e. the electrode is in a standard state.

The overall reaction is:

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} 2PbSO_4 + 2H_2O$$
$$E_0 = +2.048 \text{ V} \tag{3}$$

where E_0 is the standard cell voltage. On discharge, sulfuric acid is consumed and water is formed, with the converse on charging. The SoC of the battery can, therefore, be determined by measuring the relative density of the electrolyte, which is typically 1.27 - 1.30 for a fully charged cell. The lead-acid battery is unique in this regard.

The capacity (Ah) exhibited by a lead-acid battery when discharged at a constant rate depends on a number of factors, among which are the design and construction of the cell, the cycling regime (history) to which it has been subjected, its age and maintenance, and the prevailing temperature. Typical discharge curves for lead-acid batteries at varying rates are shown in Figure 1. It is immediately apparent how the realisable capacity is strongly dependent on the rate of discharge, e.g. the capacity obtained from a 30-min discharge is only a fraction of that from a 10-h discharge. Moreover, the cell voltage is much reduced and thereby results in an even greater reduction in available energy (Wh).
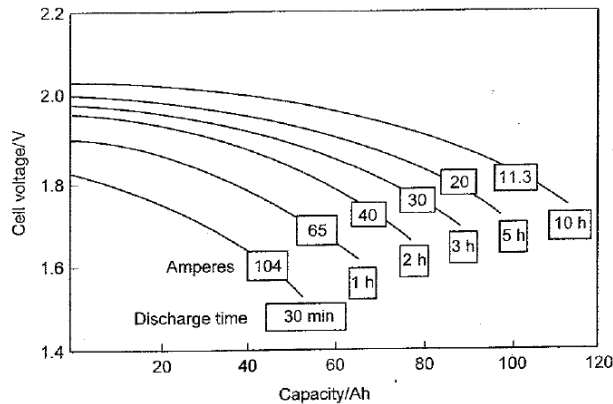

Fig. 1. Typical discharge curves for lead-acid traction batteries.

The life of a battery is generally defined as the number of charge-discharge cycles that will sustain before the capacity fails to 80% of its initial value or, alternatively, before the power output at 80% DoD falls below a specified value. For lead-acid batteries, the life is very temperature-dependent. These batteries operate best from 10 to 25ºC - premature failure can occur on continuous operation above 25ºC, while output falls off sharply at temperatures below 0ºC.

Battery life is also dependent on the DoD that is employed; this factor is much more critical for some types of lead-acid battery than for others. Kinetics, mass transfer effects, current production, current distribution, and other characteristics exhibited by operational lead-acid battery systems have been considered in previous papers [14-16]. A perspective on the present stages of several generic types of lead-acid battery is as follows.

3. TYPES OF LEAD-ACID BATTERIES

3.1 Traditional Flat-Plate Batteries

The first lead-acid batteries were of the flooded design, i.e. the sulphuric acid is a free liquid to a level above the top of the plates and above the busbars that connect plates of the same polarity together. Both the positive and negative plates are produced by machine application of a paste of the active materials (lead oxides, additives, sulfuric acid) onto a rectangular, lattice-type grid that is gravity cast from a lead-antimony alloy (see schematic in Figure 2 (a)). (Note: pure lead is sometimes used for negative grids.) Porous separators, typically made of polyethylene, are placed between each adjoining positive and negative pasted plates to provide electrical insulation and, hence, prevent short-circuits. After assembly, the plates are "formed" (charged) to convert the active materials to lead dioxide (PbO_2) and spongy lead (Pb) at the positive and negative electrodes, respectively.

Until about 20 years ago, all automobiles used the above design as it is the cheapest form of lead-acid battery. The duty cycle does not normally involve deep discharge and, for most of the time, the battery is in a charge state. The battery is unsealed and liberates gas on charging (oxygen at the positive plate, hydrogen at the negative), and it is therefore necessary to periodically replenish the water ("topping-up") that has been lost from the battery through this electrolysis. Screw caps are provided at the top of each cell for this purpose. The life of the battery, normally several years, is seriously shortened if it is subjected to deep-discharge cycling. The principal reason for this is the molar volume expansion of the positive active material on discharge. The repeated mechanical stresses imparted on charge-discharge cycling weakens the active material and cause it to "soften" and, eventually, to break away from the grids ("paste shedding"). Other debilitating factors are corrosion and cracking of the grids, electrical isolation of active material from the grids, irreversible sulfation of the plates (which can become especially serious if the battery is allowed to stand for excessive periods in a discharged state), and internal short-circuits [16].

By modifying the design to incorporate glass-fibre mats around the positive plates and by the use of thicker positive grids, it is possible to produce a pasted-plate battery that is suitable for deep-discharge cycling. The glass mat serves to absorb shocks and to prevent shedding of active material from the electrodes. The deep-cycling ability is attained, however, at the expense of increasing considerably the mass and cost of the battery. This design is commonly used for leisure applications (caravans, boats, etc.) and for standby-power duties. Heavy-duty versions are manufactured as traction batteries for off-road electric vehicles, as well as for some industrial applications [17].

3.2 Low-Maintenance Flat-Plate Batteries

In recent years, a new generation of low-maintenance, flooded batteries has been introduced for automotive duties. These lose very little water and require almost no maintenance. The technological advance that made this possible was the replacement of the lead-antimony alloy used for the grids by a lead-calcium or a lead-calcium-tin alloy. These grids are produced either by gravity casting or by slitting and expansion of alloy strip (Figure 2(a)). It is this antimony component of the traditional battery that gives rise to excessive gassing and water loss on charge: antimony dissolves (corrodes) from the positive grid, diffuses through the electrolyte, and deposits on the negative plate where it increases the rate of hydrogen evolution on charging. By eliminating antimony, a great improvement is effected. Nevertheless, the batteries are still vented. Their life on deep-discharge cycling is generally shorter than that of the conventional lead-antimony batteries. Not only does the same shedding of paste occur at the positive plate, but also a highly resistive corrosion layer forms at the interface between the grid and the active material. The addition of tin to the positive-grid alloy moderates the influence of this "barrier" layer. In any event, low-maintenance batteries should not regularly be cycled to greater than 15% DoD, and never beyond 50% [7].
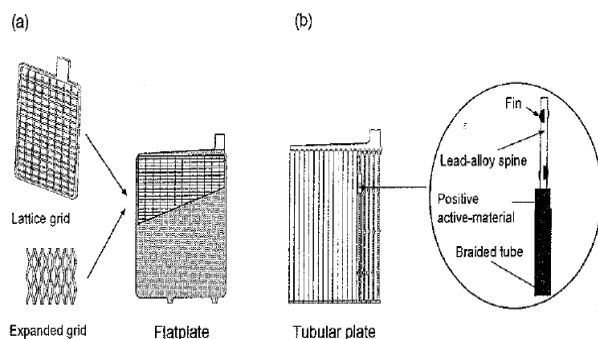
Fig. 2. Lead-acid batteries with (a) flat plates and (b) tubular plates.

3.3 Tubular-Plate Batteries

The tubular battery is a technology of long standing that is designed for deep-discharge cycling. The batteries are used extensively as power sources for many types of low-speed electric vehicles, e.g. forklift trucks, golf carts, milk floats, tractors. A 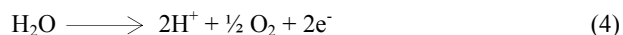lead-antimony alloy casting of parallel rods replaces the positive grid of the automotive battery (Figure 2 (b)). These rods (or "spines") are attached to a common header, rather like a coarse comb with well separated "teeth". Each rod is inserted into a vertical tube made of braided glass-fibre that it surrounded by a sheath of perforated polyvinyl chloride. The active material is then packed into the tubes around the rods, which act as the current-collectors. The flexibility in the glass-fibre tubes allows for expansion and contraction of the active material during cycling.

As the positive active material is constrained by the tubes, the batteries can withstand deep-discharge cycling. They are, however, more expensive than flat-plate batteries and still require regular topping up with water. It is possible to minimise maintenance (water replenishment) by lowering the level of antimony in the positive grid, or by using lead-calcium alloys. The latter option restricts operation to shallow cycling. At least one manufacturer does market such a battery specifically for solar photovoltaic applications. This battery would be suited to remote applications where the cost of servicing a conventional tubular battery would be so high that it is more economical to buy a battery pack several times larger than would be required for deep cycling, and then allow only shallow discharge, e.g. 20% DoD [7,9,16,18]
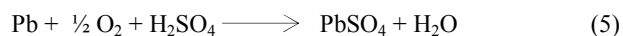
3.4 Valve-Regulated Batteries

For many battery applications, including a high proportion of solar photovoltaic installations, maintenance-free batteries are an essential requirement. In these cells, the problem of water loss through electrolysis during charging has been side-stepped by arranging for the oxygen released at the positive electrode to "recombine" within the cell. This is made possible by using a non-flooded ("electrolyte-starved") design in which the sulfuric acid is held in the interstices of an absorbent, fibre-glass mat that also serves as the separator. Only the minimum quantity of acid required for the electrode reactions is used and there is sufficient void in the glass mat to allow oxygen gas to diffuse through the separator and discharge chemically at the negative electrode. This process is known as the "internal oxygen cycle" and operates as follows.

At the positive electrode:

$$H_2O \longrightarrow 2H^+ + \tfrac{1}{2} O_2 + 2e^- \tag{4}$$

At the negative electrode:

$$Pb + \tfrac{1}{2} O_2 + H_2SO_4 \longrightarrow PbSO_4 + H_2O \tag{5}$$

$$Pb\,SO_4 + 2H^+ + 2e^- \longrightarrow Pb + H_2SO_4 \tag{6}$$

Since the negative electrode is simultaneously on charge, the discharge product is immediately reduced electrochemically to lead, via Equation 6, and the chemical balance of the cell is restored. A corresponding internal cycle for hydrogen is not possible because oxidation of the gas at the positive plate is too slow. This, together with the fact that oxygen recombination is typically 95-99%, requires each cell to be fitted with a one-way valve as a safeguard against excessive

pressure build-up. Accordingly, the technology is known generically as the "valve-regulated lead-acid battery" (VRLA) battery. There are two versions of this battery; in one the sulfuric acid is held in an absorptive glass mat ("AGM" technology), as described above, while in the other the acid is fixed in a silica gel ("gel" VRLA) [19-21].

Because no water maintenance is required, VRLA batteries are particularly suited to remote-area power supply (RAPS) sites where access is difficult. Although essentially maintenance-free, VRLA batteries are not ideally suited to deep discharge, but they may be used for cycles at medium depths-of-discharge. The latter is gaining favour in the RAPS community and is known as "partial-SoC" (PSoC) duty. This controls the battery below a full SoC for extended periods between full recharges (Figure 3 (a)). Such a strategy significantly decreases the overcharge delivered to the battery compared with traditional operating methods, and thus prevents electrolyte dry-out (which increases the internal resistance of the battery), as well as reduces corrosion and other related damage to the positive plate during charging. The gel design of VRLA battery has been found to give particularly good cycle-life under PSoC duty. For example, the lifetime ampere-hour throughput of a gel battery performing PSoC cycles between 40 and 70% SoC has been shown to be three times greater than that obtained under 100% DoD cycling. Given this practical benefit from PSoC operation, the gel battery has become the preferred VRLA technology for many RAPS applications. For example, gel batteries have been chosen for the RAPS facilities that are being installed in the Amazon Region of Peru to provide continuous power to villages. The batteries (Figure 3 (b)) and their dedicated PSoC management system have been designed and produced by Battery Energy Power Solutions Pty Ltd. and CSIRO in Australia.

(b)

Fig. 3. Schematic of PSoC operating procedure (a); and gel VRLA batteries awaiting installation in Peru RAPS sites (b).

The first VRLA cells to become commercially successful were made in 1971 by Gates Energy Products, Inc. in the USA, and were marketed under the Cyclon™ brandname. This is an AGM design in which a single pair of positive and negative plates is separated by a layer of the separator, and then spirally wound (Figure 4 (a)). Busbars are welded to the exposed lugs before the assembly is inserted in the container. The tightly wound plate-group enables the separator to be maintained under high compression and thus helps to retain the positive active material during cycling. In addition, the use of thin electrodes provides an active-mass surface that is significantly larger than in conventional, flat-plate batteries. This reduces the internal electrical resistance and provides exceptionally high power. By virtue of these attributes, interest in spiral geometry has re-awakened. For example, a spiral battery has recently been developed for automotive applications (Figure 4 (b)) [22].
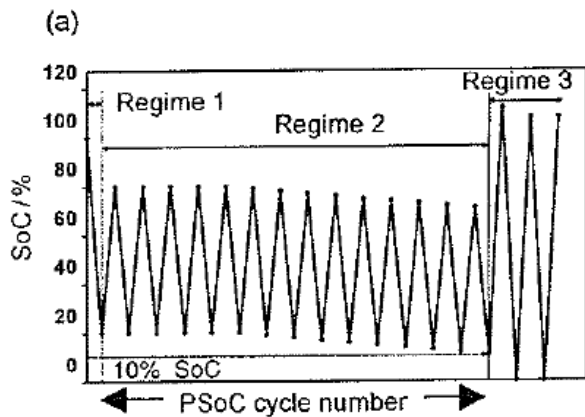
(a)
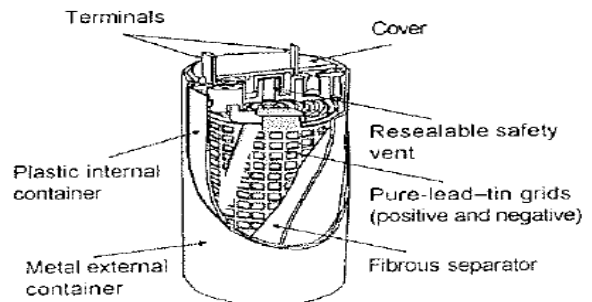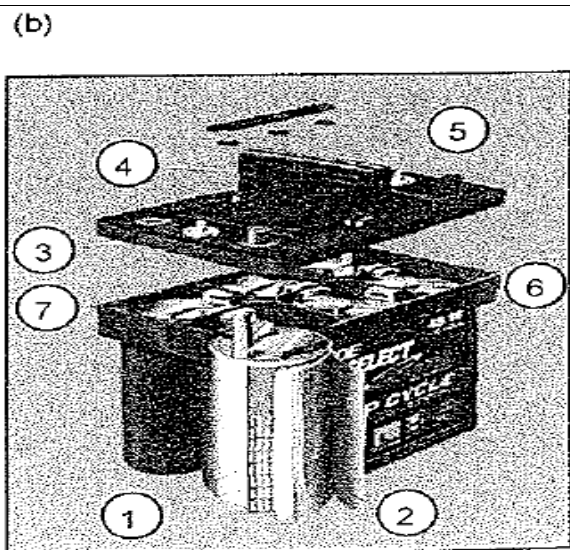
Fig. 4. Cyclon™ cell (a); and spiral-wound battery for automotive applications (b): (1) lead-tin grids, (2) AGM separator, (3) terminals, (4) fold-away handles, (5) pressure-relief valves, (6) through-the-wall cell connection, (7) busbar.

The possibility of employing spiral-wound lead-acid batteries in hybrid electric vehicles as a more affordable alternative to the present use of expensive nickel-metal-hydride batteries is also being explored [23-26]. The extra-ordinary high levels of power demanded by such vehicles are well within the capability of lead-acid, but consideration must be given to optimising the current-collection function of the grid and reducing heat generated in the cell through overpotential and resistive losses. It is well established that the performance of lead-acid batteries can be adversely affected by a non-uniform distribution of current over the plates. This effect becomes more pronounced the higher the rate of charge and discharge and the larger the plate. At the highest rates, the voltage drop down at the grid causes heterogeneous utilisation of the active material (that near the current take-off "tab" is worked harder than that further away) and increases the heat produced. Research conducted by CSIRO in Australia has demonstrated that the addition of a second current take-off tab, symmetrically placed opposite the first, results in more uniform utilisation of the active materials and safeguards against the development of high operating temperatures. These benefits, in turn, translate into improved power capability and longer cycle-life. In more recent developments, CSIRO and Hawker Energy Products, Inc. in the UK have applied the "dual-tab" concept to the spiral-wound Cyclon™ cell (Figure 5 (a,b)). In early 2004, a Honda "Insight" retrofitted with a pack of these batteries and a purpose-built management system (Figure 5 (c)) underwent successful road trials in the RHOLAB project, which was funded jointly by the UK government and the Advanced Lead-Acid Battery Consortium (ALABC). For further details of the Honda "Insight" and other hybrid electric vehicles see [27].

36-V battery modules
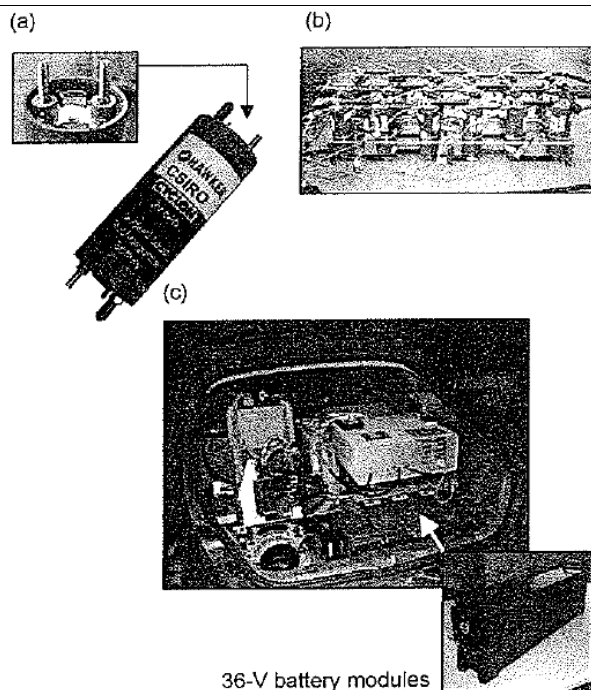
Fig. 5. Spiral-wound cell with dual tabs (a); 36-V battery of dual-tab cells under test (b); and dual-tab battery system installed in Honda "Insight" (c).

4. PROSPECTS FOR LEAD-ACID BATTERIES

The lead-acid battery finds wide use in a variety of applications, ranging from automotive starting/lightning/ ignition (SLI) and industrial batteries for motion power, to large stationary batteries for standby-power, including small sealed cells for portable application. The unique combi-nation of low cost, chemical and physical stability, and rechargeability are unmatched by other rechargeable systems. Its specific energy is 35-50 Wh kg^{-1} and peak power is 150-400 W kg^{-1}.

Although stored energy and peak power per unit mass are the most commonly cited numerical values for advanced batteries, it should be emphasized that these are not necessarily the most important criteria for particular applications. Even more significant considerations may be initial cost, overall electrical efficiency, reliability, freedom from maintenance, performance under fluctuating ambient temperatures and effective lifespan under deep-discharge cycling.

Environmentally, the inevitable drawback of the toxicity risk of lead has been almost overtaken. Today, lead–acid batteries are fully and effectively recycled without economic support and are never dispersed to the environment. Plant emissions are fully controlled and the health of plant workers is protected by precisely defined measures [12].

What are the prospects of further advances in lead-acid battery technology, after nearly 150 years of history? The theoretical limit to the specific energy of a battery is set by the free energy of the electrochemical reaction (which determines the cell voltage), the number of electrons transferred in the reaction, and the mass of the electrodes.

Generally, the theoretical cell energy, calculated in this way, is three to five times that which is practically achievable. The reason for this huge discrepancy is that the practical value has to take account of the mass of all the other cell components (electrolyte separators, container, current-collectors, terminal posts, etc.) as well as the coulombic inefficiencies arising from side-reactions, such as corrosion, self-discharge and voltaic inefficiencies associated with overpotential and resistive loss. Most of these equations that can create economic and commercial feasibility problems have now been overcome. Nevertheless, there is still enormous scope for further improving the lead-acid batteries already in existence by means of advanced and novel materials/cell components and better methods of construction, quality control and cell design.

REFERENCES

[1]   C.A.C Sequeira, P.S.D. Brito, R.P.C. Neto, Y. Chen, N.R. Sousa, P.M.R. Borges and V.M. Magueijo, *Ciencia e Tecnologia dos Materiais* **12** (2000) 66-74.

[2]   C.A.C. Sequeira, *Ingenium* **27** (1998) 95-98.

[3]   D.A.J. Rand, P.T. Moseley and C.D. Parker, eds., Valve-Regulated Lead-Acid Batteries, Elsevier, Amsterdam (2004).

[4]   M.K. Hubert, *Scientific American* **225** (1971) 61-70.

[5]   World Energy Outlook 2000, International Energy Agency, Paris (2000).

[6]   D.P. Dias, I.C. Teixeira, J.P. Teixeira and C.A.C. Sequeira, *Ciência e Tecnologia dos Materiais* **8** (1996) 19-28.

[7]   R.M. Dell and D.A.J. Rand, Understanding Batteries, Royal Society of Chemistry, Cambridge (2001).

[8]   D.R. Battlebury, *J. Power Sources.* **80** (1999) 7-11.

[9]   R.M. Dell, *Solid State Ionics* **134** (2000) 139-158.

[10] P.T. Moseley and D.A.J.Rand, *J. Power Sources,* **133** (2004) 104-109.

[11] R.D. Prengaman, *J. Power Sources,* **78** (1999) 123-129.

[12] E. Razelli, *J. Power Sources,* **116** (2003) 2-3.

[13] K.R. Bullock, *J. Power Sources,* **116** (2003) 8-13.

[14] C.A.S. Faria and C.A.C. Sequeira, *Técnica* **92** (1993) 167-171.

[15] P.S.D. Brito and C.A.C. Sequeira, *Ciência e Tecnologia dos Materiais* **8** (1996) 13-15.

[16] K.V. Kordesch, Batteries, Vol. 2, Lead-Acid Batteries and Electric Vehicles, Marcel Dekker, New York (1977).

[17] A.C. Lyons, A. Hill, K.G. Ellis, T. J. Partington and J.M. Hill, *J. Power Sources* **144** (2005) 329-337.

[18] E. Karden, P. Shinn, P. Bostock, J. Cunningham, E. Schoultz and D. Kok, *J. Power Sources* **144** (2005) 505-512.

[19] M.L. Soria, F. Trinidad, J.M. Lacadena, A. Sanchéz and J. Valenciano, *J. Power Sources* **168** (2007) 12-21.

[20] T. Ohanae, T. Hayashi and N. Inoue, *J. Power Sources* **116** (2003) 105-109.

[21] J.-S. Chen, *J. Power Sources* **85** (2000) 172-177.

[22] J. Wang, H.K. Liu, S.X. Dou, S. Zhong, Y. Zhu and C. Fu, *J. Power Sources* **113** (2003) 241-244.

[23] A. Cooper, *J. Power Sources* **144** (2005) 385-394.

[24] M.L Soria, J. Valenciano, A. Ojeda, G. Raybaut, K. Ihmels, J. Deiters, N. Clement, J. Morales and L. Sanchéz, *J. Power Sources* **116** (2003) 61-72.

[25] Y. Nakayama, E. Hojo and T. Koike, *J. Power Sources* **124** (2003) 551-558.

[26] D. Berndt, *J. Power Sources* **154** (2006) 509-517.

[27] M.A. Weiss, J.B. Heywood, E.M. Drake, A. Schafer and F.F. AuYeung, On the Road in 2020: A Life-Cycle Analysis of New Automobile Technologies, ELR-MIT EL 00-003, Massachusetts Institute of Technology, Cambridge, MA (2000).