

Aging mechanisms and service life of lead–acid batteries

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Abstract

In lead–acid batteries, major aging processes, leading to gradual loss of performance, and eventually to the end of service life, are:

- Anodic corrosion (of grids, plate-lugs, straps or posts).
- Positive active mass degradation and loss of adherence to the grid (shedding, sludging).
- Irreversible formation of lead sulfate in the active mass (crystallization, sulfation).
- Short-circuits.
- Loss of water.

Aging mechanisms are often inter-dependent. For example, corrosion of the grids will lead to increased resistance to current flow, which will in turn impede proper charge of certain parts of the active mass, resulting in sulfation. Active mass degradation may lead to short-circuits. Sulfation may be the result of a loss of water, and so forth.

The rates of the different aging processes strongly depend on the type of use (or misuse) of the battery. Over-charge will lead to accelerated corrosion and also to accelerated loss of water. With increasing depth-of-discharge during cycling, positive active mass degradation is accelerated. Some aging mechanisms are occurring only upon misuse. Short-circuits across the separators, due to the formation of metallic lead dendrites, for example, are usually formed only after (excessively) deep discharge. Stationary batteries, operated under float-charge conditions, will age typically by corrosion of the positive grids. On the other hand, service life of batteries subject to cycling regimes, will typically age by degradation of the structure of the positive active mass. Starter batteries are usually aging by grid corrosion, for instance in normal passenger car use. However, starter batteries of city buses, making frequent stops, may age (prematurely) by positive active mass degradation, because the batteries are subject to numerous shallow discharge cycles. Valve-regulated batteries often fail as a result of negative active mass sulfation, or water loss. For each battery design, and type of use, there is usually a characteristic, dominant aging mechanism, determining the achievable service life.

Temperature has a strong influence on aging. Grid corrosion rates, and rates of water loss due to evaporation or hydrogen evolution at the negative plates (self-discharge), increase with increasing temperature. On the other hand, a (moderate) temperature increase may improve service life in applications involving severe cycling.

Aging also depends on acid concentration (and concentration variations, for instance due to acid stratification). In general, very low acid concentrations, as prevailing in the discharged state, are harmful to the grids. On the other hand, at very high acid concentrations, service life also decreases, in particular due to higher rates of self-discharge, due to gas evolution, and increased danger of sulfation of the active material.

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1. Introduction

The lead–acid battery is an old system, and its aging processes have been thoroughly investigated. Reviews regarding aging mechanisms, and expected service life, are found in the monographs by Bode [1] and Berndt [2], and elsewhere [3,4]. The present paper is an up-date, summarizing the present understanding. New aspects are: interpre-

tation of hydrogen and oxygen evolution on open-circuit in terms of a thermodynamic “open-circuit hydrogen and oxygen over-voltage”, as influenced by acid concentration, and discussion of acid stratification considering the effects of diffusion potentials.

The major aging processes in lead–acid batteries are:

- Anodic corrosion (of grids, plate-lugs, straps, posts).
- Positive active mass degradation (shedding, sludging) and loss of adherence to the grid.
- Irreversible formation of lead sulfate in the active mass (crystallization, sulfation).

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- Short-circuits.
- Loss of water.

Aging mechanisms are often inter-dependent. For example, irreversible formation of lead sulfate in the active mass is usually the result of insufficient charge. The latter may arise from excessively high acid concentration, due to loss of water; but it could also be the result short-circuits. The latter, in turn, may result from positive active mass degradation.

Several aging mechanisms may contribute simultaneously to loss of performance. However, for each battery design, and each type of use, there is usually one characteristic, dominant aging mechanism, determining the achievable service life.

2. Anodic corrosion (of grids, plate-lugs, straps and posts)

2.1. Positive plates

Regarding positive plates, grid corrosion is the “natural” aging mechanism, causing finally “natural” death. Metallic lead in the positive plate is thermodynamically unstable and anodic corrosion is thus practically unavoidable. Fortunately, the formed corrosion film is protecting the metallic substrate, such that corrosion kinetics becomes sufficiently slow, to allow satisfactory service life. Nevertheless, positive grid corrosion is probably still the most frequent, general cause of lead–acid battery failure, especially in prominent applications, such as for instance in automotive (SLI) bat-

teries and in stand-by batteries. Pictures, as shown in Fig. 1 taken during post-mortem inspection, are familiar to every battery technician. One must, however, immediately add the remark, that (occasional) misuse, or abuse conditions, may strongly contribute to accelerated corrosion, as will be discussed in the following.

In fully charged condition of the positive plates, a dense layer of PbO_2 protects the positive grid from rapid anodic attack (Fig. 2). The interface between the metallic (lead alloy) grid and the PbO_2 corrosion layer is thought to comprise a very thin interlayer, having a nominal composition of PbO_x , whereby x has a value of 1–1.5. This interlayer has apparently an almost negligible ohmic resistance, and has possibly a thickness of a few molecular layers only. (Thicker inter-layers may be present in dry-charged positive plates, or in washed and dried electrode samples, as prepared for microscopic investigations). The intermediate (two-valent) state is thus quite elusive.

Regarding ionic transport, it is unlikely that Pb^{4+} ions, formed at the Pb/PbO_2 interface, could move across the corrosion layer, towards the $\text{PbO}_2/\text{electrolyte}$ interface, to be hydrolyzed and precipitated there, to form PbO_2 . Although the $\alpha\text{-PbO}_2$ structure appears to contain cation vacancies [5], the latter are known to be practically immobile, at least at temperatures below 200 °C. The above transport mechanism would also raise questions, how to explain inter-crystalline grain-boundary corrosion.

Much more likely is an ion transport mechanism across the corrosion layer involving the movement of surface-adsorbed water, from the electrolyte/ PbO_2 interface to the PbO_2/Pb interface. Water may react at the inter-crystalline surface of

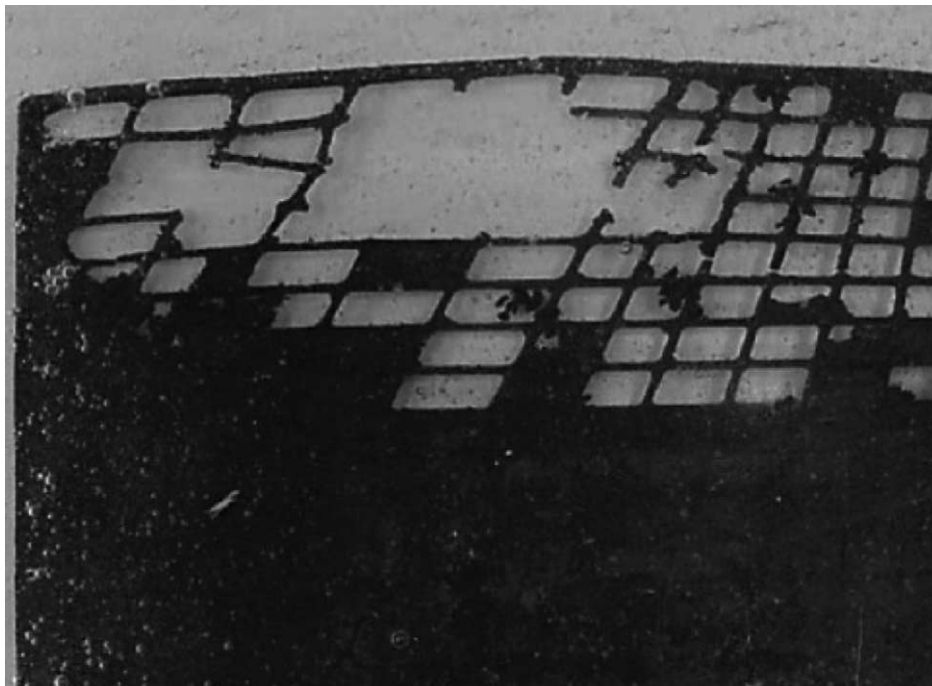


Fig. 1. Corroded positive plate of a starter battery, at the end of 5 years of service life in a passenger car.

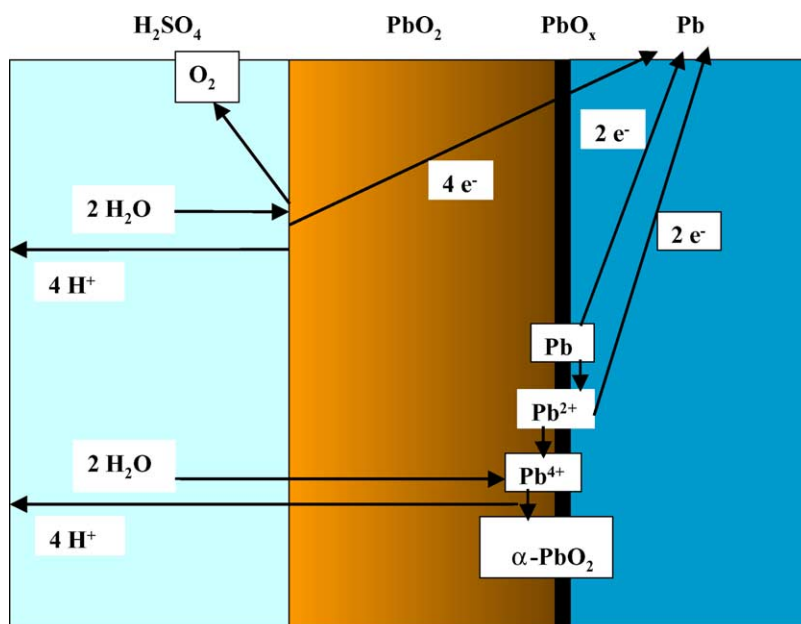
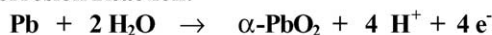
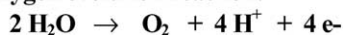
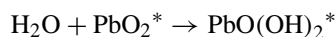
**Corrosion Reaction:****Oxygen evolution reaction:**

Fig. 2. Anodic corrosion mechanism in positive plates, during float-charge or over-charge.

PbO₂ particles [6,7], to form surface OH groups, according to



where * designates surface sites.

The surface OH groups may provide sites for relatively mobile surface protons, allowing ionic current flow, as required for the electrochemical corrosion process. Newly formed PbO₂ would thus precipitate at the Pb/PbO₂ interface, as illustrated schematically in Fig. 2, rather than at the PbO₂/electrolyte interface. This is confirmed by experiments, using ¹⁸O as tracer element [8]. Since PbO₂ has a lower density than Pb, the existing PbO₂ layer would have to be pushed upwards, in order to make room for newly formed PbO₂ material. The latter precipitates, in absence of sulfuric acid, in form of the *α-modification* [9]. The corrosion layer acts as “ion-selective membrane” which is impervious to SO₄²⁻ ions. This mechanism could possibly also explain the detrimental influence of certain alloy constituents, such as antimony, on the corrosion rate. Anodic dissolution of antimony, and accumulation of hydrated antimony oxides in the corrosion layer, could possibly lead to an enhanced transport rate of surface OH groups. Clearly, the transport rate of water is of decisive influence on the corrosion rate.

At highly anodic potentials, in the region corresponding to float-charge or over-charge, the rate of anodic corrosion of positive grids increases with increasing anodic polarization. A quantitative, theoretical treatment, regarding this dependence, has not been given. At least part of any forced, overall

potential increase must be attributed to polarization at the electrolyte/PbO₂ interface, and only the rest would then be available for accelerating the ionization (and ion transport) process near the PbO₂/Pb interface. Experimentally determined Tafel slopes for the anodic corrosion reaction have been reported to be 150–250 mV per decade of current [10]. This is indeed about two to three times higher than that of the oxygen evolution reaction (80 mV per decade of current), confirming that only part of the total polarization is active for the lead ionization process.¹

Since the corrosion rate depends on *potential*, comparisons between different alloys should preferably be made at the *same* (constant) electrode potential, and not at the same current. In order to obtain the best service life, over-charge of batteries should be avoided, and charging should be carried out by appropriately limiting end-of-charge voltage. At the operating potential of the positive electrode, corrosion is accompanied by oxygen evolution. In view of the high electronic conductivity of PbO₂, oxygen evolution takes place at the PbO₂/electrolyte interface. At high anodic potentials, the oxygen evolution current is typically about 100 times larger than the corrosion current. Fig. 3 illustrates the corrosion mechanism under open-circuit conditions. The *anodic* oxidation of lead at the Pb/PbO₂ interface is now being

¹ Recently, the author has been informed, through a private communication, that L.T. Lam has found a Tafel slope of 60 mV per decade of corrosion current, which is in discrepancy with the above results reported by Berndt.

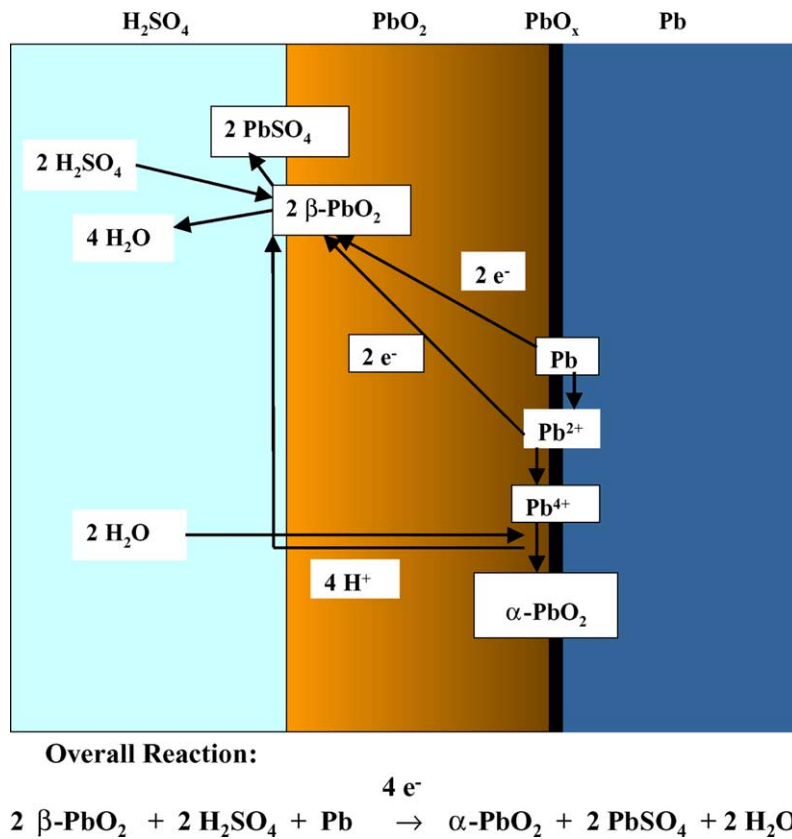
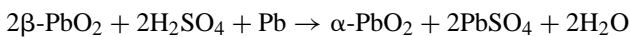


Fig. 3. Anodic corrosion mechanism in positive plates at open-circuit.

driven by a simultaneous *cathodic* reduction of PbO_2 at the $\text{PbO}_2/\text{electrolyte}$ interface [11]. The overall reaction is then



with a standard free enthalpy of reaction of $\Delta_r G^\circ = -176.8 \text{ kJ}$ (for the transfer of four electrons!).

It should be mentioned, that some oxygen evolution takes place (at low rates) also under open-circuit conditions, resulting in self-discharge of the positive electrode, as will be discussed later. The formation of lead sulfate in the corrosion layer will lead to mechanical stress, causing the formation of crevices, or cracks, which in turn may accelerate water transfer and thus increase the corrosion rate.

Fig. 4 depicts schematically (quasi) steady-state anodic corrosion currents on pure lead electrodes, as a function of electrode potential, over the entire potential range occurring in lead–acid batteries. This figure was derived from early experimental work, regarding anodic behavior of pure lead, or lead–calcium alloys, at constant potential [12,13]. These experiments indicated that, after an initial period of about 24 h, the corrosion current remains almost constant, for extended periods of time. The steady-state currents of Fig. 4 are estimated values, for a temperature of 25 °C. Insufficient experimental data is, in fact, available concerning the long-term behavior at potentials just above the reversible Pb/PbSO_4 electrode potential. Part of the data of Fig. 4 is

thus guesswork. Potentials in Fig. 4 are expressed against $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrodes in the *same* solution as the test electrode.

The increase of the corrosion current at potentials above 1.20 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ (corresponding to the range of potentials of the positive plates during charge or over-charge), in accordance with the above-mentioned Tafel slope, is accompanied by a rapidly increasing oxygen evolution rate. At lower potentials, namely at about 50 mV above the reversible $\text{PbO}_2/\text{PbSO}_4$ potential, the anodic corrosion current reaches a minimum. For 5 molal acid (32.9%), this is at 1.18 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$. This then would represent the preferred float potential of positive plates, for this particular acid concentration. At still lower potentials, the corrosion rate is observed to increase sharply, to reach a maximum at about 50–100 mV below the reversible open-circuit potential. The corrosion layer now contains also PbSO_4 . The latter has a considerably lower density than PbO_2 , causing increased mechanical stress within the layer, which could lead to the formation of crevices, or cracks, wherein water could be transported even more readily to the Pb/PbO_2 interface, thereby increasing the corrosion rate.

Fig. 4 illustrates that the optimum float voltage must be carefully adapted to acid concentration. It is important to note, that the corrosion rate, particularly at potentials near or below the open-circuit potential, where the corrosion film is partly, or completely, composed of PbSO_4 , increases

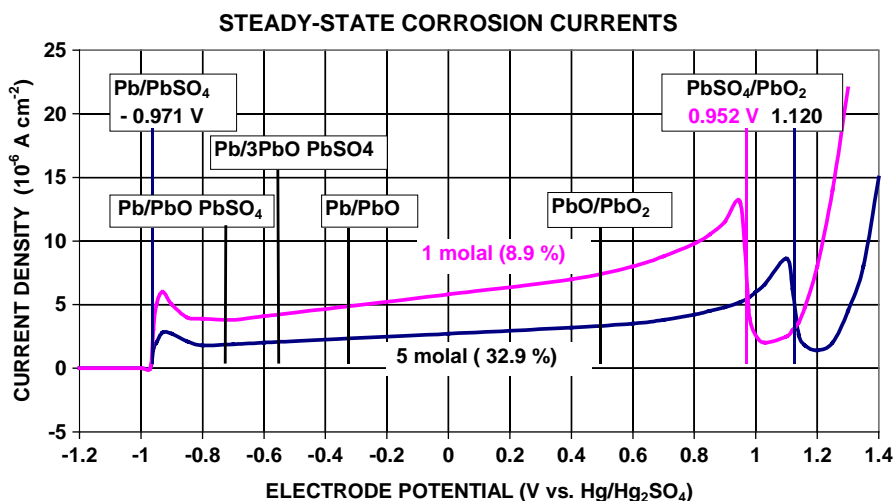


Fig. 4. Schematic representation of long-term, steady-state anodic corrosion currents, at constant potential and at 25 °C. Theoretical electrode potentials of corrosion processes occurring underneath the “ion-selective” PbSO₄ layer, according to Table 1.

strongly with decreasing acid concentration [12,13]. The PbSO₄ corrosion film becomes then less and less protective. This may be related to the increased solubility of lead sulfate, as the acid concentration decreases. The float voltage should preferably also be adapted to the operating temperature, typically about by $-3 \text{ mV}/^\circ\text{C}$.

Determination of anodic currents at potentials *below* the reversible (open-circuit) potential of the positive electrode, and *above* the reversible potential of the negative electrode, at a given, constant acid concentration, is, of course, only possible with small test electrodes in a large excess of acid. In a real battery, positive plates kept at potentials below open-circuit potentials, and negative electrodes kept at potentials above open-circuit potentials, would undergo discharge, leading to a corresponding decrease of acid concentration. This, in turn, would accelerate corrosion, as illustrated in Fig. 4.

In Fig. 4, the minimum corrosion rate in 5 molal acid, at 1.18 V versus Hg/Hg₂SO₄, is shown to be approximately $2 \mu\text{A}/\text{cm}^2$. In the literature, also lower values have been quoted, down to $0.2 \mu\text{A}/\text{cm}^2$. However, the value of $2 \mu\text{A}/\text{cm}^2$ is probably more representative for the average condition in practical float service, which may include also occasional (partial) discharge. This quasi steady-state corrosion current remains nearly constant over the entire life-span of the battery. The rate of $2 \mu\text{A}/\text{cm}^2$ corresponds theoretically to a corrosive attack (transformation of metallic Pb to PbO₂) of about 0.03 mm depth per year [2,14]. Regarding batteries with tubular-plate positives (spine diameter 3 mm), one would then calculate, under optimum float voltage conditions, a theoretical maximum service life of about 20 years. In fact, a service life of this order may probably be achieved in practice with modern, gravity-cast, low-antimony (1.8% Sb) grid alloys, operated at a float voltage of 2.20 V at 20 °C [15]. Obviously, the service life of a battery, as determined by anodic corrosion, will depend not only on the type of alloy, but also on the thickness of

the positive grids. It must be pointed out, that the corrosive attack may not be uniform. Inter-granular corrosion is a frequent phenomenon. Alloy constituents acting as grain-refiners, and appropriate casting techniques (cooling rates), producing a fine-grain metallographic structure, will have a beneficial effect on service life. Examples for such alloy constituents are selenium in antimony–lead alloys, and aluminum in lead–calcium–tin–tin alloys [16,17]. The addition of arsenic (0.15–0.25%) improves the corrosion resistance of lead–antimony alloys drastically.

As will be discussed later, valve-regulated batteries must be operated at considerably higher float voltages than tubular (flooded) batteries, in order to avoid sulfation of the negative plates. The float voltage recommended for valve-regulated batteries is typically 2.25–2.27 V. This is mainly due to the higher acid concentration, used in valve-regulated batteries. However, since the cathodic over-voltage at the negative plates is notoriously low, this would mean that the positive electrodes will operate at much higher potentials (50 mV and more), than those of positive electrodes in tubular-plate (flooded) batteries, with correspondingly adverse effects on the corrosion rates. The corrosion rate in valve-regulated batteries may then be as much as two times higher than in tubular (flooded) batteries. Under optimum conditions, their service life may be estimated to reach about 10 years. In practice, a service life of 10 years is usually not being achieved, because of other life-limiting factors, causing premature failures [18]. Automotive batteries, with very thin positive grids, will have an average service life, as regards to grid corrosion resistance, of about 5 years [15].

2.2. Negative plates

In flooded lead–acid batteries, corrosion at the negative plates is never hardly a problem. During float service, the grid is cathodically protected, the electrode potential

being maintained at about 50–100 mV below the reversible Pb/PbSO₄ potential. Only during discharge, the potential of the negative plates is forced temporarily to values positive to the reversible Pb/PbSO₄ potential, where anodic oxidation of Pb to PbSO₄ can occur. However, upon recharge, formed PbSO₄ is being reduced back metallic lead.

The anodic behavior of lead, in the range of negative plate potentials, is shown in the left part of Fig. 4. The reversible Pb/PbSO₄ potential versus Hg/Hg₂SO₄ in the same solution, is at –0.971 V, independent of acid concentration. The quasi steady-state anodic corrosion currents just above the equilibrium potential are surprisingly high, and strongly dependent on acid concentration. One must also remember that the corrosion reaction is here the transformation of Pb to PbSO₄, a two-electron process, causing for the same current a corrosion penetration depth twice as high as that of anodic oxidation of Pb to PbO₂. A small peak may be observed at potentials just above the reversible Pb/PbSO₄ potential (reminiscent of the corresponding peak in linear-sweep voltammetry curves). As the PbSO₄ corrosion layer increases in thickness, it becomes impervious to SO₄^{2–} ions and then acts as ion-selective membrane [19].

At potentials above –0.734 V versus Hg/Hg₂SO₄ (in 5 molal acid), the corrosion film may contain, underneath an outer PbSO₄ layer, an inner layer of PbO·PbSO₄, at potentials above –0.560 V an inner layer of 3PbO·PbSO₄, at potentials above –0.341 V an inner layer of PbO and at potentials above 0.490 V an inner layer of α-PbO₂ (Table 1). These values were calculated using standard free enthalpies of formation as per reference [20] and activity coefficients and activities of water as per reference [21,22], and they are considered to be more precise than those given earlier [19]. In particular, the standard free enthalpies of formation of the basic sulfates, given in [20], differ considerably from the values used earlier. During deep discharge, plate potentials pass successively through regions, where the composition of the corrosion film, that is the various crystallographic phases present, may vary. The resulting mechanical stress in the film is likely to increase the corrosion rate.

Alloys containing a high percentage (2% or more) of tin are known to be relatively resistant against corrosion at potentials slightly above the reversible Pb/PbSO₄ potential, probably because (selective) anodic dissolution of lead results in a tin-enriched surface layer, which will limit further dissolution of lead. Anodic oxidation of Sn to SnO is only possible at a potential above –0.694 V, that is nearly 300 mV above the Pb/PbSO₄ potential (see Table 2). However, even at potentials above this value, the advantage offered by Sn seems to persist, possibly due to the formation of mixed tin–lead oxides. Antimony would theoretically be even more noble than tin. However, antimony alloys are undesirable. Antimony oxides are relatively soluble in sulfuric acid, causing increased hydrogen evolution at the negative electrode, particularly at elevated temperature.

Regarding negative plates of valve-regulated batteries, anodic corrosion can become a problem, even under normal

Table 1

Calculated electrode potentials (vs. Hg/Hg₂SO₄) of corrosion processes on lead in sulfuric acid at 25 °C

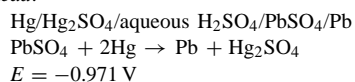
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /Pb PbSO ₄ + 2Hg → Pb + Hg ₂ SO ₄ E = –0.971 V
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /PbO·PbSO ₄ /Pb PbO·PbSO ₄ + H ₂ SO ₄ + 4Hg → 2Pb + 2Hg ₂ SO ₄ + H ₂ O E = –0.7459 + 0.0148 log(a _s /a _w) E = –0.734 V
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /3PbO·PbSO ₄ /Pb 3PbO·PbSO ₄ + 3H ₂ SO ₄ + 8Hg → 4Pb + 4Hg ₂ SO ₄ + 3H ₂ O E = –0.5784 + 0.0222 log(a _s /a _w) E = –0.560 V
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /PbO/Pb PbO + H ₂ SO ₄ + 2Hg → Pb + Hg ₂ SO ₄ + H ₂ O E = –0.3654 + 0.02958 log(a _s /a _w) E = –0.341 V
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /PbO/PbO ₂ PbO ₂ + H ₂ SO ₄ + 2Hg → PbO + Hg ₂ SO ₄ + H ₂ O E = 0.4665 + 0.02958 log(a _s /a _w) E = 0.490 V
Hg/Hg ₂ SO ₄ /aqueous H ₂ SO ₄ /PbSO ₄ /PbO ₂ PbO ₂ + 2H ₂ SO ₄ + 2Hg → PbSO ₄ + Hg ₂ SO ₄ + 2H ₂ O E = 1.0718 + 0.05916 log(a _s /a _w) E = 1.120 V

As the outer PbSO₄ layer builds up in thickness, acid diffusion becomes impeded and inner corrosion products are formed, at increasingly higher pH. In accordance with international norms, the potential-determining reactions are written as electrochemical reduction processes. The calculated numerical values refer to 5 molal sulfuric acid at 25 °C. Acid activity a_s = 4m³f_{+/-}³ = 4.506 and water activity a_w = 0.7032; values as per reference [22]. Standard free enthalpies of formation as per reference [20]. For each process, the first line shows the electrochemical system, including the Hg/Hg₂SO₄ electrode as anode; the second line shows the potential-determining electrochemical reaction; the third line shows the standard potential and the dependence on acid and water activity and the fourth line the numerical value, calculated for 5 molal acid (bulk electrolyte, containing the reference electrode). The double oblique line indicates the liquid junction between bulk electrolyte and acid-depleted electrolyte at the interface.

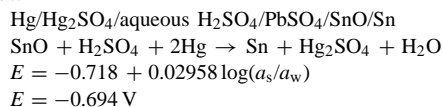
Table 2

Theoretical potentials (vs. Hg/Hg₂SO₄) at 25 °C for anodic dissolution of alloy constituents^a

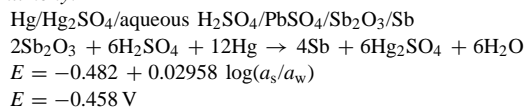
Lead:



Tin:



Antimony:



Calculations as per Table 1.

^a The free enthalpy of the alloying reaction between lead and the respective constituent is neglected.

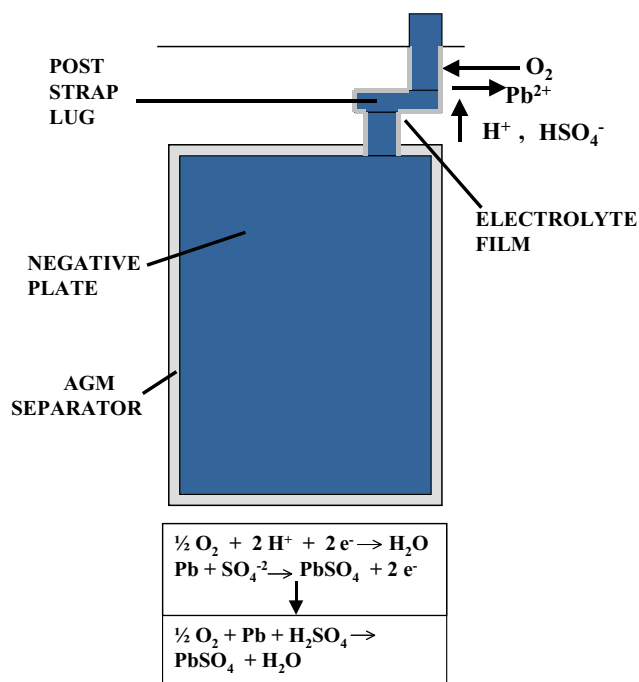
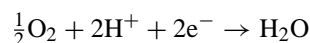
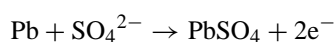


Fig. 5. Corrosion of plate-lugs, straps or posts of negative plates in valve-regulated batteries.

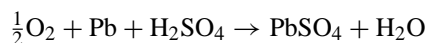
float-charge condition, in particular on those metallic plate parts (lugs, straps, posts) which are not in direct contact with the micro-fiber glass separators (Fig. 5). This is due to insufficient “throwing power” of the cathodic current into the electrolyte film covering these parts. The latter may thus lose their cathodic protection [23]. In valve-regulated batteries, the electrolyte film on plate-lugs, straps and posts is not being periodically renewed by acid spray, and may thus be thinner, and more dilute, than that on equivalent parts in flooded batteries. Oxygen gas, evolved at the positive plates, will readily diffuse through the thin electrolyte film and will be cathodically reduced at the metallic surface, according to



Cathodic oxygen reduction requires the flow of ions (protons), up into the electrolyte film, resulting in a corresponding ohmic voltage drop in the film, forcing the electrolyte film to increasingly negative potentials, with increasing height above the separators. The metallic surface of plate-lugs, straps or posts, on the other hand, is being kept at the *same* potential throughout, because of metallic conduction. The result is, that the local electrode potential (electrode–solution interface) is polarized to correspondingly more positive values, with increasing length of the film above the separators. At sufficient height above the separators, the local electrode potential of the film-covered metal surface may finally reach a value where metallic lead will anodically corrode, according to



The sum of the two above processes results in the formal overall process:



This reaction will, of course, also take place under open-circuit conditions. With increasing length of the electrolyte film above the separators, the local acid concentration decreases, which tends to accelerate corrosion. At locations far above the separator, the local electrode potential should finally reach a value corresponding to the mixed potential established by cathodic oxygen reduction and anodic lead dissolution. Experiments have shown, that the anodic corrosion rate seems to reach a maximum at a distance of 10–20 mm above the separators. Further up, the corrosion current starts to decrease, because of acid depletion.

Instead of oxygen reduction, other cathodic processes, such as accelerated evolution of hydrogen on antimony-contaminated plate-lugs, straps or posts may also drive their surfaces into the potential range, where anodic dissolution takes place, in particular under conditions of high temperature [24].

In order to avoid the described problem, valve-regulated lead–acid batteries are often maintained at an excessively high float voltage, again with correspondingly adverse effects on grid corrosion, as already mentioned. Keeping the length of the metallic parts above the separator edge as short as possible, and using for plate-straps and posts antimony-free lead alloys, with a high content of tin (for instance 2%), anodic corrosion of these parts may, in practice, be almost completely avoided.

3. Positive active mass degradation and loss of coherence to the grid

Loss of coherence between individual particles of the positive active mass, or loss of contact between positive active mass and grid, is a dominant aging factor in batteries subjected to cycling regimes. Transformation of PbO₂ into PbSO₄, during discharge occurs via a dissolution–precipitation mechanism [25,26]. PbSO₄ has a completely different morphology and crystallographic structure, and occupies considerably more volume, than PbO₂. Upon recharge, PbO₂ may be re-deposited in a slightly different morphology than the one having existed before discharge. With continued cycling, this may lead to a morphological “shape-change” of the positive active mass. It has been speculated that the “necks” connecting individual PbO₂ particles may slowly become thinner, resulting finally in loss of coherence between particles [27].

With prolonged cycling, the positive mass will become softer and softer and will finally be subject to what is called “shedding” or “sludging”. Fig. 6 shows a “post-mortem” picture of a starter battery positive plate having served in a city bus for 6 months. In this application, the battery has experienced about 3000 shallow cycles (5–10%

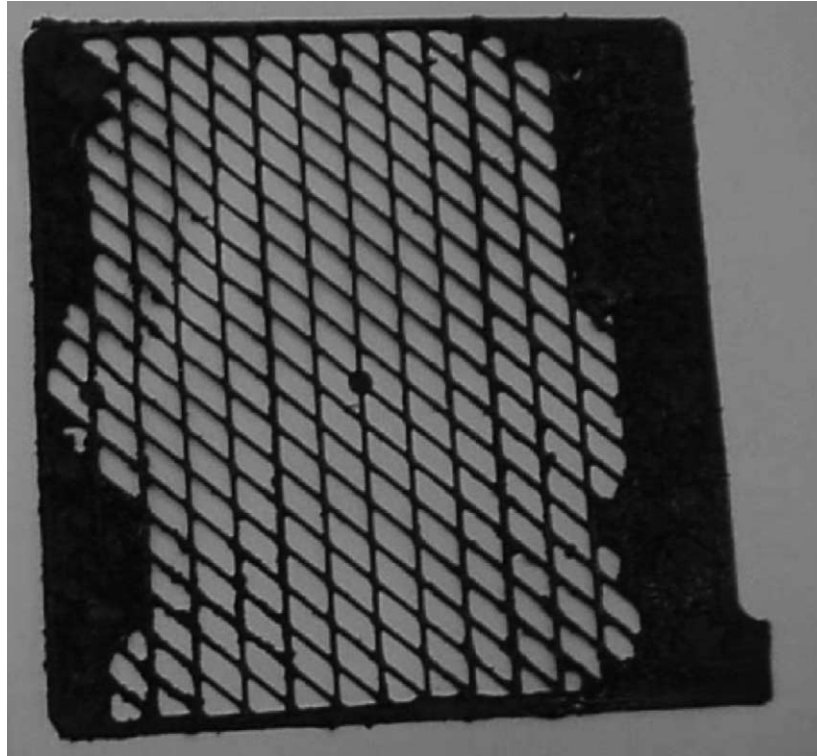


Fig. 6. Picture taken at “post-mortem” inspection of a starter battery, having served in a city bus for 6 months.

depth-of-discharge). The active material is totally disintegrated.

It has been known for many years, that positive plates with *antimony-free grids* alloys will suffer degradation during cycling more rapidly than plates with lead–antimony grids. This has been called the “antimony-free effect”. It appears that antimony, dissolved anodically from the grid, will be retained in the positive active mass in form of hydrated antimony oxides and these tend to act as “cement” between PbO_2 particles, and between active mass and grid, in promoting a more dense and coherent PbO_2 structure during recharge. However, antimony is an undesirable additive, because it decreases corrosion resistance, and increases self-discharge.

The so-called “premature capacity loss” during cycling is probably due to deterioration of the (mechanical and electronic) contact between grid and active material. During discharge at high currents, the active material adjacent to the grid surface is being discharged preferentially (utilizing acid within the pores of the active mass). During recharge at low rates, PbO_2 is being re-deposited (via dissolution of PbSO_4) more uniformly, over the entire plate cross section. With continued cycling, there is then a slow displacement of active mass, away from the grid, towards the plate surface. With time, the porosity of the active mass near the grid may become too large. Too much acid is then available near the grid surface. Upon discharge, PbSO_4 formed there will interrupt the electronic contact to the rest of the active mass. The capacity deteriorates prematurely. The addition

of tin to the grid alloy (preferably more than 0.7%) improves the contact between grid and active material, possibly aided by the formation of conducting, mixed lead–tin oxides [29].

Cycle life is dependent on a number of construction factors. One important aspect is active mass utilization during discharge. The thicker the plates, the lower is usually active mass utilization, and the better will be the cycle life. Similarly, a higher active mass density (that is a lower porosity), will decrease active mass utilization, and increase cycle life. High active mass density can be achieved by using high density pastes, and by curing at high temperature, resulting in the formation of tetra-basic lead sulfate. Active mass utilization can also be simply restricted by limiting the quantity of acid in the battery.

Active mass degradation can be counteracted by appropriate charging techniques. Charging at high currents has a favorable effect on cycle life [30–32]. The effect of high charge currents may, at least partly, be attributed to the resulting higher temperatures. It has been known for a long time, that cycle life improves with increasing temperature [33]. Better coherence between individual PbO_2 particles is achieved during charge at elevated temperature. Conversion of PbSO_4 to PbO_2 occurs via dissolution [25,28] and it is possible that the increased solubility of Pb^{2+} ions is responsible for this effect. However, at excessive temperature (e.g. above 60°C), grid corrosion, or plate sulfation, may become the life-limiting factors. There appears thus to be an optimum temperature, for best service life during cycling.

An effective means to decrease positive active mass degradation is mechanical compression [34–36]. Regarding valve-regulated lead–acid batteries, micro-fiber glass separators having a good resiliency will help to maintain mechanical pressure on the positive plates [37–40]. An excellent way to keep the positive active material under compression is realized in tubular-plate positive electrodes. Such batteries may achieve routinely 1500 cycles, to a depth-of-discharge of 80% at $C/5$. With valve-regulated lead–acid batteries, one obtains up to 800 cycles. Standard SLI batteries, on the other hand, will generally not even reach 100 cycles of this type.

4. Irreversible formation of lead sulfate in the active mass (crystallization, sulfation)

The phenomenon called “sulfation” (or “sulfatation”) has plagued battery engineers for many years, and is still a major cause of failure of lead–acid batteries. The term “sulfation” described the condition of a battery plate, in which highly crystalline lead sulfate has formed in an practically irreversible manner. This type of lead sulfate cannot, or only partially, be reconverted back to an electrochemically active form, resulting in a corresponding loss of capacity. The danger of re-crystallization of PbSO_4 always exists, when the plates remain in a (partly) discharged condition for prolonged periods of time. This can arrive, when batteries are not being charged sufficiently, or not frequently enough. In fact, the active material should, at least from time to time, be completely converted back to the charged state, to Pb in the negative plates, and to PbO_2 in the positive plates, in order to avoid sulfation. Long periods of open-circuit stand, or long periods of discharge at very low rates, can result in sulfated plates, especially at elevated temperature. Self-discharge can thus be an important factor regarding sulfation. Charging rates and charging intervals must be such, as to compensate self-discharge.

Negative plates have a larger tendency to become sulfated, than positive plates. In order to avoid formation of highly crystalline sulfate during cycling, the negative active mass must contain the so-called “expanders”, that is an addition of typically about 0.3% BaSO_4 , about 0.2% ligno-sulfonates, plus about 0.1% of carbon black.

Water loss, as a result of gas evolution, or evaporation, leads to an increase in acid concentration. Insufficient attention is sometimes paid to the fact, that increased acid concentration results in a higher reversible cell voltage, requiring theoretically a correspondingly higher float voltage, or a correspondingly higher charge voltage, to maintain an adequate state of charge. Furthermore, as will be discussed later, at high acid concentration, self-discharge due to gas evolution, is increased, requiring a correspondingly higher float-charge current, in order to avoid sulfation. Water loss and its effects will be further discussed in Section 4.

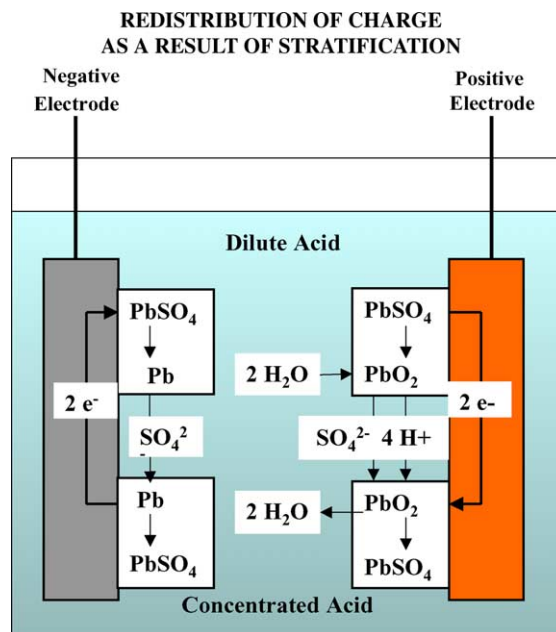


Fig. 7. Mechanism of the redistribution of charge, resulting from acid stratification.

In tall, vented cells with a height above about 25 cm, sulfation may occur as a result of acid stratification. This is a condition of high acid concentration at the bottom of the cell, and low concentration at the top. Stratification may be initiated by preferential discharge of the top portion of the battery, due to a lower ohmic resistance for current flow to upper part of the plates. The electrolyte concentration in the upper part of the battery will then (temporarily) be lower than at the bottom. Under these conditions, a diffusion potential should develop between top and bottom [41]. The diffusion potential is, however, being short-circuited by the electronically conducting plates, leading to discharge of their bottom part, and charge of their top part, as illustrated in Fig. 7. This aggravates the unequal charge distribution between top and bottom. Upon subsequent recharge, the top part will reach the state of full charge quicker than the bottom part and the latter may possibly even never reach full charge, with the result that the active material will sulfate. An effective means to avoid stratification is the installation of an electrolyte circulation pump.

In valve-regulated lead–acid batteries, negative active material can become sulfated at locations which are not sufficiently wetted with sulfuric acid, and not sufficiently protected by cathodic polarization. Then, the same phenomenon can result in the negative active material, as that already described for corrosion of negative lugs, straps or posts. In these locations the negative active mass may then become inactive. Similar conditions may arrive in liquid electrolyte cells, in which the acid level is so low, that the acid does no longer cover the plates. Regarding valve-regulated batteries, ingress of atmospheric oxygen, because of defects in seals or valves, may aggravate sulfation.

5. Short-circuits

5.1. Short-circuits across the separators

Short-circuits across the separators are practically always the result of prolonged deep discharge. In automotive (SLI) batteries, or in train-lighting batteries, such inadvertent abuse conditions arrive relatively frequently. In dilute acid, lead sulfate tends to precipitate in a voluminous form, filling the separator pores. Upon recharge, the lead sulfate in the separator pores may then be converted to dendritic, metallic lead, causing “metallization” of the separators.

This phenomenon is related to the fact, that the solubility of PbSO_4 increases sharply as the acid concentration drops to near zero. While in 0.1 M acid, the solubility of PbSO_4 at 25 °C is only about 1.6×10^{-5} mole/l, it rises in pure water to 1.5×10^{-4} mole/l. The relatively high solubility of PbSO_4 in acid concentrations near zero can be drastically reduced by the addition of Na_2SO_4 to the battery electrolyte. A concentration of about 0.1 mole per liter is sufficient to prevent impregnation of the separators. Separator types with large pores are more prone to become metallized than separators with very fine pores. The thinner the separator, the larger the danger of such short-circuits.

5.2. Short-circuits due to mossy, metallic deposits, or due to sludge

Short-circuits of this type are usually a result of positive active mass degradation. Once the PbO_2 particles have lost mechanical and electric contact, their surface will be slowly converted to PbSO_4 , due to self-discharge (oxygen evolution). Loose, and partly sulfated, PbO_2 particles may become suspended in the electrolyte (causing the latter to turn dark-brown) and can then be transported by electrolyte convection to the top- and side-edges of the negative plates. There, they may be reduced to metallic lead, to form mossy deposits. These can provoke short-circuits.

On the other hand, loose positive active material can form sediments (sludge) at the bottom of the cells. Such sediments can produce short-circuits as well. Finally, it should be mentioned, that inter-granular corrosion of positive grids can result in growth of the positive plates, such that their edges can touch the negative plates and thus provoke short-circuits. In the fight against the development of such short-circuits, pocket-type separators are frequently used today in many applications. Cells with short-circuits usually end up in a permanent state of insufficient charge, resulting in sulfated plates, as already discussed.

6. Loss of water

6.1. Vented batteries

In vented cells, loss of water is, as such, not an aging mechanism leading to a decrease of service life. It is, in

the first place, a nuisance, requiring maintenance in form of water addition. Today, batteries are required to be as maintenance-free as possible. A remarkable improvement, regarding maintenance requirements, was achieved already years ago, by the decrease, or total elimination, of the antimony content in the grid alloys. In this manner, water loss could be greatly decreased. Many types of batteries, such as most SLI batteries, or modern, low-antimony, tubular-plate stationary batteries, are today practically maintenance-free over a service life of several years, if the charge voltage is properly regulated. This is, unfortunately, not always the case. Over-charge leads to a rapid loss of water through electrolysis. In order to minimize water consumption, charging of tubular-plate traction batteries, for instance, should preferably involve not more than about 4% over-charge. Mixing of the acid should be done by means of a circulation pump, rather than by over-charge.

Electrolysis of water takes place not only during charge and over-charge, but also on open-circuit, although at lower rates. However, in many applications, batteries are experiencing relatively long periods of open-circuit stand. Water loss by “self-discharge electrolysis”, that is oxygen evolution at the positive plates, and hydrogen evolution at the negative plates, may then represent an important part of total water loss [42]. The rate of these reactions depends on temperature and acid concentration. The dependence on acid concentration has not, in the past, received sufficient attention. Regarding oxygen evolution, one must consider that the reversible (open-circuit) potential of the $\text{PbO}_2/\text{PbSO}_4$ electrode is 0.4–0.5 V higher than the potential of a (hypothetical) reversible O_2 electrode in the same solution. This “thermodynamic” over-voltage for oxygen evolution can be readily calculated from thermodynamic data. Fig. 8 illustrates, how it increases with acid concentration. I believe, that it has never been pointed out, that the experimentally (volumetrically) measured (self-discharge) oxygen evolution rate, on open-circuit, is increased by a factor of 10, when the acid concentration is increased such, as to increase the “thermodynamic” over-voltage by about 80 mV. This is, for example, the case when the acid concentration increases from 1 to 5 M. The “thermodynamic” polarization has thus a similar “Tafel slope” as a current–voltage polarization curve. Regarding hydrogen evolution, one must consider that the potential of the reversible Pb/PbSO_4 electrode is 0.3–0.4 V below the potential of a reversible hydrogen electrode in the same solution. This “thermodynamic” over-voltage for hydrogen evolution at the lead electrode increases with acid concentration, as illustrated by Fig. 8. It is of interest to note, that hydrogen evolution on open-circuit (as measured for instance volumetrically) increases with acid concentration by a factor of 10, when the acid concentration is increased such as to increase the “thermodynamic” over-voltage by about 120 mV. This corresponds to the Tafel slope of current–voltage polarization curves for the hydrogen evolution reaction. The hydrogen evolution rate may be strongly influenced by certain impurities in the electrolyte.

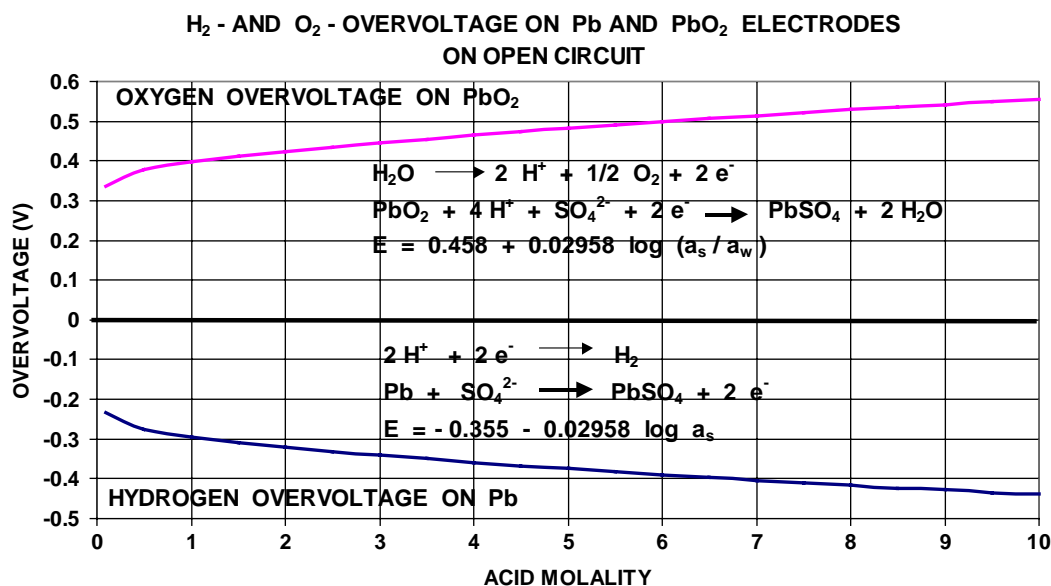


Fig. 8. “Thermodynamically imposed” over-voltage for oxygen evolution on positive electrodes, and for hydrogen evolution on negative electrodes, at 25 °C, as a function of acid concentration. The calculated over-voltages correspond to the voltages of the electrochemical couples O₂/H₂O/aqueous H₂SO₄/PbSO₄/PbO₂, respectively H₂/H₂O/aqueous H₂SO₄/PbSO₄/Pb. Calculations based on data of references as given in Table 1.

For vented cells, loss of performance, due to the loss of water, only arises, when maintenance intervals are not being properly respected. Then, the acid concentration rises, which results in an increase of the reversible electrode potential. Theoretically, the (float) charge voltage should then be adapted, in order to keep the battery properly charged. This is, however, often overlooked. Increase in acid concentration also leads to an important increase of the rate of self-discharge due to gas evolution, as discussed above. This again would require an increase in the charging current. This is also usually being neglected. The result is then an insufficient state of charge, and sulfation of the plates. If the electrolyte level is below the plate edges, the part of the plates above the acid level cannot be charged properly, and this part of the plates will then undergo sulfation as well.

6.2. Valve-regulated batteries

Valve-regulated batteries are expected to be totally maintenance-free, over their entire service life. During charge, oxygen evolved at the positive electrode is being reduced at the negative electrode. This is the so-called oxygen cycle. Inevitably, some hydrogen will, however, evolve at the negative electrode, even under open-circuit conditions, and more so under charge conditions. Hydrogen cannot be re-oxidized to water at the PbO₂ electrode, at least not at significant rates, unless special means such as auxiliary electrodes or catalyst plugs are employed. Without such means, hydrogen must thus be vented from the battery. This represents a loss of water. Water may also be lost by evaporation and diffusion of water vapor across the battery container walls, especially when batteries are operated at elevated temperature.

Water loss must be kept as small as possible, in order to avoid an undue increase of acid concentration, with the mentioned adverse effects. This again shows, how much the aging factors may be inter-dependent.

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