

Silver–silver sulfate reference electrodes for use in lead-acid batteries

Paul Ruetschi

Leclanché SA, Laboratories of Leclanche, CH-1400 Yverdon-les-Bains, Switzerland

Abstract

Electrochemical properties of silver–silver sulfate reference electrodes for lead-acid batteries are described, and the following possible applications discussed:

- Determination of individual capacities of positive and negative plates.
- Monitoring individual electrode behavior during deep discharge and cell reversal.
- Optimization charge or discharge parameters, by controlling the current such that pre-determined limits of positive or negative half-cell potential are respected.
- Observation of acid concentration differences, for example due to acid stratification, by measuring diffusion potentials (concentration-cell voltages).
- Detection of defective cells, and defective plate sets, in a string of cells, at the end of their service life.

Silver–silver sulfate reference electrodes, permanently installed in lead-acid cells, may be a means to improve battery management, and therewith to improve reliability and service life. In vented batteries, reference electrodes may be used to limit positive plate polarization during charge, or float-charge. Limiting the positive half-cell potential to an upper, pre-set value would permit to keep anodic corrosion as low as possible. During cycling, discharge could be terminated when the half-cell potential of the positive electrode has dropped to a pre-set limit. This would prevent excessive discharge of the positive electrodes, which could result in an improvement of cycle life. In valve-regulated batteries, reference electrodes may be used to adjust float-charge conditions such as to assure sufficient cathodic polarization of the negative electrodes, in order to avoid sulfation. The use of such reference electrodes could be beneficial particularly in multi-cell batteries, with overall voltages above 12 V, operated in a partial-state-of-charge.

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1. Introduction

Recently, I have developed silver–silver sulfate reference electrodes for measuring, and monitoring, individual electrode potentials in lead-acid batteries [1]. Such reference electrodes are easy to construct at low cost, in a variety of geometries. They have a precisely defined electrode potential, which is readily reproducible to ± 1 mV, and which is very stable, even at elevated temperatures, over extended periods of time. The reversible electrode potential of the Ag/Ag₂SO₄ reference electrode is about 1 V positive with respect to the Pb/PbSO₄ electrode, and about 1 V negative with respect to the PbO₂/PbSO₄ electrode. Silver–silver sulfate reference electrodes are practically free of self-discharge. Reduction of silver sulfate to metallic silver by dissolved hydrogen in the electrolyte, and oxidation of metallic silver to silver sulfate by dissolve oxygen in the electrolyte, are insignificantly small, and have opposite

effects. Silver–silver sulfate reference electrodes appear thus to be suitable for long-term use, and could be permanently installed in batteries, over their entire service life. Silver–silver sulfate reference electrodes are mechanically robust and shock-proof. Finally, they are free of toxic substances, such as mercury or cadmium. A patent has been applied for lead-acid batteries with integrated silver–silver sulfate reference electrodes.

As illustrated in Fig. 1, Ag/Ag₂SO₄ reference electrodes may be housed in a thin, flexible tubing (3) of inert plastic, preferably of Teflon. The electrode shown in Fig. 1 makes use of a tubing having an outer diameter of 4 mm, an inner diameter of 3 mm, and a length of 120 mm. The design is readily adaptable to other dimensions, for instance to tubes of smaller diameter, or increased length. A dense plug of micro-fiber glass separator material (5) is placed at the lower end (in Fig. 1 to the right) of the tubing, separating the active material mixture (4) from the battery electrolyte. The length

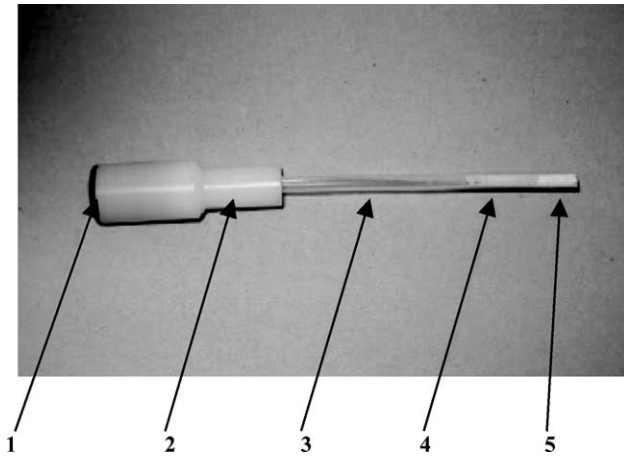


Fig. 1. Silver–silver sulfate reference electrode as used in the present study: (1) safety connector socket; (2) turned plastic sleeve; (3) Teflon tubing; (4) active material mixture; (5) micro-fiber glass separator plug.

of the micro-fiber separator plug of the electrode shown in Fig. 1 is 12 mm. However, the length may be adapted according to specific requirements, regarding inhibition, or permission, of acid equilibration, between battery electrolyte and reference electrode electrolyte. The active material consists of a 1:1 mixture (per mole) of silver powder and silver sulfate. A silver wire makes electric contact to the active material mixture. At the upper end, the silver wire is soldered to a safety connector (1). The soldering point is protected from acid spray, or acid creep, by potting it into acid-resistant resin (not visible in Fig. 1). An acid-resistant, turned sleeve (2) covers the electric connection. The latter has a gold-plated, 4 mm diameter contact socket. The individual parts are shown in Fig. 2.

The major concern regarding long-term use of these reference electrodes is the relatively high solubility of silver sulfate. In sulfuric acid solutions, Ag_2SO_4 dissolves mainly

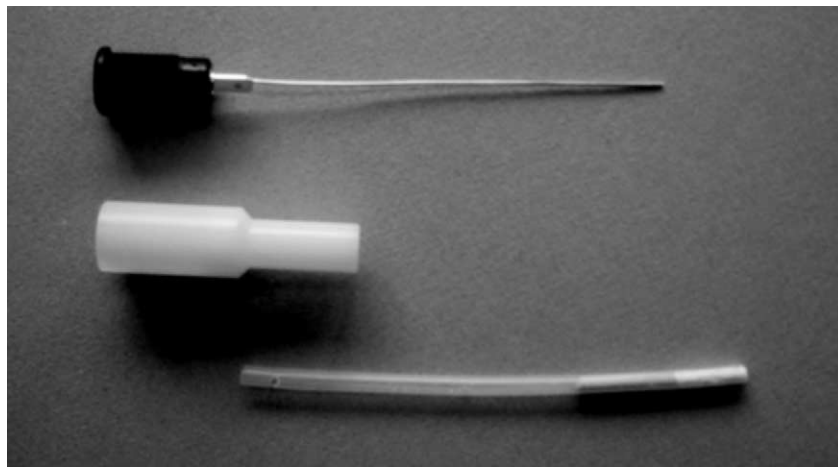


Fig. 2. Individual parts of the $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode.

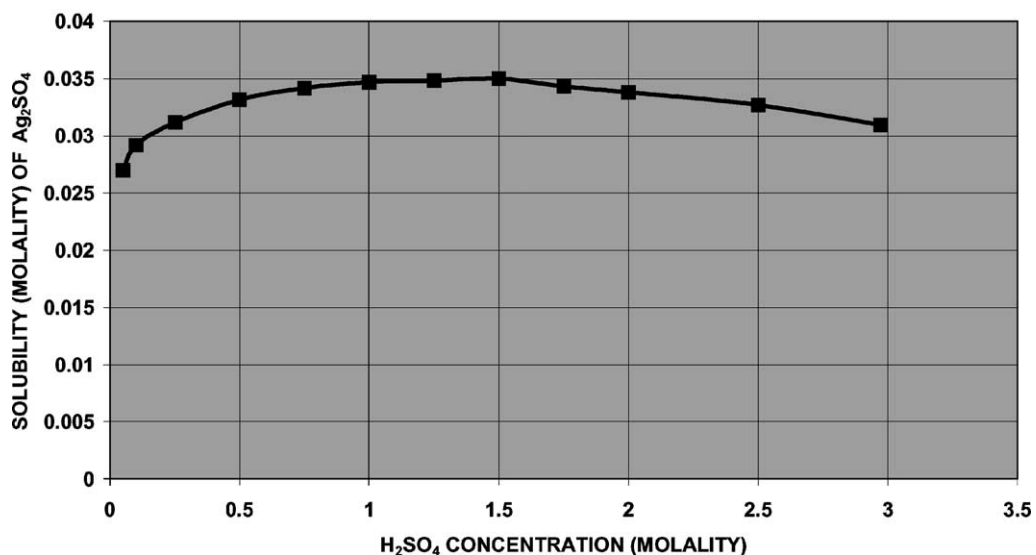


Fig. 3. Solubility of Ag_2SO_4 in sulfuric acid solutions at 25 °C.

in non-dissociated form, and the solubility is almost independent of acid concentration [2,3]. As illustrated in Fig. 3, the solubility (at 25 °C) is about 0.03 mol/1000 g H₂O. The solubility increases, however, with temperature. If silver sulfate diffuses into the battery electrolyte, metallic silver could get deposited on the negative plates. Fortunately, metallic silver has a relatively high hydrogen over-voltage, and contamination of the negative electrodes with small quantities of metallic silver should have only a minor effect on their self-discharge. Diffusion of silver sulfate into the battery electrolyte can be restricted by decreasing the diameter of the micro-fiber glass plug separator, by increasing its length and its density (compactness), and by adding a gelling agent. On the basis of Fick's law, one can estimate that it should be possible to limit the diffusion into the battery electrolyte (at 25 °C) to less than 0.1 mg of metallic silver per year.

Regarding the reversible (open circuit) electrode potential of the *negative plates* (Pb/PbSO₄ electrodes), as measured against a Ag/Ag₂SO₄ reference electrode, in the *same* sulfuric acid solution, one calculates from thermodynamic data, for 25 °C, a value of

$$E(\text{Pb}/\text{PbSO}_4)\text{ versus }E(\text{Ag}/\text{Ag}_2\text{SO}_4) = -1.0091 \text{ V} \quad (1)$$

This value is independent of acid concentration.

Regarding the reversible (open circuit) electrode potential of the *positive plates* (PbO₂/PbSO₄ electrodes), as measured against a Ag/Ag₂SO₄ electrode in the *same* solution, one expects from thermodynamics, at 25 °C, the following relation:

$$E(\text{PbO}_2/\text{PbSO}_4)\text{ versus }E(\text{Ag}/\text{Ag}_2\text{SO}_4) = 1.0334 + 0.05916 \log\left(\frac{a_s}{a_w}\right) \quad (2)$$

Table 1
Electrode potentials vs. Ag/Ag₂SO₄

Acid molality	Concentration, % H ₂ SO ₄	Potential, Pb/PbSO ₄	Potential, PbO ₂ /PbSO ₄
0.1	0.9713	-1.0091	0.7894
0.5	4.6748	-1.0091	0.8727
1	8.9320	-1.0091	0.9137
1.5	12.825	-1.0091	0.9424
2	16.399	-1.0091	0.9661
2.5	19.692	-1.0091	0.9874
3	22.735	-1.0091	1.0075
3.5	25.555	-1.0091	1.0269
4	28.177	-1.0091	1.0457
4.5	30.621	-1.0091	1.0636
5	32.904	-1.0091	1.0811
5.5	35.041	-1.0091	1.0980
6	37.047	-1.0091	1.1143
6.5	38.932	-1.0091	1.1302
7	40.708	-1.0091	1.1457
7.5	42.383	-1.0091	1.1604
8	43.966	-1.0091	1.1747
8.5	45.465	-1.0091	1.1888
9	46.885	-1.0091	1.1996
9.5	48.234	-1.0091	1.2152
10	49.515	-1.0091	1.2278

where a_s and a_w designate the activity of sulfuric acid and water, respectively. Treating sulfuric acid as 2:1 electrolyte, the activity a_s is given by

$$a_s = 4m^3 f_{\pm}^3$$

where f_{\pm} is the mean ionic activity coefficient and m the acid molality. Values for f_{\pm} and a_w are readily available in the literature [4,5].

Calculated electrode potentials for the negative and the positive electrode, at various acid concentrations, are listed in Table 1.

Experimentally measured values are found to be in excellent agreement with these calculated ones.

In the following, various uses of silver–silver sulfate reference electrodes will be described.

2. Determination of individual discharge capacities of positive and negative plates

In order to measure electrode potentials of the positive and negative plates of a particular cell, a small hole is drilled into the cell cover, fitting tightly the plastic tubing of the reference electrode. The reference electrode is introduced through the hole, such that the lower end of the tubing touches the electrolyte level, or the electrolyte-wetted separators. The feed-through area is then sealed by means of a suitable, acid-resistant hot-melt adhesive or wax. When taking electrode potential measurements under current flow, measured values will include ohmic potential drops in the electrolyte. The magnitude of such ohmic potential drops may be evaluated using current-interruption techniques. Ohmic drops usually constitute only a small fraction of total polarization. The local, physical position of the reference electrode has thus only a minor influence on the measured value.

Fig. 4 shows potential–time curves obtained with a 200 Ah, tubular-plate, lead-acid (train-lighting) battery, discharged at 20 A (to 1.85 V) and charged at 40 A. Comparison of the half-cell potentials of negative and positive electrodes demonstrates, that it is the negative electrode which limits the cell capacity. Carrying out such half-cell potential measurements at the end of useful service life allows to determine, which plate set has limited service life.

The use of reference electrodes offers the possibility to stop discharge, during cycling, when the potential of the *positive electrode* reaches a defined (end of discharge) limit. The positive electrode can thus be protected from excessively deep discharge. In this manner, cycle life might be improved.

3. Monitoring battery plate behavior during deep discharge and cell reversal

In certain applications, individual cells may occasionally be subject to deep discharge, or even to reversal. This is the case in SLI- and train-lighting applications. In order to

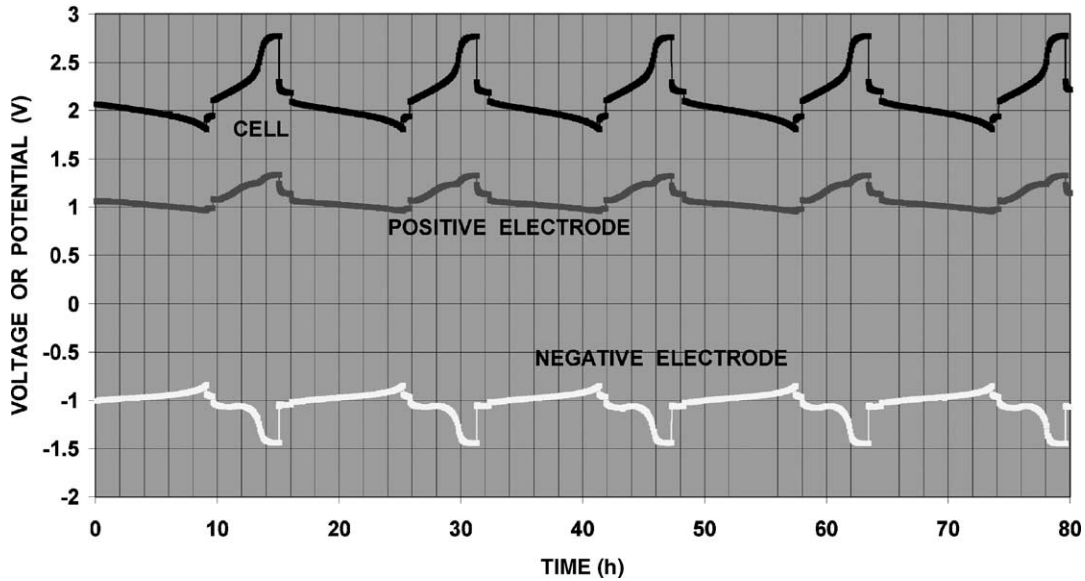


Fig. 4. Cell voltage and individual electrode potentials of a 250 Ah train-lighting battery (Leclanché EPR-2) with tubular positive electrodes, during cycling. Discharge at 20 A to 1.85 V, charge at 40 A.

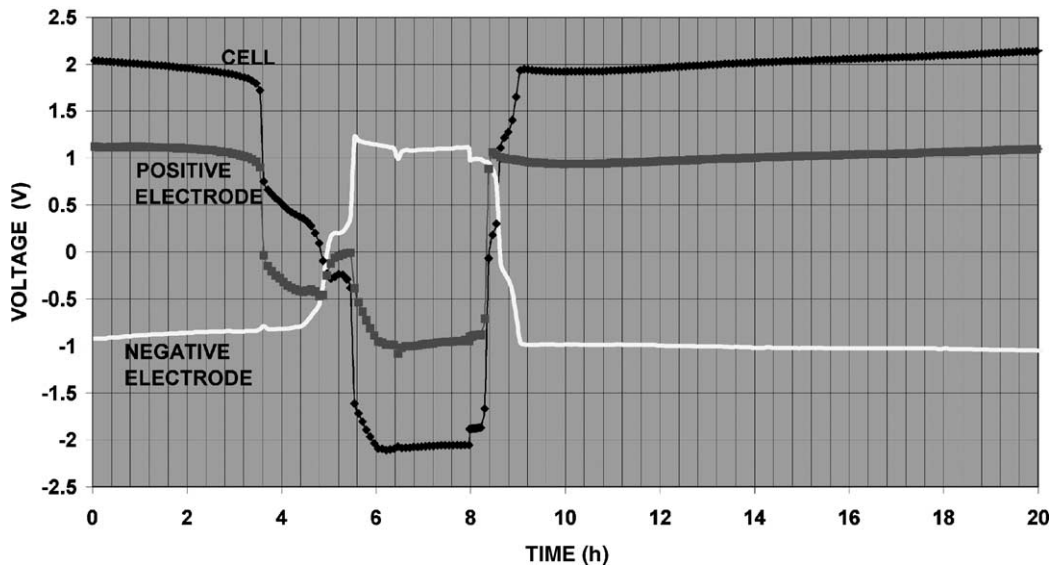


Fig. 5. Cell voltage and individual electrode potentials of a 150 Ah valve-regulated battery (Leclanché SP 150) during a reversal test. Discharge and reversal at 15 A, charge at 15 A.

assure satisfactory service life, such batteries should thus be as resistant as possible against over-discharge.

In developing batteries of this type, studies with reference electrodes are particularly helpful. Such investigations have been carried out at Leclanché SA on various types of train-lighting batteries. Fig. 5, illustrates the behavior of cell voltage and individual electrode potentials during a reversal test on a 150 Ah valve-regulated lead-acid battery (Leclanché SP 150). The battery was initially 70% discharged. The curves of Fig. 5 relate to the continuation of discharge, at 15 A, into reversal condition. They demonstrate that the cell capacity is here limited by the positive electrode. Upon continuation of discharge, the potential of the positive electrode shows a

plateau, at about -0.5 V versus $\text{Ag}/\text{Ag}_2\text{SO}_4$, followed by a recovery to about 0 V. Finally, the potential drops to a value corresponding to that of a negative electrode. The intermediate potential plateau and potential recovery is due to discharge of active material in the interior of the positive plates, under conditions of acid depletion.

4. Optimization of charge parameters, as monitored by positive or negative half-cell potentials

Suitable charging techniques play an important role in optimizing service life of lead-acid batteries. In recent years,

much effort has gone into the development of high-rate charge techniques [6]. Usually, the charge current is being reduced, when a defined upper limit of the *cell voltage* (corrected for temperature) has been reached. In this manner, it is hoped to avoid excessive over-charge, and thus excessive corrosion of the positive grids. However, the cell voltage, especially in vented cells, is strongly influenced also by the negative half-cell potential. If the negative half-cell potential is low, that is when hydrogen over-voltage is low, the positive electrode is forced to correspondingly higher potentials, where corrosion could occur more rapidly.

In *vented batteries*, the use of reference electrodes would theoretically permit the adjustment of charge parameters independent of negative half-cell potential, regulating the charge current only with respect to *positive half-cell potential*. Thus, the charge current, and the duration of charge, could be limited when the positive electrode has reached a defined half-cell potential. In this manner, corrosion could be kept low, and service life could be optimized. Similarly, for stationary batteries, the float-charge current could be regulated such as to assure optimum conditions regarding positive half-cell potentials. It is generally believed that the optimum float-charge potential of the positive electrodes is about 40–60 mV above the reversible (open circuit) potential. In this potential range, the corrosion rate reaches a minimum. Half-cell potential measurements with reference electrodes could thus be used to assure optimum conditions during float-charge.

In *valve-regulated batteries*, polarization of the negative electrode during charge is notoriously low, due to the reduction of oxygen (oxygen cycle). This incurs the risk of sulfation. The use of reference electrodes would permit to control the charge current as to regulate *polarization of the negative plates* to a sufficiently negative value, for instance typically to about 20–30 mV below the reversible (open circuit) potential.

This would assure sufficient cathodic protection for the negative active material. In this manner, sulfation could be avoided. If a sufficiently negative potential cannot be reached, this could be an indication that the cell has lost water and has become too dry. One could then consider to add water to the electrolyte. Reference electrodes thus provide an additional means to check on the health of a battery.

Fig. 6 illustrates schematically polarization curves of positive and negative electrodes, as expected to be measured when using silver–silver sulfate reference electrodes (in the same electrolyte). These curves were calculated by assuming an acid concentration of 5 molal, and thus a reversible cell voltage (at 25 °C) of 2.090 V. The reversible potential of the Pb/PbSO₄ electrode would then be –1.009 V (versus Ag/Ag₂SO₄) and the reversible potential of the PbO₂/PbSO₄ electrode +1.081 V (versus Ag/Ag₂SO₄).

In flooded (flat-plate or tubular-plate) batteries, the Tafel slope for hydrogen evolution at the negative electrode is usually found to be 120 mV per decade of current [7,8]. At float currents below about 20 μA/Ah, the Tafel line starts to deviate from linearity. The deviation to lower over-voltage values (as shown in Fig. 6) can be explained by the influence of two factors: (a) the increase of current due to oxygen reduction and (b) the acceleration of the hydrogen evolution rate due to adsorbed sulfate anions [9,10]. At float currents below about 10 μA/Ah, the negative electrode cannot be maintained at full charge, because of the self-discharge processes. The sum of the hydrogen evolution current and the oxygen reduction current will then tend to become larger than the supplied charge current. The electrode surface would then, with time, become covered with lead sulfate films, which will cause a decrease of hydrogen evolution and oxygen reduction rates. The Tafel line would then tend to deviate to higher over-voltage values, rather than to lower ones (deviation to lower currents).

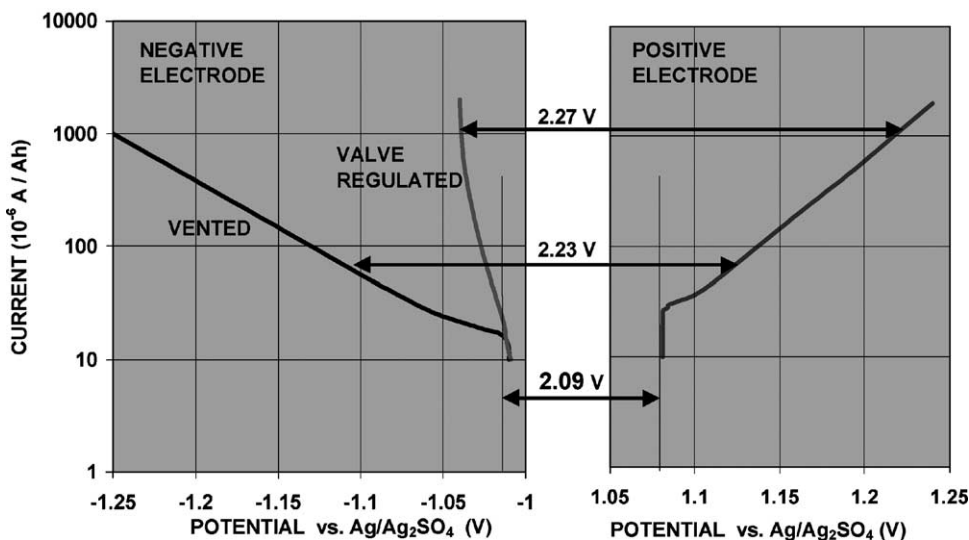


Fig. 6. Expected polarization curves of positive and negative electrodes, when measured against silver–silver sulfate reference electrodes. This figure serves to demonstrate that the positive electrodes of valve-regulated batteries are subject to much higher potentials than the positive electrodes in vented batteries.

Regarding valve-regulated batteries, Fig. 6 illustrates that the negative plate polarization is quite low, usually below 30 mV only, under ordinary float-charge conditions, due to the internal oxygen cycle.

A Tafel slope of 80 mV is usually observed for the oxygen evolution process on positive electrodes [7,8]. At float currents below about 40 $\mu\text{A}/\text{Ah}$, the Tafel line may start to deviate from linearity, as indicated in Fig. 6, because of the influence of the corrosion current. If the applied float current becomes smaller than the sum of the self-discharge currents (oxygen evolution plus corrosion), the positive plate cannot be kept at full charge. Solid lead-sulfate films may then start to form on the PbO_2 surface. This, in turn will tend to decrease oxygen evolution [11]. The Tafel line would then tend to deviate to higher over-voltage values, rather than to lower ones (deviation to lower currents).

Fig. 6 serves to illustrate, that the positive electrodes of valve-regulated batteries, operated at a float voltage of 2.27 V, are subject to half-cell potentials which may be as much as 100 mV higher than those of positive electrodes in vented (flat-plate or tubular-plate) batteries, the latter being floated typically at a voltage of 2.23 V. The positive grids in valve-regulated batteries will corrode correspondingly quicker. It should, however, be mentioned that the acid concentrations used in valve-regulated batteries are generally somewhat higher than those used in vented batteries. This means that the reversible electrode potential of the positive electrode in valve-regulated batteries is correspondingly higher, and the electrode polarization (at a cell voltage of 2.27 V) correspondingly lower. Nevertheless, positives in valve-regulated batteries are generally operated at less favorable potentials than positives in vented batteries, with correspondingly adverse effects on grid corrosion. The higher acid concentration used in valve-regulated batteries

results also in a higher (self-discharge) hydrogen evolution rate during open circuit stand [12].

5. Observation of acid concentration differences (for example acid stratification) by measuring diffusion potentials (concentration-cell voltages)

When measuring half-cell potentials of battery electrodes, one must be aware of the fact, that the measured value may include a *diffusion potential*. This is always the case when the acid concentration in the reference electrode differs from the one in the battery. This situation presents itself, for instance, during discharge. Then the (local) acid concentration in the battery may become lower than that in the reference electrode, although acid inter-diffusion will tend to (slowly) equalize the concentration difference between reference electrode and battery. The rate of acid inter-diffusion is determined by the length, diameter and compactness of the micro-fiber glass diffusion barrier of the reference electrode. For reference electrodes as described in Fig. 1, acid inter-diffusion will occur at a rate such as to decrease the concentration difference by about a factor of two, within about 48 h [1]. The micro-fiber separator plug can be designed as to comply with specific requirements regarding acid inter-diffusion rate.

The diffusion potential E_D can be calculated theoretically as *concentration-cell voltage* between two reference electrodes, one containing acid of (reference) activity a_1 , the other acid of activity a_2 , corresponding to the (local) acid concentration in the battery. The electrode in the more dilute acid is positive with respect to the electrode in the more concentrated acid.

$$E_D = t_+ \left(\frac{RT}{2F} \right) \log \left(\frac{a_1}{a_2} \right) \quad (3)$$

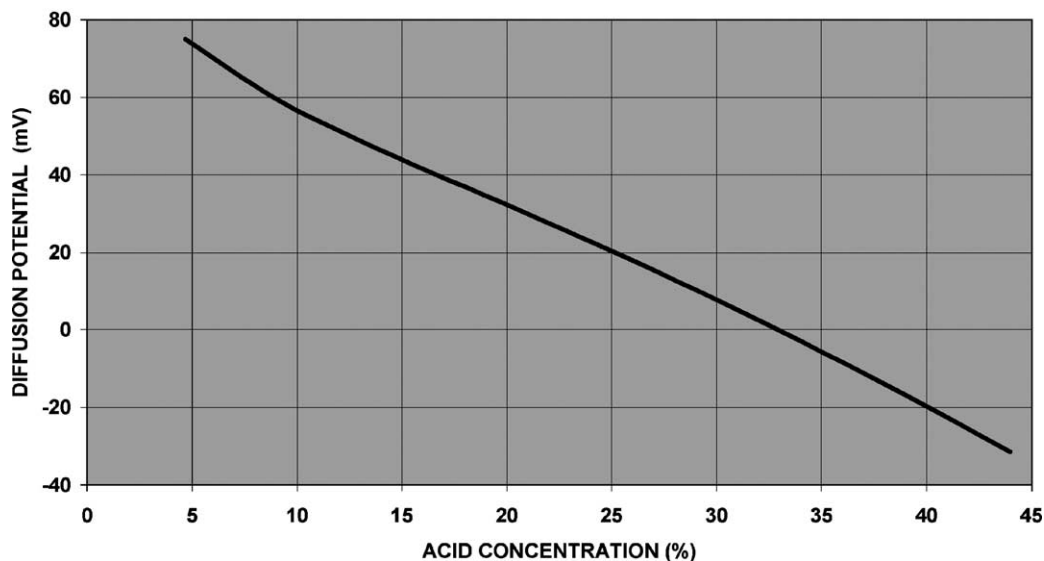


Fig. 7. Calculated diffusion potentials between two reference electrodes, the first one in 5 molal acid, the second one in acid of a concentration as given on the abscissa.

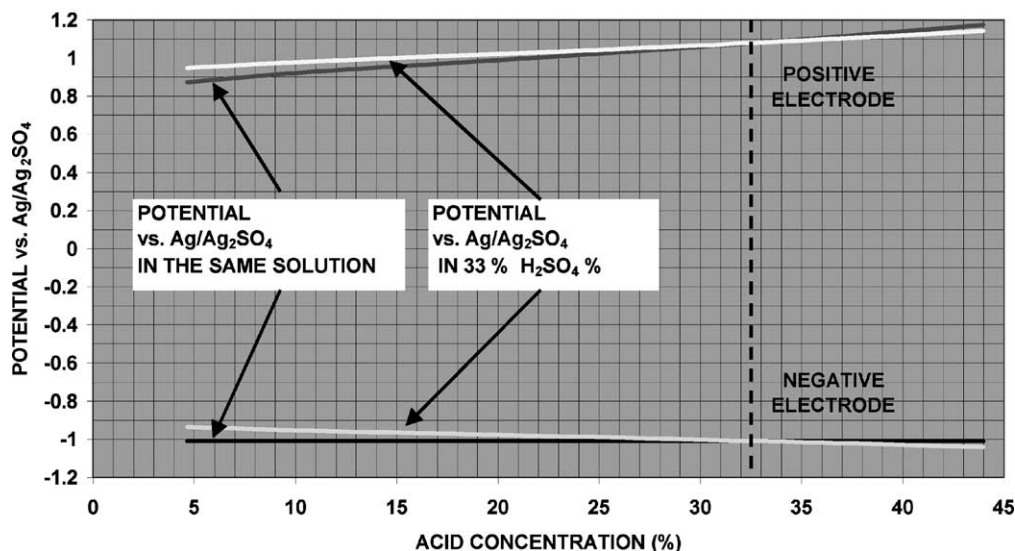


Fig. 8. Expected electrode potentials, when measured (a) against a $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode in the *same* solution as the battery electrode, and (b) against a $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode in 5 molal acid.

where t_+ is the transfer number of cations (protons). Experimentally, the transfer number t_+ has been found to have an (average) value of 0.75.

Fig. 7 shows calculated diffusion potentials, as a function of acid concentration in the battery, when assuming in the reference electrode a constant acid concentration of 5 molal, corresponding to an acid concentration of 32.9% per weight (activity a_1). As demonstrated by Fig. 7, the diffusion potential can reach values of up to 80 mV, and more. The diffusion potential is positive when the acid activity a_2 in the battery is lower than the acid activity a_1 in the reference electrode.

Experimentally measured half-cell potentials will correspond to the *sum* of (a) the calculated potential against a reference electrode in the *same* solution, as described by Eqs. (1) and (2) and (b) the above-described diffusion potential E_D , as expressed in Eq. (3). Fig. 8 illustrates

how diffusion potentials are expected to influence the measured half-cell potential.

Diffusion potentials should also exist between top and bottom of a battery subject to acid stratification [1,12]. Under the presumption that stratification persists for a sufficiently long period of time, as to equilibrate acid concentrations in the respective reference electrodes with the local acid concentration in the battery, diffusion potential measurements could provide a means to evaluate the importance of stratification. Fig. 9 illustrates this type of measurement. Concentration differences between top and bottom could then be evaluated on the basis of the data of Fig. 7.

6. Detection of defective cells, and defective plate sets, in a string of cells, at the end of their service life

At the end of life-tests, or at the end of useful service life, it would often be desirable to know, which cell, or which plate-set, is actually responsible for battery failure. Measurements using reference electrodes can be helpful to identify the defective cell, or plate-set. Post-mortem visual inspection can then possibly be limited to that particular cell.

This technique is illustrated in Fig. 10. Small holes were drilled into each cell cover, and reference electrodes introduced into each cell. The feed-through areas were sealed with acid-resistant wax. Voltage readings (at open circuit) were taken between reference electrodes and the positive, or negative battery terminals. For the end-cells, one would expect to measure a value of about +1 or –1 V, respectively. For the intermediate cells, the voltage readings for two successive cells should differ by about 2.1 V. Fig. 10 shows that the readings designated “3+” and “4+” differ only by 1.592 V, and the readings “3–” and “4–” differ only by 1.593 V. This then proves that the third cell from the left

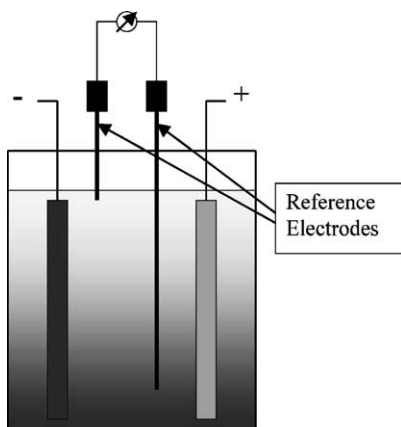


Fig. 9. Measurement of diffusion potentials in a cell showing acid stratification, using silver–silver sulfate reference electrodes.

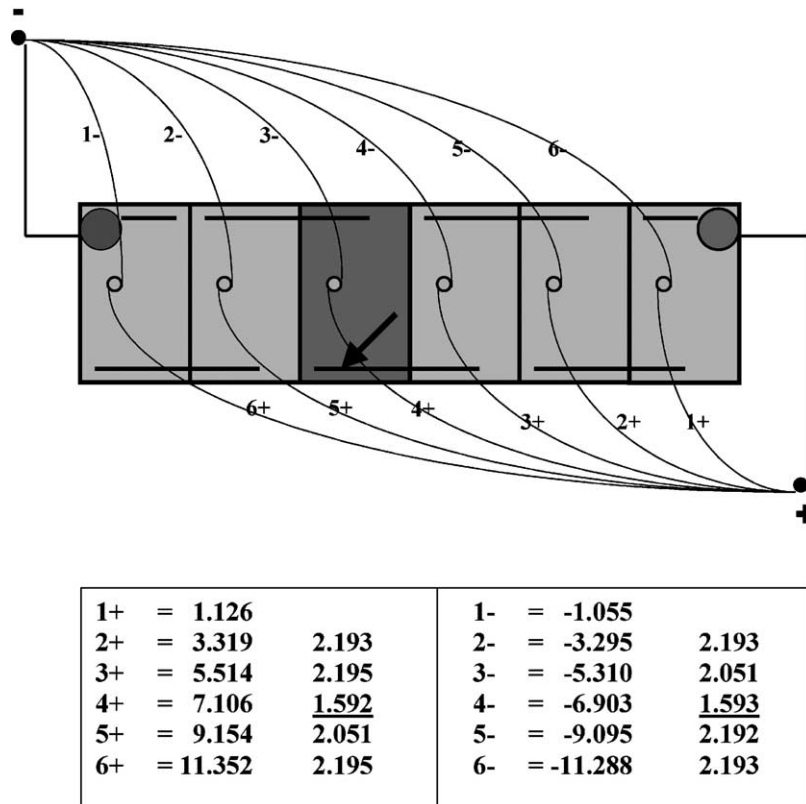


Fig. 10. Detection of defective cells, and defective plate sets, at the end of service life, by means of measurements with silver–silver sulfate reference electrodes.

(shaded cell) is defective, and it is in fact the positive plate set of that particular cell which is causing the failure.

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