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# LEAD-ACID BATTERY EVOLUTION AXIS

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**ABSTRACT:** The recent environmental requirements had compelled the automobile and energy production industries to look for new solutions. The hybrid and electric vehicles and the photovoltaic and wind systems are examples of this research.

Thus, it became necessary to find energy storage systems (ESSs) for these new applications. This study is developed in this direction, taking as starting-point the most common SAE: the lead-acid (LAB). Subsequently, alternatives to LAB were studied. The work focused in two points: electrodes and their components. The solutions implicate the total or partial substitution of the lead electrodes by polymers, ceramic or fiber glass, being almost ready to commercialization bipolar batteries with ceramic base that announce the double of specific energy. These ceramics can also be added to the positive paste. The negative paste has been less investigated than the other.

As alternative, the Li-ion battery is close to reach its development peak and his mineral reserves are an order of magnitude lower than the ones of lead/nickel. The nickel is used in the hybrid vehicles NiMH batteries, also constituted by other elements that limit their production and increase the battery cost. ZEBRA Battery is a valid option, although it requires working with temperatures above 200ºC.

The ultra battery, based in LAB, can be an alternative in a near future, as well as the bipolar ones. The conclusion for storage systems for renewable energy sources is that the LAB will continue to prevail in the next decade.

**Keywords:** lead-acid, lead electrodes, active mass, hybrid vehicle, photovoltaic power system, Li-ion

**RESUMO:** As recentes imposições ambientais obrigaram a indústria automóvel e a de produção de energia a procurar novas soluções. Os veículos híbridos e eléctricos e os sistemas fotovoltaicos e eólicos são casos paradigmáticos dessa pesquisa.

Assim, torna-se necessário encontrar sistemas de armazenamento de energia (SAE) para estas novas aplicações. É neste sentido que este estudo se desenvolve, tomando como ponto de partida o SAE mais difundido: o chumbo ácido (PbA). Foram posteriormente estudadas alternativas ao PbA. Devido à elevada complexidade deste, o trabalho incidiu em dois pontos: os eléctrodos e os seus constituintes. As soluções passam por substituir total ou parcialmente o chumbo dos eléctrodos por polímeros, cerâmicos ou fibra de vidro, estando próximas da comercialização baterias bipolares com base cerâmica que anunciam o dobro da energia específica. Estes cerâmicos podem também ser aditivados à matéria activa positiva. A matéria activa negativa tem sido pouco investigada.

Dentro das alternativas, a bateria de Li-ião está a alcançar o seu limite de desenvolvimento e as reservas minerais estão uma ordem de grandeza abaixo das do chumbo/níquel. O níquel é utilizado nas baterias de NiMH dos veículos híbridos, constituídas também por outros elementos que limitam a sua produção e aumentam o preço da bateria. A bateria ZEBRA é uma opção válida, embora seja necessário trabalhar a temperaturas acima dos 200ºC.

A ultra bateria, baseada no PbA, poderá ser uma alternativa a médio prazo, bem como as bipolares. Nos SAE para fontes de energia renováveis, concluiu-se que nenhum conseguirá substituir o PbA na próxima década.

**Palavras-chave:** chumbo ácido, eléctrodos de chumbo, matérias activas, veículo híbrido, aplicação fotovoltaica, Li-ião
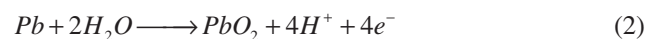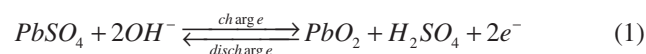
# 1. INTRODUCTION

The energy storage systems (ESS) industry is at this moment in a turnout point of its history. The new demands to the ESSs lead to the creation of new systems which, by consequence, have earned the market of the already established ESSs. The most common of the conventional systems is the lead-acid, which is used, for example, in Starting, Lightning and Ignition (SLI) batteries for Internal Combustion Engine (ICE) vehicles. In this way, it matters how the investigators and the biggest lead-acid batteries makers are dealing with this situation and what they are doing to recover their lost importance in the battery market.

For this purpose were investigated ways for improve the performance of the lead-acid battery (LAB), taking in account two key points: the lead electrodes (or grids) and the active masses. It has already been done a brief introduction to the alternative ESSs, as well as a performance comparative between them and the LAB. In the end the applicability of the LAB to the new applications (hybrid and electric vehicles and renewable power sources) was discussed.

# 2. DEVELOPMENT OF LEAD ACID BATTERY ELECTRODES

It has been a goal for battery engineers and scientists to provide lighter weight and more reliable battery systems, by selecting corrosion resistant materials, active electrochemical couples and combining them in a well engineered system. The goals are often incompatible, as the failure of the materials of construction often frustrate the aims.

Such problems have been evident in the lead-acid battery and have concerned the industry for many years. Corrosion of the lead/lead alloy substrates is the major failure mode in the lead-acid battery, especially in the positive battery plate. The persistent corrosion of the lead/lead alloy grid occurs during the recharge of the system as shown in the following equation (1):

$$PbSO_4 + 2OH^- \underset{disch\,arg\,e}{\overset{ch\,arg\,e}{\rightleftarrows}} PbO_2 + H_2SO_4 + 2e^- \qquad (1)$$

$$Pb + 2H_2O \longrightarrow PbO_2 + 4H^+ + 4e^- \qquad (2)$$

Naturally the exposed lead grid will oxidize to lead dioxide also, see equation (2). As the grid ages it suffers stress corrosion, creep and electrochemical attack. Stress corrosion in particular accelerates the failure of the lead grid, and therefore the grid is made from much thicker cross section than is necessary from electrical conductivity considerations, in order to prevent premature failure [1].

It's not expected that many of the proposed solutions will be a total success. The high oxygen overvoltage necessary to recharge the lead sulfate severely restricts the choices of materials to use in this system – three of the most promising choices studied nowadays are the *Ebonex* substrate battery (commercial trademark of titanium suboxides), the carbon foam battery and the reticulated vitreous carbon substrate

(RVC) battery which, in consequence of their intrinsic properties, allows the construction of bipolar batteries [1]. These solutions are patented and are in an embryonic production state, besides their high production costs due to adopted raw materials.

Therefore, it is also relevant to mention some of the investigated solutions like the polymer-based substrates, which have as premise the considerable reduction of lead amount present in the grid.

## 2.1. Polymer-based electrodes

One of the investigated hypotheses was the substitution of actual lead grids (mechanical support of the active masses and collectors of the current produced during the charge and discharge reactions) by the best-suited material for each function: high strength fiber material for the support of the active mass and copper for the current collector function. The new grid has therefore been developed as a lightweight metalized polymeric network structure (PNS) with a high surface area due to the reduced mesh dimensions in comparison to conventional grids. The network was then coated with conductive materials and corrosion resistant layers to conduct the current flow.

The PNS grids developed in this project can substitute the conventional positive and negative grids, which can also be used in a hybrid configuration (PNS/conventional) according to specified characteristics. The optimized PNS grids developed in the project show lower weight than standard grids (approximately 1/3) with the same conductivity properties, proper weight homogeneity in the same batch and metal distribution on the grid surface, good adhesion of the metallic layers, enough thermal stability under pressure for the application and higher mechanical strength than standard grids.

The biggest difference observed between PNS and conventional grids is attributed to the mesh size, much smaller in first one. The influence of the grid geometry in active mass (AM) utilization follows a well known pattern: smaller the mesh size, bigger the AM utilization. But, by other side, with conventional lead grids, a smaller mesh size involves an important grid weight increase. In the present case, with polymeric electrodes, it's possible to reduce the mesh side while maintaining a low grid weight.

The best ratio 'performance/grid weight' for all the solutions developed during the project was achieved with electrodes, with a 3 mm×3mm mesh, a coknitted copper filament and enhanced copper density in the lug region. The total grid weight was 34g, against 43g of the equivalent conventional grid.

Exploitation of results strongly depends on the final production costs, once achieved a lifetime, quality and reliability levels similar to standard batteries [2].

In a different way, the project now referred describes the polymeric structure – ABS (Acrylonitrile Butadiene Styrene) –, covered with a copper (Cu) conductive layer, which is covered with a lead protective and conductive layer.

To protect the lead from corrosion were experimented two coatings: polyaniline (PANI) and tin dioxide ($SnO_2$). The

ABS was coated with copper by electrolysis and the lead was deposited on copper by electrochemical deposition. A new room-temperature process (RTACRP – Rapid Thermally Activated Chemical Reaction Process) was used to corrosion protect the lightweight lead-acid battery grids coated with a lead metal layer by electrodepositing polyaniline (PANI). To test this solution were build batteries with a ¼ of the conventional battery weight. These batteries are also capable of rapid charge/discharge cycles. Tests were made to determinate the corrosion rate in ABS/Cu/Pb grids with and without PANI and $SnO_2$ layers in a 4,5M (relative density of approximately 1.27) $H_2SO_4$ electrolyte.

The results permitted to verify that PANI and $SnO_2$ coatings allow a considerable reduction of corrosion rate (between 60 and 90%) [3, 4]. The polymer-based grid batteries have an energy density of about 50Wh/kg, even though this value can be increased.

## 2.2. Ceramic-based electrodes

One of the alternative configurations to the typical positive and negative plates battery is the bipolar one. (Fig. 1) A battery with a bipolar configuration is known to be advantageous over the conventional monopolar configuration in terms of power output. In a conventional battery, the current generated by active materials travels to a current collector and through an outer circuit to reach the next cell. In the bipolar configuration, active materials of opposite polarities are placed on the two surfaces of a bipolar substrate. Current can thus flow through the substrate to the next cell. Because of a much shorter electrical path, power loss due to ohmic drop in the circuit is minimized. The volume of the battery is reduced due to elimination of the outer circuit materials such as straps, posts and tabs.
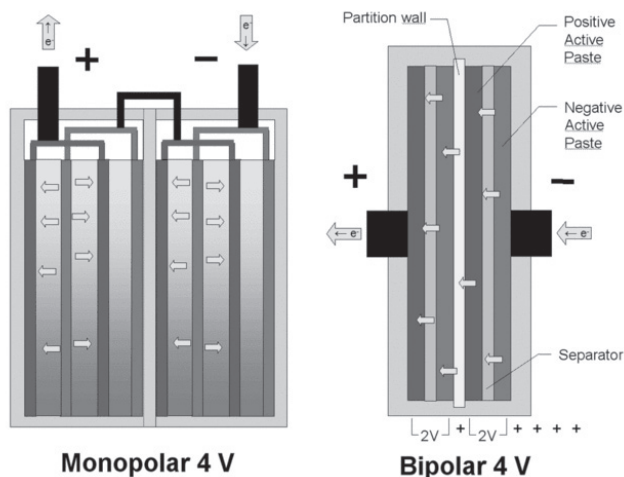


**Fig. 1.** Schematic representation of monopolar and bipolar batteries [5].

The bipolar battery with *Ebonex* substrate will be available on market shortly through a company with the utilization rights of this technology, *Atraverda Limited*. *Ebonex* is a commercial denomination for a substoichiometric titanium dioxide or titanium suboxide ($Ti_nO_{2n-1}$ or TiO abbreviation), with perovskite structure and conductivity equal to carbon, a material used as electrode that will be discussed latter. This material is still very expensive, although it's expected that

when the mass production begins the price starts to fall, like other ESSs.

The ceramic used according to the present invention is extremely resistant to corrosion and attack by hydrogen, both of which could occur during cell reversal, or if the substrate was used as a cathode. In the bipolar case the ceramic is extruded as a star shaped pin that is molded into a plastic wall made of a material such as polypropylene. A battery paste or powder is applied and held in place with a porous fabric separator tube [1]. Fig. 2 shows images of the *Ebonex* substrate before pasted with active masses.
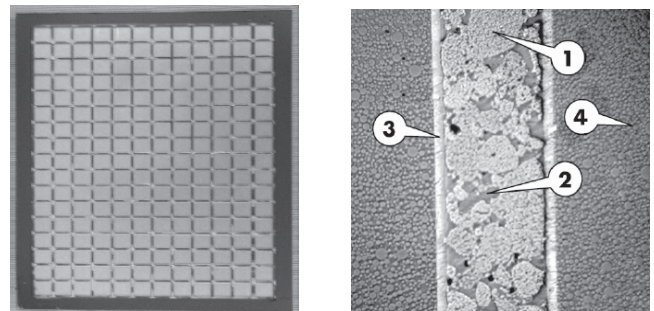


**Fig. 2.** *Ebonex* substrate images before pasting with active masses. At left, plan view of *Ebonex* plate prior to pasting with active materials. At right, cross section of unpasted bipolar plate: 1 – titanium suboxide particles, 2 – polymer binder, 3 – interface lead alloy foil, 4 – potting resin for microscope sample [6]

According to *Atraverda Limited*, a bipolar battery with *Ebonex* substrate have a higher active mass (AM) utilization that the standard, both positive and negative. In first case the utilization increases to the double (from 30% PAM utilization on conventional grids to 60% utilization in *Ebonex* substrate), while NAM utilization increases about 70% (from 30% to 50% utilization).

Regarding to energy and power densities, the announced difference by *Atraverda* turns lead-acid battery (LAB) a new competitor for new applications of energy storage. Although at present the NiMH (about 70 and 85Wh/kg) or Li-ion (about 90 and 150Wh/kg) batteries possess higher energy densities, the bipolar *Ebonex* LAB (about 45 and 60Wh/kg) will have certainly a lower Wh/kg cost than the first two. Thus, it's predictable that the future of LAB passes along bipolar *Ebonex* batteries, but not only. Besides these batteries, another very promising approach uses carbon substrates to substitute a larger part of lead present on grid, announcing higher energy density values.

Nowadays two companies have patented technologies and are starting to license and produce bipolar batteries (although monopolar batteries can also be produced) based in this substrate: *Firefly Energy, Inc*. and *Power Technology, Inc*. (Fig. 3). The principal difference between the two companies adopted grids by is that the *Firefly* grid is lead-free, while the *Power Technology* grid has a Pb-Sn (1% w/w) coat applied by galvanic deposition in a fluoroborate bath. The layer thickness ranges between 200 and 300μm in positive grid and between 80 and 120μm in negative grid.

The carbon foam used to form carbon foam layers of composite material is electrically conductive. In certain forms, the carbon foam may offer sheet resistivity values of less than about $1\Omega/cm$. The electrical conductivity of carbon foam layers allows composite material to be used as current collectors in batteries without the need of lead coatings.
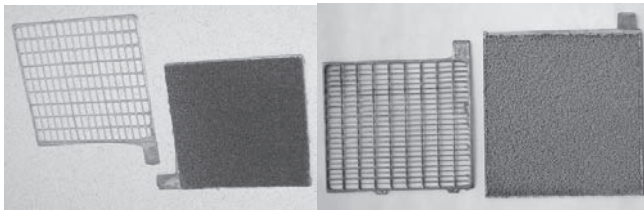


**Fig. 3.** Comparison between conventional lead grid (left of both images) and carbon-based grids. At left, the carbon foam grid used by *Firefly Energy, Inc*.; at right, the RVC grid used by *Power Technology, Inc.* [7, 8].

The carbon foam used to form carbon foam layers of composite material is also resistant to corrosion. In general, carbon oxidizes only at very high temperatures and will resist corrosion even in corrosive environments. The carbon foam used in composite material retains this corrosion resistance, and therefore, composite material may be used, for example, in the corrosive environment of a lead-acid battery [9].

Nevertheless, carbon has overvoltage of 1.46V, too low for the charging process to take place. That is, oxygen is evolved rather than the conversion of lead or lead sulfate to lead dioxide and consequently the electrode does not become charged up efficiently [1]. With the purpose of verify this question, cyclic voltammetry studies of electrodeposited Pb and $PbO_2$ on RVC showed that the carbon substrate had virtually no effect on the apparent electrochemical behavior of either Pb or $PbO_2$. On the other hand, the presence of a Pt layer in between RVC and electrodeposited Pb diminished the peak current density for $PbO_2$ reduction after the first voltammetric sweep.

Therefore, it was concluded that bare RVC could serve as an effective substrate material for lead–acid battery current collectors [10]. Additionally, carbon foam layers are lightweight (calculating the total battery weight was verified that the collectors weight contributed just 2% for the total weight [10]) due to the presence of a network of pores. In a determined embodiment the carbon foam may have an open porosity value of at least about 90%. This open network of pores may result in a density of less than about 0.6 gm/cm$^3$ for each layer of carbon foam [9].

Besides that, these present a rapid recharge capacity and good discharge performance in adverse conditions (high rate/low temperature) [7]. So, the increased specific power values offered by these batteries may also translate into reduced charging times. Therefore, the batteries may be suitable for applications in which charging energy is available for only a limited amount of time. For instance, in vehicles, a great deal of energy is lost during ordinary braking. This braking energy may be recaptured and used to charge a battery of, for example, a hybrid vehicle. The braking energy, however, is available only for a short period of time (i.e., while braking is occurring). In view of their

reduced charging times, these batteries may provide an efficient mean of storing such braking energy. The porous nature of the carbon foam current collectors also creates an improved substrate for retaining the chemically active paste of the energy storage device. By impregnating the paste into pores of the carbon foam current collectors, the paste is less likely to separate from the current collectors. This property is important in vehicle and other applications where vibration is common [9].

In this way, the carbon substrate it's a serious competitor to the titanium suboxides, since the producers that adopted this technology announced energy density values until 100Wh/kg, as well as volume and weight reductions between 40 and 75% when compared with the conventional LAB. The upper value is announced by the new Firefly's battery, with the new "3D$^2$ Technology" (Fig. 4) [7].
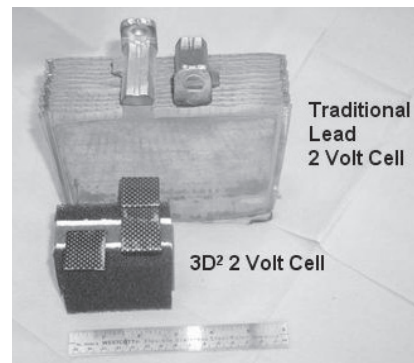


**Fig. 4.** Image that allows comparing the volume difference between the traditional lead 2V cell and the 2V "3D$^2$" cell by *Firefly Energy, Inc.* [7].

## 3. PRESENT STATUS OF THE LEAD ACID BATTERY ACTIVE MASSES

### 3.1. Positive active mass (PAM)

A persistent frustration for developers of the lead-acid battery is that the utilization of active material, particularly in the positive plate, remains very low (typically around 30% at the $C_1$ rate) while strenuous efforts are being made to increase the specific energy of the system. The electric vehicle market in particular would certainly respond positively to the increase in specific energy that would result from raising the active material utilization at the $C_1$ rate to even 60%.

The discharge capacity available from the battery, especially at high rates, is generally limited by the kinetics of supply of reactants in the discharge reaction:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O \qquad (3)$$
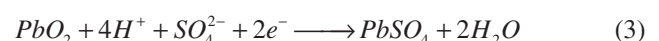
At the site of the reaction – distributed over the surface area of the liquid/solid interface of the porous positive electrode – there must be an adequate supply of acid and of electrons to sustain the reaction at the required discharge rate. Simultaneously, the porous electrode structure must allow the diffusion of the reaction product (water) away from the reaction site and the accommodation of a solid reaction

product ($PbSO_4$) with a greater molar volume than the solid reactant ($PbO_2$).

It may be that at some discharge rates the limiting factor would be electronic conductivity while at other rates the limiting factor would be acid diffusion. Therefore, it is very important to take account of the rate at which the battery will be discharged when seeking improvement by the use of additives to promote the discharge reaction.

In a similar way, the thickness of the active mass between the current collector and the bulk electrolyte also affects the degree of utilization and may dictate whether it is conductivity or diffusion that needs to be supported. The motive behind much of the work on positive plate additives is the promotion of the supply of reactants to the site of the discharge reaction in pursuit of a higher active material utilization. In all instances beneficial effects are sought with a minimum amount of additive since such materials do not themselves contribute to the discharge capacity. The issues that must be taken into consideration in the planned use of solid additives are the enhancement of the acid supply and conductivity and the stability of the additives [11].

The persulfate salts were approached in a project that had as objectives the development of positive plates for lead-acid battery (LAB) with high porosity and specific area, aiming to deliver a very high current density, about 1 A/cm$^2$. The high porosity and specific area were achieved by using a combination of fine particles of lead oxide and/or basic lead sulfates with an adequate amount of persulfate and water. The relationship between the positive paste phase composition and the high rate performance of the plate was also studied.

The highly porous plate is able to deliver a very high current owing to more acid being available in the plate structure. In the low rate applications when acid diffusion from the bulk becomes the limiting factor, the high-performance plate is less advantageous than the conventional starting, lighting, and ignition (SLI) plates. At the end, a comparative performance test with the best masses attained versus conventional, as well as this one with barium metaplumbate addition, one of the best additives to increase conductivity, has been conducted. The results showed that at higher discharge rates the persulfate plates had higher AM utilization. At lower rates there are now substantial differences, with the persulfate mass AM utilization being even lower than the standard with $BaPbO_3$ [12].

The next project referred studied the addition of Dynel fibers coated with tin dioxide to the PAM. A rapid thermally activated chemical reaction process (RTACRP), already referred, has been used to coat tin oxide onto Dynel fibers. Preparing tin oxide by conventional methods requires a calcination process at temperatures ranging between 450 and 600ºC. Hence, coating tin oxide onto low melting substrates, such as Dynel fibers, without affecting their mechanical integrity by RTACRP is the novelty of this study. The process is simple, less time consuming and cost-effective, therefore looking commercially attractive. It has been possible to accelerate the formation process, improve the positive active material utilization at higher discharge rates and enhance the cycle-life of lead–acid cells by the aforesaid process.

The tin oxide coating appears to be porous and non-uniform. The additived cells were found to form within three charge–discharge cycles, while the conventional cells attained their maximum capacity in five charge–discharge cycles. During formation, the cells were charged at $C_{20}$ rate followed by the discharge at $C_5$ rate. It is clear that the faradic efficiency of additived cells is superior to that of the conventional cells, and is found to be about 90%. Moreover, the additived cells deliver higher discharge capacity than do conventional cells. Furthermore, the higher plateau voltage during discharge suggests that the additived plates offer a lower internal resistance and provide a wider effective capacity window. In brief, it has been possible to improve the positive active mass utilization in lead–acid cells by coating Dynel-fiber additive with tin oxide, and particularly so at higher discharge rates [13].

Besides the addition of Dynel fibers, the carbon fibers added to PAM appears to improve capacity ratings of 10–20%, especially at high rate charge/discharges. Moreover, it appears to remain stable in the battery during charge and discharge procedures and significant increases in cycle life were observed on addition of 0.25w/w chopped carbon fibers. The manner in which the carbon fibers contribute to the improvements in performance is not yet clear, although is most likely to be due to the following factors working individually or together [14]:
- Increase in mechanical integrity.
- Increase in porosity leading to greater acid access.
- Increase in active material electrical conductivity.

Besides the utilization as substrates, perovskites can be used as additives to PAM. In this case, the utilization of barium metaplumbate ($BaPbO_3$) it's more common than *Ebonex*, on the contrary of substrates. The bulk electrical conductivity of an *Ebonex* plate was measured using a probe with DC current about $5,0\times10^2$ $\Omega^{-1}.cm^{-1}$, which was lower than that of barium metaplumbate (between $1,2\times10^3$ and $2,0\times10^3$ $\Omega^{-1}.cm^{-1}$). From the cyclic voltammogram, it was believed that *Ebonex* could be oxidized irreversibly at an anodic potential higher than that for decomposition of water and become passivated. The electrode passivated at -1.0 V vs. $Hg/Hg_2SO_4$. The passivation was suspected to be caused by formation of titanium hydride, which is an insulator. Based on these results, *Ebonex* is considered stable in the positive plate of a lead-acid battery but passivation of the additive may occur if the plate is heavily overcharged or reversed.

$BaPbO_3$ has no effect on the plate cycle life if loading is below 1%. At a higher loading level, the plate cycle life is reduced due to decomposition of the additive to form barium sulfate. Unlike $BaPbO_3$, *Ebonex* had no significant impact on the cycle life of a formed positive plate even at 5% loading level. When *Ebonex* decomposes or passivates the surface of the additive turns into less conductive high oxides which are inert to the plate chemistry. Passivated *Ebonex* additive, however, may have a negative effect on the charging efficiency of a positive plate, because the overall conductivity of the plate would be reduced. Formation enhancement by additives appears to be more significant in the early stage of formation when the overall plate conductivity is low. Beyond 80% of theoretical input capacity, the impact of conductive additives diminishes [15].

## 3.2. Negative active mass (NAM)

Although the negative electrode system is simpler than that of the positive electrode system and many papers concerning the negative electrode have been published recently, its kinetics and mechanism are not yet well understood. The passivation of the negative plate is still one of the main reasons for the shortening of the battery life. Therefore, it is very important to study the structure and the passivation mechanism of the active mass on the negative plate (NAM). It was found that in the recrystallization and self-discharge, many big $PbSO_4$ crystals are formed on a seriously passivated negative plate (Fig. 5). The micropores in the active mass become very narrow and long and even their passageways are greatly blocked. The porosity in the active mass decreases obviously. The mass transfer of ions in it becomes very difficult. In charge/discharge cycles, many small $PbSO_4$ crystals are formed over the big crystals which are very difficult to be reduced [16].
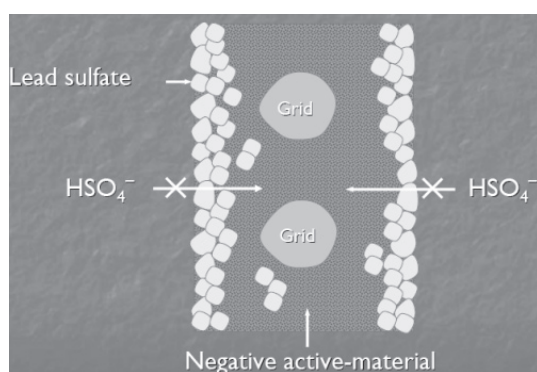


**Fig. 5.** The acid diffusion for inside and outside the plate is blocked by $PbSO_4$ [17].

The batteries used in hybrid vehicles are exposed to very different duty cycles than any other lead-acid battery (LAB) actual duties. These operate in a high rate partial state of charge (HRPSoC) instead of a full charge state, besides the charges and discharges tend to be of short duration but high rated. In these conditions, the conventional duties designed LAB (for example, SLI or deep cycle) rapidly fails due to negative plates sulfatation. During HRPSoC operation, the high rate discharge it's the responsible key factor for the growing of a compact lead sulfate layer on the negative plate surface and the subsequent charges increase the premature hydrogen evolution. The hydrogen evolution is yet aggravated when a high charge current is used [18].

Expanders are used in every lead-acid battery produced in the world. The most common expanders are lignosulfonates, which exert physical, chemical and electrochemical effects on negative pastes and active materials. Vanisperse-A, an organic additive, it's the most common lignosulfonate used in LAB industry. It seems that cycle life is limited by two phenomena: the additive progressive deactivation by a so far unknown mechanism and an insufficient NAM polarization at high oxygen recombination efficiencies, allowing that selfdischarge occurs [19].

A more recent a study [20] concluded that those synthetic lignins are more efficient than natural ones in HRPSoC, the operation mode of hybrid and electric vehicles. Barium sulfate ($BaSO_4$) particles in various sizes and synthetic

lignin were added to the negative active-material to control $PbSO_4$ particle size during HRPSoC cycle-life. The efficacy of this synthetic lignin has been evaluated under an EV schedule (with deep discharge and full recharge). The results for batteries show that the cycle-life performance of the battery with synthetic lignin is superior to that with natural lignin, whereas the other factors such as $BaSO_4$ size or carbon fiber extended less influence [20].

Besides the barium sulfate and synthetic lignin additions, has been attained in another study [18] an increase in hybrid vehicles LAB cycle life adjusting the carbon materials types and quantities. It appears that carbon materials used in negative plates designed for HRPSoC exert a beneficial effect by maintaining a conductive network through the negative plate material, especially at low states-of-charge. Additionally to carbon materials, it was also tested a new glass microfiber to increase the effective electrode surface area of the plate, together with low specific area graphite. In the end, the best cycle life performance in HRPSoC has been attained with expanded graphite addition to NAM that increases the conductivity of active mass through life cycle. However, the use of graphite has been detrimental for cycle life due to its lower surface area. On the other hand, the use of micro-fiberglass in NAM increases the NAM surface area, although the effect on cycle life is still unclear [18]

Another recent study [21] contradicts the affirmation that the graphite addition increases NAM conductivity. This has been verified after an extensive investigation of the resistance of the negative electrode active mass both in the charged and discharged states at various mechanical pressures and at increasing numbers of charge–discharge cycles. The resistance of the active mass between two neighboring ribs ranged from 0.2 e 0.5 m$\Omega$, the differences between the values in the charged and discharged states being within experimental errors. (For comparison, the values for the positive electrodes were 7-8 m$\Omega$ in the charged state and 20-50 m$\Omega$ in the discharged state). In view of these facts, any attempts to improve the conductivity of the negative active mass by the addition of graphite (a far less conductor than lead) would obviously have no sense.

Two sorts of additives were used in the negative active mass: either powdered graphite of about 4$\mu$m nominal particle size and 13m$^2$/g specific surface area, or pure titanium dioxide ($TiO_2$) of particle size 1-3$\mu$m according to SEM microphotograph. The highest cycle life was attained by the cell with negative electrode containing 2.5% $TiO_2$, namely 205,000 cycles, and by that with 2.5% graphite, namely 197,000 cycles. At this stage, it seems that the graphite additive can be replaced by titanium dioxide with equally good results, hence that the effect of graphite is not due to electric conductivity according to the idea outlined at the beginning [21].

It will now be explored the strategy to suppress the accumulation of lead sulfate on the negative plates under PSoC duty. Sodium salt of polyaspartic acid (PASP) has been selected from the commercially available functional polymers acting as crystal modifiers. Polyaspartates are water soluble dispersants having effect on the crystal morphology. They are known to inhibit the precipitation of calcium carbonate, calcium sulfate and barium sulfate and

find an application as scale inhibitors and complexing agent for heavy metals.
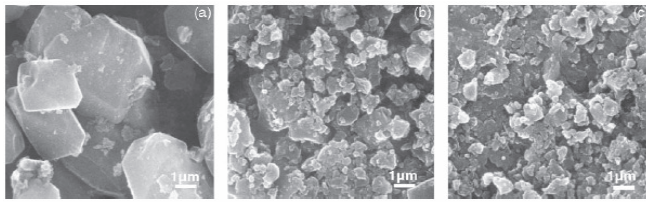


**Fig. 6.** Negative plate surface SEM micrograph at the end of tests in HRPSoC regime: (a) conventional cell; (b) cell with 0.2% w/w of PASP in electrolyte; (c) cell with 0.1% w/w of PASP in negative mass [22].

The results of this investigation indicate that the use of polyaspartate as additive to the paste and to the electrolyte has a beneficial effect on the performance of the negative plate under HRPSoC operation. The additive controls the crystallization of $PbSO_4$ and modifies the shape and size of the crystals (Fig. 6). The addition of PASP to the paste and to the electrolyte improves the utilization of the negative active material and reduces the internal resistance of the negative plate. The results obtained during cycling of lead-acid cells under simulated HRPSoC duty show that addition of PASP increases the cycling ability of the negative plates and thus decreases the frequency of equalization charging during operation [22].

## 4. ALTERNATIVES TO LEAD ACID BATTERIES

Nowadays two applications put challenges to Electric Storage Systems (ESSs): the hybrid (HEV) and electric (EV) vehicles and the renewable power sources. It's predictable that these applications would have a preponderant role in our society, so LAB performance will be compared with the alternative ESSs in these domains. The alternative technologies to compare will depend on the designed application, so for better perception of their characteristics differences, has been decided to introduce various technologies in the next paragraphs.

### 4.1. Lithium-based batteries

Lithium batteries can be classified into four principal types according to the electrodes and electrolyte materials: lithium metal, lithium metal polymer, lithium ion and lithium ion polymer.
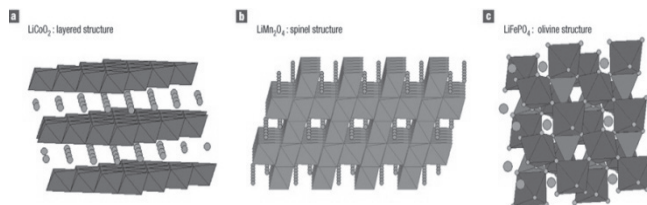


**Fig. 7.** Front left to right: layered structure (a), spinel structure (b) and olivine structure (c) of the lithium battery positive electrode [23].

Inside the different categories, those that nowadays are more interesting are lithium ion (namely those with $LiCoO_2$, $LiMn_2O_4$ and more recently $LiFePO_4$ cathodes, represented

in Fig. 7) and lithium ion polymer. Today the main field of application is the consumer market with portable products, like cellular phones or computers. With major programs in both high capacity and high power Li-ion technology, battery makers have developed a family of products which can address the power and energy storage needs for vehicles, utilities, aviation, satellites, and other applications where light weight, long life, and excellent energy or power storage capabilities are needed [24]. However, the recently occurred safety problems reduced somehow the enthusiasm around the application of this technology to HEVs and EVs. A few months ago, Wall Street Journal noticed that *Toyota Motor Corp.* decided to delay the introduction of Li-ion batteries in the next generation of the best-seller Prius HEV due to concerns about this technology safety [25].

### 4.2. Nickel-based batteries

The nickel-based battery technology it's almost as old as lead-acid battery (LAB) technology, since NiCd batteries are used since the end of XIX century. The principal advantages of nickel-based batteries are long cycle life in certain conditions with a suitable management, a good liability and an excellent performance when long term storaged.

These batteries may be classified according to the type of the active material used in the electrodes: nickel-cadmium (NiCd) batteries, nickel-zinc (NiZn) batteries and nickel-metal hydride (NiMH) batteries. The NiMH market drop between the end of 2001 and the beginning of 2002 was due to the slope of lithium price, becoming competitive with NiMH. The NiCd batteries for industrial applications are today a niche product in a marked dominated by LAB. The NiCd have a significant share in portable batteries, but are nowadays challenged by NiMH and Li-ion batteries. Only one type of NiZn battery is available on the market for scooters, electrical bicycles and similar applications. The NiMH batteries dominate the HEV market. The principal limitations of NiCd are the high cost per Wh and the cadmium content; in the NiMH case, its great limitation is the high selfdischarge [24].

### 4.3. Redox flow batteries

The Redox Battery is an electrochemical energy storage device. It stores or releases electrical energy by means of a reversible electrochemical reaction between two salt solutions (the electrolytes) coming from outside containers. The reaction (reduction/oxidation) occurs within an electrochemical cell, which has two compartments, one for each electrolyte, physically separated by an ion-exchange membrane (no mixing of electrolytes). The first researches concerning Redox flow battery were made on the basis of the iron-titanium (Fe-Ti) couple and then iron-chromium (Fe-Cr) to get better performance. The main problem encountered was the use of an expensive ion selective membrane needing high maintenance. Today new couples are investigated (some batteries are already operating in the field) such as vanadium-vanadium couple (all-vanadium system), zinc-bromine couple and bromine-sulfur couple.

The battery is composed by the following main components as it can be seen in Fig. 8: a negative electrolyte tank with a pump, a positive electrolyte tank with a pump and a series of membranes or electrochemical cells ("the cell stack") through which the electrolyte flows (or is pumped).
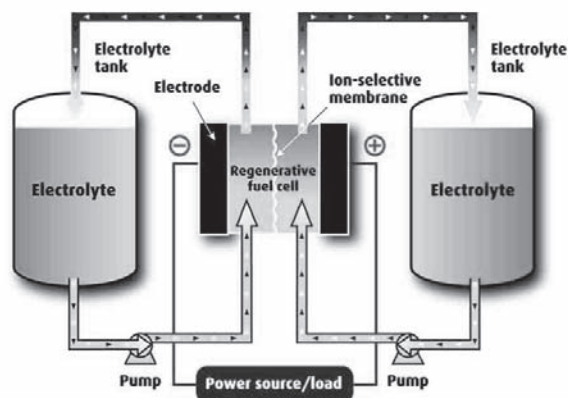
**Fig. 8.** Schematics of a Redox flow battery [24].

The vanadium redox battery VRB has been referred to as "The Green Battery" due to the materials used in its construction (vanadium, carbon, plastic, copper and iron) and for its ability to integrate with natural power sources such as wind and solar. The electrolytes used in VRB have an indefinite life, so there are no disposal issues as the electrolytes are completely reusable. However, vanadium compounds are considered to have variable toxicity (decreasing with oxidation state and solubility) and toxic effects are acute but seldom chronic. For bromine/sulfur and zinc/bromine batteries, there are potential environmental impacts during production, use and disposal due to the presence of bromine and zinc [24].

### 4.4. Sodium-based batteries

Sodium is most attractive as a negative electrode reactant on account of its high electrochemical reduction potential of -2.71V (cf. Zn -0.76V). When coupled with an appropriate electropositive material, it is capable of giving a cell of voltage superior to 2V. Moreover, sodium is abundant in nature, cheap and non-toxic. It is also of low atomic mass (23.0) and the combination of high voltage and low mass leads to the possibility of a battery of high specific energy. The disadvantages of sodium metal as a negative reactant are that an aqueous electrolyte cannot be employed and it is a potential fire hazard.

Although these problems have been addressed in detail in sodium sulfur (NaS) battery, with some measure of success, most of the industrial development programs have now been terminated (with the notable exception of that in Japan) for a mixture of technical and commercial reasons [26].

In parallel with the NaS program, there has been a development program on a related battery system, the sodium nickel chloride battery ($NaNiCl_2$). This maintains many features of the NaS battery (the beta alumina electrolyte, the sodium electrode, hot operation etc.) but replaces the liquid sulfur electrode by a solid nickel chloride electrode ($NiCl_2$). A second (liquid) electrolyte, sodium chloraluminate $NaAlCl_4$, is added to the positive electrode compartment so as to make good ionic contact between the solid $NiCl_2$ and the solid electrolyte. In contrast to NaS, there are almost no safety problems with the $NaNiCl_2$ battery [26].

This type of battery is being developed primarily for electric utility power quality and load leveling applications and for electric vehicles due to its potential performance (in particular, its energy density) and the use of common materials [24]. Also in contrast to the sodium sulfur technology, the development of the sodium metal chloride system has been pursued by a successive progression of single, integrated organizations for one primary application – electric vehicles. To date, development has focused almost exclusively on the higher voltage nickel variant but using iron as a doping addition to the positive electrode [27].

### 4.5. The supercapacitor

The supercapacitor resembles a regular capacitor with the exception that it offers very high capacitance in a small package. Energy storage is by means of static charge rather than of an electrochemical process that is inherent to the battery. Applying a voltage differential on the positive and negative plates, the supercapacitor is charged.

Whereas a regular capacitor consists of conductive foils and a dry separator, the supercapacitor crosses into battery technology by using special electrodes and some electrolyte. There are three types of electrode materials suitable for the supercapacitor. They are: high surface area activated carbons, metal oxide and conducting polymers. The high surface electrode material, also called Double Layer Capacitor (DLC), is least costly to manufacture and is the most common. It stores the energy in the double layer formed near the carbon electrode surface. The electrolyte may be aqueous or organic [28].

Supercapacitors were initially used by the US army to start the engines of tanks and submarines. Most applications nowadays are in the field of electric vehicles (regenerative braking) and power quality devices (UPS) for large supercapacitors and portable electronic devices (computer memory, video camera, TV set) for small supercapacitors.

### 4.6. The ultra battery

The ultra battery is a hybrid energy-storage device, which combines an asymmetric supercapacitor and a lead-acid battery in one unit cell, without extra electronic control, answering to the HRPSoC solicitations, one of the VRLA battery limitations. The schematic structure of the ultra-battery is shown in Fig. 9.
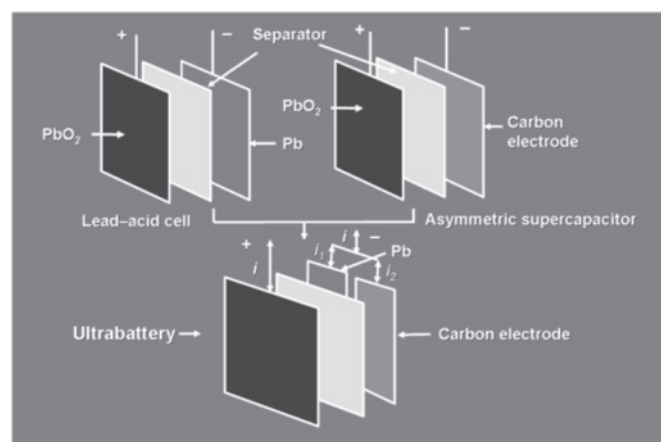


**Fig. 9.** Ultra battery schematic configuration [29].

A lead-acid cell comprises one lead-dioxide positive plate and one sponge lead negative plate. On the other hand, an asymmetric supercapacitor composed by one lead-dioxide positive plate and one carbon-based negative plate (i.e., capacitor electrode). Since the positive plates in the lead-acid cell and the asymmetric supercapacitor have the common composition, these two devices can be integrated into one unit cell by connecting internally the capacitor electrode and the lead-acid negative plate in parallel. Both electrodes now share the same lead-acid positive plate. With this design, the total discharge or charge current of the combined negative plate is composed of two components: one is the capacitor current and the other is the lead-acid negative plate current. Accordingly, the capacitor electrode can now act as a buffer to share the discharge and charge currents with the lead-acid negative plate and thus prevents it being discharged and charged at the high rates.

However, it does not mean that the ultra-battery can be easily achieved by just inserting any capacitor electrodes into a lead-acid battery. This is because there is a difference in the operational potential range between the capacitor electrode and the lead-acid negative plate [29]. This difference has been solved with proper supercapacitors and VRLA batteries, which are still being tuned and tested.

## 5. APPLICABILITY STUDIES

Energy storage systems (ESSs) have the potential to play a key role. Although they have been little studied for this application in Europe, ESSs appear to be complementary to ICT and power-electronic based solutions, since they can provide large capacity with a short response time and provide ancillary services such as uninterruptible power supply (UPS).

It is therefore pertinent to consider more precisely the role of energy storage systems and evaluate their market potential. Since many different storage technologies are claimed to fulfill the technical requirements of the above applications, it is necessary to compare their performances and costs so as to identify the best candidates. The results presented in Fig. 10 are taken from work conducted by the INVESTIRE Thematic Network [24].
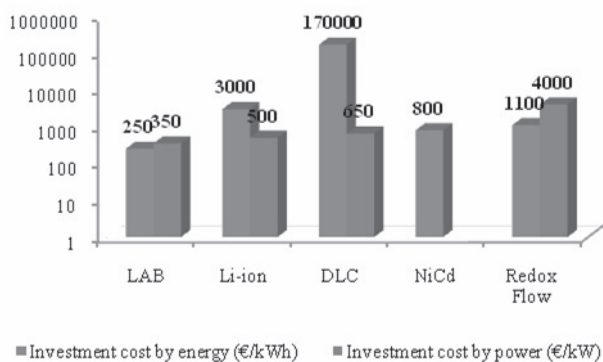


**Fig. 10.** Investment cost by power or energy for the different technologies considered [24].

It is clear that lead-acid batteries are the cheapest option for both power and energy. Rather than the investment cost, the cost of ownership is the determining criterion for the selection of one or another technology. The cost of ownership of a storage system (i.e., cost of 1 kWh transited through the system without taking into account the price of the input electricity) includes the costs of maintenance and replacement over system life. For this purpose, the losses associated with each storage technology are also included [30].

The main conclusion is that, at present and for the near future, no energy storage technology is able to replace lead-acid batteries in this category of stationary applications due to economic and/or technical limitations. However lead-acid batteries still require performance improvements especially in terms of cycle life time. If these improvements are implemented, lead-acid batteries are unlikely to be supplanted in the next 10 years [24].

Lithium, besides being abundant as element, has raised many doubts to the analysts about the actual lithium reserves and the necessary quantities to be used in lithium-based batteries for electric vehicles. As it can be seen in Table 1, the *United States Geological Survey* calculated reserves shows that the available lithium, both reserve, reserve base or world resources is always at least one order of magnitude below lead or nickel.

**Table 1.** 2007 values of the main metals adopted in batteries (in European Million Tons) [31]

|          | Reserves | Reserve base | World Resources |
|----------|----------|--------------|-----------------|
| Lead     | 67       | 140          | 1500            |
| Lithium  | 4.1      | 11           | 13.8            |
| Nickel   | 64       | 140          | 130             |

Regarding nickel, the NiMH battery is rugged, proven, has high cycle life and has many years development behind it. However, it is also heavier than Li-ion and very Nickel intensive: between 3 and 6 kg of Nickel metal are required per kWh of capacity depending on the cathode type. It also requires Cobalt. Cobalt is an extremely expensive strategic metal and production is limited. Total global production of Cobalt in 2005 was about 50,000 tones. There is certainly insufficient Cobalt to mass produce large NiMH batteries for a global sized fleet of HEVs, PHEVs or EVs. The lack of Cobalt as well as its high price is another reason Li-ion battery manufacturers will not use the $LiCoO_x$ cathode type in EV batteries, as used in consumer Li-ion batteries, apart from the unacceptable safety of a Cobalt containing Li-ion cathode for an EV battery [32].

Regarding lead-acid, the use of lead–acid batteries is seen as a relatively safe way to use a toxic metal, given the ease of managing and recovering spent batteries. Environmental releases associated with lead–acid battery use are confined to a limited area and are not subject to widespread dispersion of the metal as is lead in gasoline. The continued use and recycling of lead–acid batteries promises an efficient and environmentally benign means of using a toxic substance. However, as our results show, recycling cannot meet the entire demand for lead in the US as the light duty vehicle fleet continues to grow, and especially if micro-

hybrid vehicles using lead–acid battery packs reach even modest infiltration (10%).

Even if alternative technology systems are introduced, depending on the battery requirements, there will continue to be a need for importation and production of lead. Micro-hybrid vehicles that use lead–acid batteries (with a factor of four increase in the amount of lead per vehicle), even at a mild introduction rate, are predicted to increase the lead releases to air and land by 26 tons in 2015. This is an increase of 6% increase over 2004 TRI lead releases and is 1.4 times greater than the current total lead emissions from the fuel combustion of all transportation. The results of all three cases show the need for continued mining and processing of lead ore, even in the presence of a highly reliable recycling system [33].

## 6. CONCLUSIONS

It has been verified that the main direction of development of lead-acid batteries, with reference to substrate, is the production of bipolar substrates. These would allow the attainment of energy densities double of the current ones, with lower volume and the well-known reliability of this system. However, the final prices remain unknown.

In other way, it's necessary to improve the active masses utilization, although in this case the choice of a direction is not so clear. Therefore, it's pertinent to study the various additives suggested in the desired operation conditions, in order to determinate the cost/benefit relationship of each additive.

Concerning to the utilization of the different technologies in HEV and EV, it can be observed that the NiMH usage in medium and total hybrids is an intermediate solution, since it's applied not by its qualities, but by the lack of stability and safety of lithium batteries and low energy density of lead-acid batteries.

VRLA batteries are nowadays used in the modest hybrid types, like micro and mild. However, the beginning of commercialization of bipolar batteries will certain replace the first ones in a medium time as it has already been referred. At a long term it's possible that ultra battery will complement the offer of lead-acid batteries (besides this is a hybrid-LAB).

If the long term sustainability problems of nickel and lithium technologies will be confirmed, bipolar batteries could be developed in a way that satisfy the necessary requests for application in total HEVs or even EVs.

Finally, nowadays the renewable power sources use LAB as one way to store produced energy, a scenario that, if the predictable developments will be accomplished, will remain inalterable in the next decade.

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