Silver–silver sulfate reference electrodes for lead-acid batteries

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Abstract

Cadmium sticks, or mercury-mercurous sulfate reference electrodes, have been widely used in the past, in order to measure half-cell potentials in lead-acid batteries. The present paper presents experimental data obtained with a new type of reference electrode, based on the Ag/Ag_2SO_4 couple. This reference electrode has a reproducible and stable electrode potential, situated 38.4 mV positive with respect to that of the Hg/Hg_2SO_4 couple.

Ag/Ag_2SO_4 reference electrodes allow a precise evaluation of diffusion potentials (concentration cell voltage) in sulfuric acid solutions.
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Keywords: Lead-acid batteries; Reference electrodes; Half-cell potentials; Diffusion potentials; Concentration cells

1. Introduction

Cadmium sticks have been widely used in the past for quality control of negative and positive plate potentials during manufacturing, while mercury-mercurous sulfate reference electrodes have generally been preferred for precise laboratory investigations. Reference electrodes of this type are commercially available. However, they are relatively costly, fragile and environmentally unfriendly.

Very scant information is available in the literature [1–3] on silver–silver sulfate reference electrodes and there are hardly no descriptions available, how to prepare such electrodes. Ag/Ag_2SO_4 reference electrodes have never been used, up to now, in studies related to lead-acid batteries. The main reason for this is probably the fear, that silver sulfate might be too soluble, and might thus contaminate the sulfuric acid battery electrolyte. The solubility of Ag_2SO_4 in sulfuric acid [4] at 20 °C has been reported to be about 0.03 mole per 1000 g H_2O. This is indeed relatively high. However, suitable separator materials are available today, allowing to create effective diffusion barriers between reference electrode and battery electrolyte.

2. Electrode potentials of Pb/PbSO₄ and PbO₂/PbSO₄ electrodes, as measured against Ag/Ag₂SO₄ reference electrodes

The voltage difference between a Pb/PbSO₄ battery electrode (negative plates) and a Ag/Ag_2SO_4 reference electrode

in *the same solution* can be calculated by considering the electrochemical cell system

$$Ag/Ag_2SO_4/aqueous\ H_2SO_4/PbSO_4/Pb$$
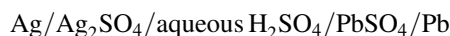
and the corresponding electrochemical process:

$$PbSO_4 + 2Ag \rightarrow Ag_2SO_4 + Pb$$
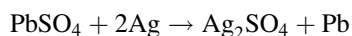
The *standard* free enthalpy of this reaction, calculated with the data of [5], amounts to

$$\Delta_r G^\circ = 194.73\ kJ$$

Under standard conditions (25 °C and 1 bar), the electrode potential difference between a Pb/PbSO₄ battery electrode and a Ag/Ag_2SO_4 reference electrode in the same solution is then given by

$$E^\circ = \frac{-\Delta_r G^\circ}{2F} = -1.0091\ V$$

This means that the Pb/PbSO₄ battery electrode is at -1.0091 V with respect to the Ag/Ag_2SO_4 reference electrode. This value is invariable, that is independent of electrolyte concentration (as long as the Pb/PbSO₄ battery electrode and the Ag/Ag_2SO_4 reference electrode are in the same electrolyte, that is at the *same* concentration).

$$E(Pb/PbSO_4)\ versus\ E(Ag/Ag_2SO_4) = -1.0091 \qquad (1)$$

It should be mentioned that the Ag/Ag_2SO_4 reference electrode is 0.0384 V positive with respect to a Hg/Hg_2SO_4 reference electrode. This difference is also independent of acid concentration.

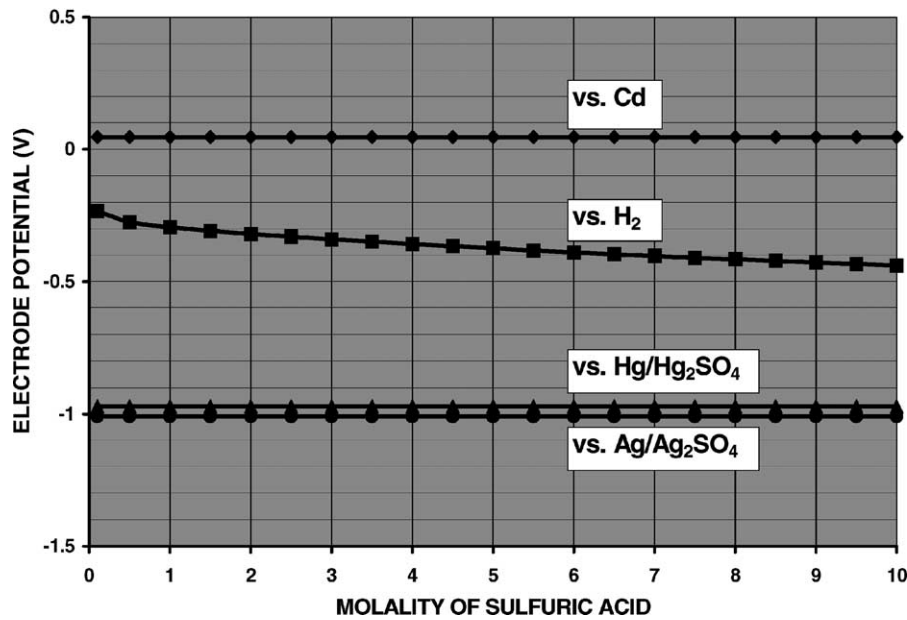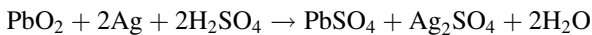*E-mail address:* paul.ruetschi@bluewin.ch (P. Ruetschi).

Fig. 1. Calculated electrode potentials of the Pb/PbSO$_4$ electrode, vs. various reference electrodes, as a function of sulfuric acid concentration.

Regarding the potential of the PbO$_2$/PbSO$_4$ battery electrode, with respect to a Ag/Ag$_2$SO$_4$ reference electrode in the same solution, it is obtained by considering the cell

Ag/Ag$_2$SO$_4$/aqueous H$_2$SO$_4$/PbSO$_4$/PbO$_2$

and the corresponding cell reaction

PbO$_2$ + 2Ag + 2H$_2$SO$_4$ → PbSO$_4$ + Ag$_2$SO$_4$ + 2H$_2$O

From the standard free enthalpy of reaction ($\Delta_r G° = -199.42$ kJ), one calculates

$E° = 1.0334$ V

The potential of the PbO$_2$/PbSO$_4$ electrode, with respect to the Ag/Ag$_2$SO$_4$ reference electrode in the same solution, depends on acid concentration in the same manner as the voltage of the lead-acid cell:

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

where a_s is the activity of sulfuric acid and a_w the activity of water. Regarding, for instance, an acid concentration of 5m, the potential of the PbO$_2$/PbSO$_4$ battery electrode versus the Ag/Ag$_2$SO$_4$ reference electrode in the same solution is calculated to be 1.0811 V, whereas at an acid concentration of 1m one obtains 0.9137 V. These values were calculated by using water activities a_w and mean ionic activity coefficients $f_\pm$ of sulfuric acid, as reported by Robinson and Stokes [6], and further by using the corresponding expression for activities of 2:1 electrolytes: $a_s = 4m^3 f_\pm^3$, where m designates the acid molality.

Figs. 1 and 2 illustrate calculated electrode potentials of PbO$_2$/PbSO$_4$ and Pb/PbSO$_4$ electrodes, against various reference electrodes (in the same solution). The potentials versus the cadmium (stick) electrode were calculated on the assumption, that the metallic cadmium surface is covered with a film of solid cadmium sulfate, and that the electrolyte at the solid–liquid interface is thus (practically) saturated with cadmium sulfate. Atmospheric oxygen readily reacts with cadmium, when wetted with sulfuric acid electrolyte, to form cadmium sulfate. The free enthalpy of formation of solid CdSO$_4$ is, according to reference [5], $\Delta_f G° = -822.72$ kJ/mole. The thermodynamically computed electrode potentials are in close agreement with experimentally observed values. Should the latter be a few millivolt higher than the calculated ones, it could simply mean, that the electrolyte at the Cd surface was not completely saturated with CdSO$_4$. In the past, the electrode potential of the cadmium (stick) electrode has sometimes been qualitatively interpreted in terms of a "mixed potential", due to (cathodic) hydrogen evolution and (anodic) cadmium dissolution. However, there is no necessity to resort to this speculative interpretation, in order to explain the experimentally observed electrode potentials.

3. Experimental

Silver–silver sulfate reference electrodes, as developed in the present study, comprise a thin-walled Teflon tubing (inner diameter 3 mm), closed at the lower end by means of a dense plug of micro-fiber glass separator material (Fig. 3). The separator plug may have a length of, for
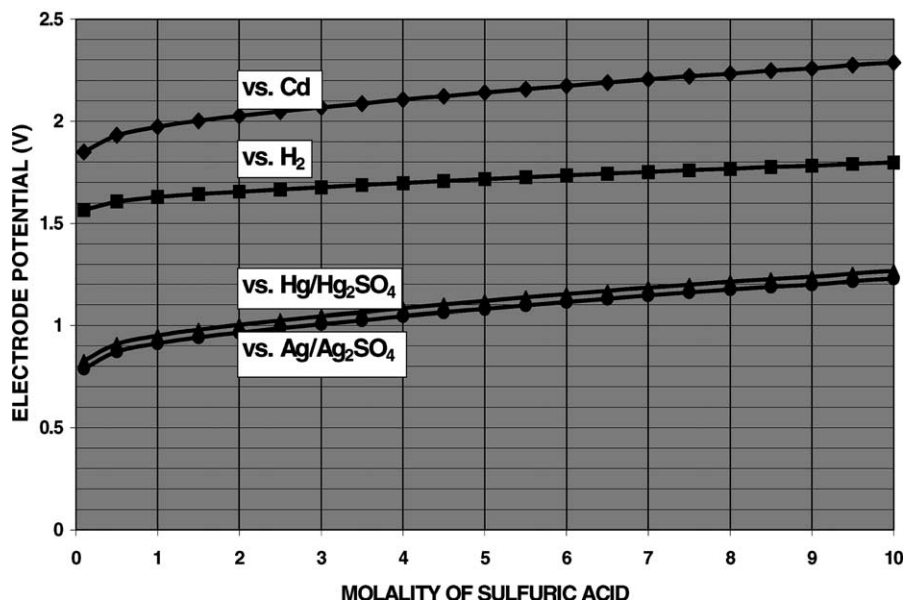
Fig. 2. Calculated electrode potentials of the PbO$_2$/PbSO4 electrode, vs. different reference electrodes, as a function of sulfuric acid concentration.

instance, 15 mm. Above the micro-fiber glass plug is placed the electrochemically active material, a mixture of silver powder, silver sulfate, (together 300 mg), a small amount of gelling agent (SiO$_2$) and sulfuric acid (all materials p.a.). The amount of sulfuric acid is calculated such as to make

Fig. 3. Construction of silver–silver sulfate reference electrodes.

sure that all the silver oxide will react to form silver sulfate. The active material mixture is dried in the Teflon tube. A silver wire makes contact to the active material mixture. At the upper end, the silver wire and its soldered connection to the socket are potted into acid-resistant epoxy resin. The safety connector has a 4 mm diameter, gold-plated contact surface. It is protected by an acid-resistant, turned plastic sleeve. Prior to use of the electrode, the micro-fiber glass plug and the active material mixture are wetted with sulfuric acid by dipping the electrode into acid of the desired concentration, during a period of preferably 100 h or more. The required amount of sulfuric acid can also be injected into the reference electrode by piercing the Teflon tubing above the active material layer, by means of a syringe. The total quantity of sulfuric acid absorbed in the reference electrode amounts to about 200 mg (for 35% acid). The electrode shown in Fig. 3 has a total length of typically 150 mm.

When using such reference electrodes in lead-acid batteries, the loss of silver sulfate to the battery electrolyte, as a result of diffusion through the micro-fiber glass plug, is estimated to be (applying Fick's law) less than a fraction of 1 mg per year (at 20 °C). These reference electrodes are mechanically quite robust and shock-proof. Their potential is easily reproducible within 1–2 mV. About 50 reference electrodes of the type shown in Fig. 3 were prepared in the course of the present study. A patent, regarding the use of Ag/Ag$_2$SO$_4$ electrodes in lead-acid batteries, has been applied for.

The reference electrodes were introduced into the lead-acid battery cells through small holes, drilled into the cell covers. The reference electrodes were placed such, that the tip was touching the electrolyte level, or, in the case of AGM
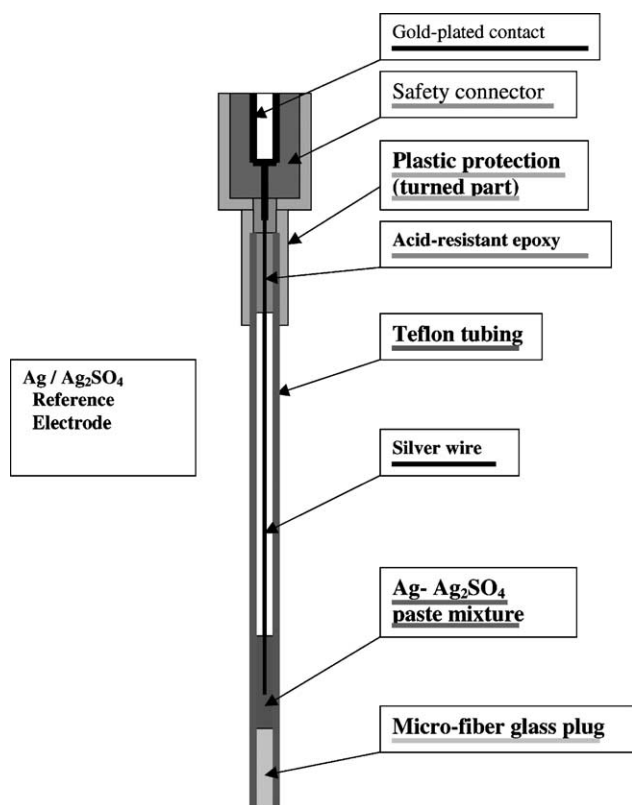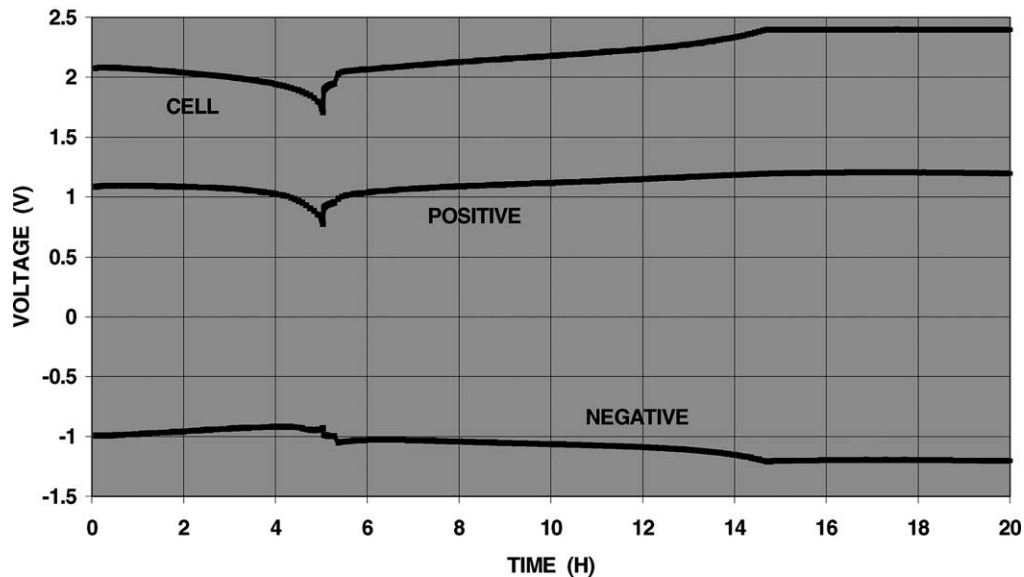
Fig. 4. Electrode potentials and cell voltage during discharge and recharge of a 150 Ah valve-regulated lead-acid battery.

cells, the electrolyte-wetted (micro-fiber separator) potentials in lead-acid cells. Fig. 4 shows measurements taken on a 150 Ah valve-regulated lead-acid battery (type Leclanché 3 SP 150), discharged at 30 A and recharged at 15 A/2.40 V. It is clearly seen that the positive electrode is limiting the cell capacity. When making measurements under current flow, the observed potential is (slightly) influenced by the position of the electrode tip, with respect to the terminal posts [7,8]. Ohmic potential drops may be evaluated using current interruption techniques.

Electrode potential measurements, using such reference electrodes, are particularly useful for diagnostic investigations at the end of service life, or during experimental abuse conditions, such as deep discharge or cell reversal.

4. Diffusion potentials as measured with Ag/Ag$_2$SO$_4$ reference electrodes

In lead-acid cells, the electrolyte concentration is not constant. It decreases during discharge and increases again during charge. Furthermore, a concentration gradient may build up between bulk electrolyte and electrolyte layers next to the electrode surfaces. Acid concentration variations are largest in the electrolyte layers near the positive plates. Especially in tall cells, concentration gradients may also be observed between top and bottom. This phenomenon is known as "stratification". *The equilibrium electrode potential of a particular electrode is determined by the local electrolyte concentration at the electrode surface.* When measuring electrode potentials in cells subject to electrolyte concentration variations, and when using *reference electrodes of constant electrolyte concentration*, one must take into account the so-called diffusion potentials, sometimes also called liquid junction potentials, or concentration cell potentials.

Silver–silver sulfate reference electrodes are particularly well suited to study such diffusion potentials. Fig. 5 shows schematically a concentration cell with two Ag/Ag$_2$SO$_4$ reference electrodes. In this figure, t_+ designates the (average) transport number of cations (protons).

The mass balance in each compartment presents itself as follows:

	Compartment I (activity a_1)	Compartment II (activity a_2)
Electrode process	$-SO_4^{2-}$	$+SO_4^{2-}$
Transported across the boundary	$+(1 - t_+)\ SO_4^{2-}$ $- 2t_+\ H^+$	$-(1 - t_+)\ SO_4^{2-}$ $+ 2t_+\ H^+$
Resulting balance	$-t_+\ H_2SO_4$	$+t_+\ H_2SO_4$

In the anode compartment (Compartment I) there will result a *loss* of t_+ mole H$_2$SO$_4$ and in the cathode compartment (Compartment II) there will result a *gain* of t_+ mole H$_2$SO$_4$.

The free enthalpy change of the overall process is then given by:

$$\Delta_D G = -2FE_D = t_+ RT \ln\left(\frac{a_2}{a_1}\right)$$

The voltage difference (diffusion potential) between two silver–silver sulfate electrodes in a concentration cell, one electrode in acid of activity a_1, and the other electrode in acid of activity a_2, is thus

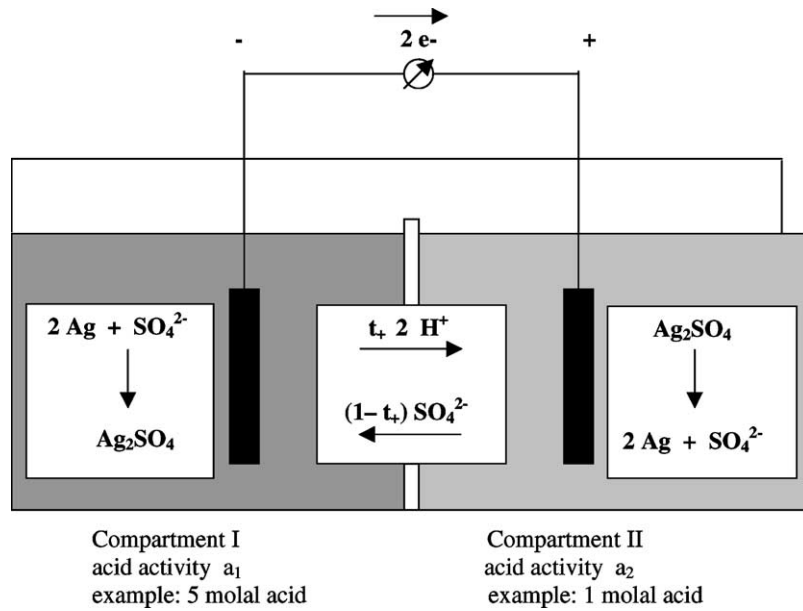$$E_D = t_+\left(\frac{RT}{2F}\right)\ln\left(\frac{a_1}{a_2}\right)$$

Fig. 5. Schematic two-compartment concentration cell with silver–silver sulfate electrodes.

where t_+ is the cation (proton) transport number. Under standard conditions (25 °C and 1 bar) the diffusion potential becomes:

$$E_D = t_+ \, 0.02958 \log\left(\frac{a_1}{a_2}\right) \tag{3}$$

Assuming, for example, an acid concentration of 5m for the first electrode (activity a_1), and of 1m for the second electrode (activity a_2), and using for t_+ a value as reported by Hamer [9] and Bode [10], that is $t_+ = 0.75$, one calculates an electrode potential difference (diffusion potential) of $E_D = 0.0598$ V. (The electrode in 1m acid is positive with respect to the electrode in 5m acid !). In reality, transport numbers are concentration-dependent [8]. However, using the above mentioned average value, one computes diffusion potentials in excellent agreement with experimentally observed values.

It is important to point out, that the result would have been the same, if the two Ag/Ag_2SO_4 electrodes in the concentration cell were replaced by other electrodes responsive to anions, such as two Hg/Hg_2SO_4 electrodes, two (saturated) $Cd/CdSO_4$ electrodes, or two lead/lead/sulfate electrodes. The diffusion potential E_D would in each case be given by Eq. (3).

When measuring electrode potentials of *negative plates in lead-acid batteries* by means of reference electrodes, the latter having an acid concentration which differs from that in the battery, the observed value will include a diffusion potential, as given by Eq. (3). If, in the course of discharge, the acid concentration near the negative plates would, for example, be lowered to a concentration of 1m (8.932%), and if one would measure the potential by means of a Ag/Ag_2SO_4 reference electrode filled with 5m acid (32.904%), the

observed potential will include a diffusion potential of $E_D = 0.0598$ V, as calculated above. The experimentally measured electrode potential is, in fact, the sum of this diffusion potential, plus the (invariant) potential difference (-1.0091 V) between the $Pb/PbSO_4$ electrode and an (imaginary) Ag/Ag_2SO_4 electrode in the *same* 1m acid. The experimentally measured potential of the negative plates is then expected to be $-1.0091 + 0.0598 = -0.9493$ V.

When measuring the potential of *positive plates*, supposed to be exposed to a local acid concentration of, for example, 1m, against a Ag/Ag_2SO_4 reference electrode, the latter
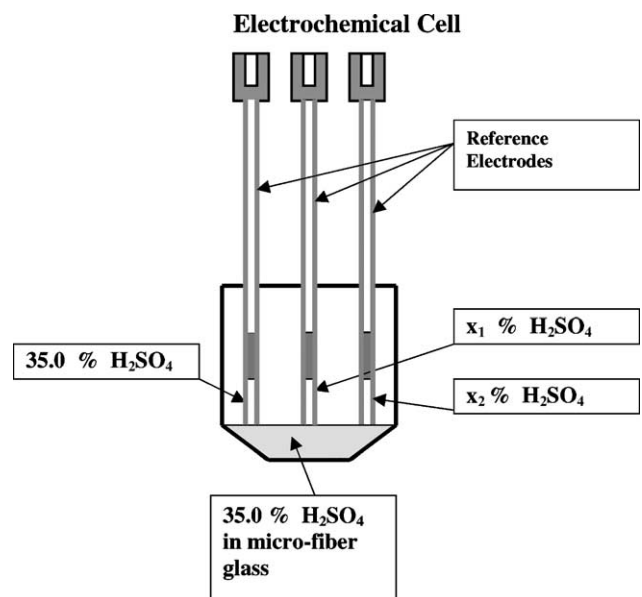

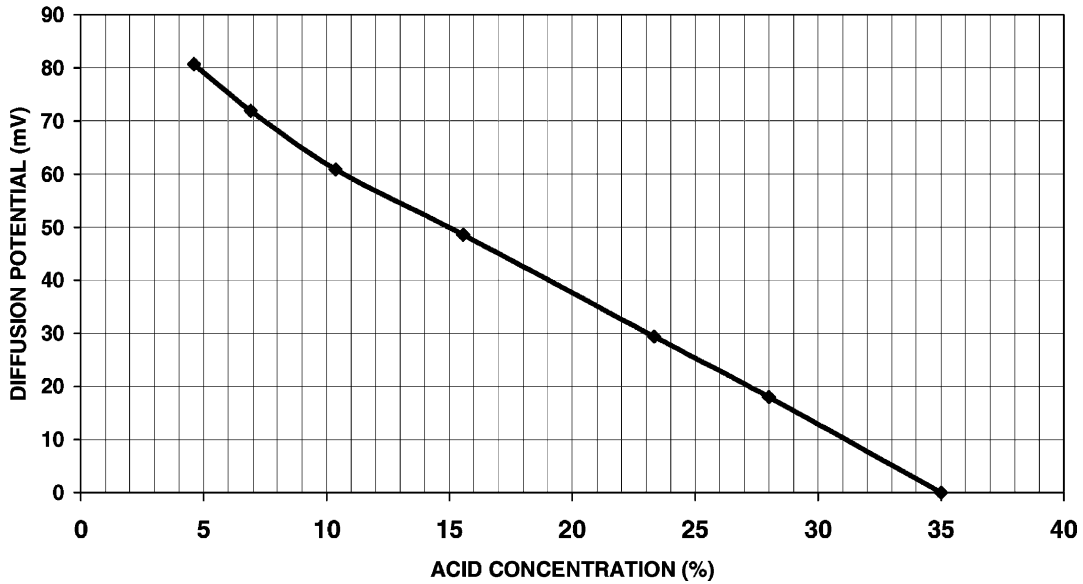Fig. 6. Experimental arrangement for the measurement of diffusion potentials.

Fig. 7. Diffusion potentials measured with silver–silver sulfate reference electrodes (dots) and calculated curve (solid line).

having itself an acid concentration of 5m, the experimentally observed potential will be given by the *sum* of the diffusion potential, as calculated above, and the potential of the $PbO_2/PbSO_4$ electrode versus an (imaginary) Ag/Ag_2SO_4 in 1m acid: $0.9137 + 0.0598 = 0.9735$ V.

Fig. 6 shows schematically the experimental glass cell, used for measuring diffusion potentials. The cell contained 20 g of 35% sulfuric acid, absorbed in micro-fiber glass separator material. The quantity of acid in the cell was thus about 100 times larger than the acid contained in the reference electrodes. Prior to placing the reference electrodes into the cell, they were wetted with acid of the desired concentration (%), by dipping them for at least 100 h in acid of precisely known concentration, between 5 and 35%. The measured diffusion potentials (at 25 °C) are shown as dots in Fig. 7. Calculated diffusion potentials (solid line), using Eq. (3), agree exactly with the measured values.

The experimentally observed diffusion potentials remained constant (within 1–2 mV) for several hours, and then began to decrease, due to equalization of acid concentration between bulk and reference electrodes, as a result of inter-diffusion. Using reference electrodes having micro-fiber glass separator plugs of 15 mm length, it took more than 100 h to equalize the
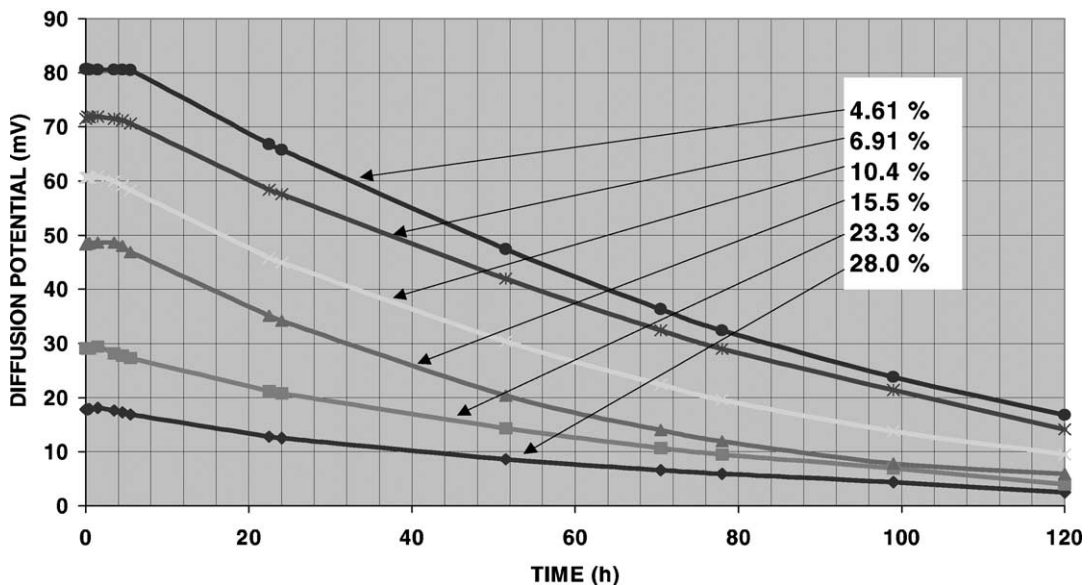

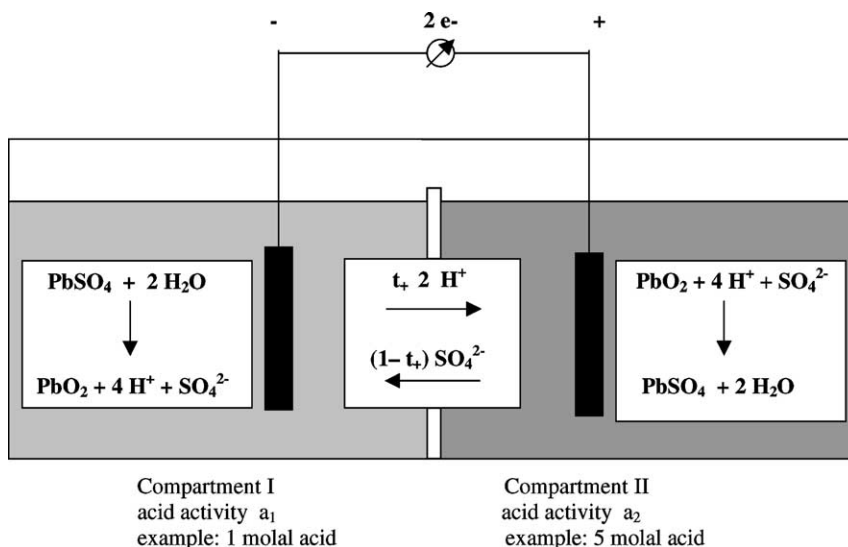Fig. 8. Decay curves of diffusion potentials.

Fig. 9. Schematic two-compartment concentration cell with $PbO_2/PbSO_4$ electrodes.

acid concentration. Diffusion potential decay curves are shown in Fig. 8. The rate of potential decay depends on compactness, diameter and length of the micro-fiber glass plug.

5. Diffusion potentials between $PbO_2/PbSO_4$ electrodes

Let us now consider a concentration cell similar to that shown in Fig. 5, but equipped with two $PbO_2/PbSO_4$ electrodes. Such a cell is depicted in Fig. 9.

Looking at the mass balance in each compartment, one has the following situation:

	Compartment I (activity a_1)	Compartment II (activity a_2)
Electrode process	$+4H^+$ $+SO_4^{2-}$ $-2H_2O$	$-4H^+$ $-SO_4^{2-}$ $+2H_2O$
Ion transfer across the liquid junction	$-t_+ 2H^+$ $+(1-t_+) SO_4^{2-}$ $-2H_2O$	$+t_+ 2H^+$ $-(1-t_+) SO_4^{2-}$ $+2H_2O$
Resulting balance	$+(2-t_+) H_2SO_4$ $-2H_2O$	$-(2-t_+) H_2SO_4$ $+2H_2O$

The free enthalpy of the overall process is given by

$$\Delta_D G = -2FE_D = (2-t_+)RT \ln\left(\frac{a_1}{a_2}\right) - 2RT \ln\left(\frac{a_{w1}}{a_{w2}}\right)$$

Under standard conditions of temperature and pressure, one obtains for the diffusion potential

$$E_D = (2-t_+) \, 0.02958 \log\left(\frac{a_2}{a_1}\right) - 0.05916 \log\left(\frac{a_{w2}}{a_{w1}}\right) \quad (4)$$

In this expression, a_{w1} and a_{w1} designate the water activity in the respective cell compartments. Assuming, for example, that Compartment I has an acid concentration of 1m (8.932%), and Compartment II an acid concentration of 5m (32.888%), and using the corresponding values for acid activity and water activity from [6], one calculates with $t_+ = 0.75$ a diffusion potential of $E_D = 0.1076$ V. (The electrode in the more concentrated acid is now positive with respect of the electrode in the more dilute acid !). For a given acid concentration ratio between the two cell compartments, the diffusion potential measured with $PbSO_4/PbO_2$ electrodes is thus considerably higher than that measured with electrodes responsive to anions, such as Hg/Hg_2SO_4, $Cd/CdSO_4$ Ag/Ag_2SO_4 or $Pb/PbSO_4$ electrodes (Fig. 10).

6. Effect of diffusion potential on acid stratification, and vice versa

Battery plates which are exposed to acid stratification will be affected by the driving force of the diffusion potential between top and bottom. The electronically conducting plates are, in fact, short-circuiting the concentration cells. Thus, the top of the *negative* plates, exposed to dilute acid, will be subject to a *cathodic* reaction (charge), and the bottom, exposed to concentrated acid, will be subject to an *anodic* reaction (discharge). A similar phenomenon, even more accentuated, occurs at the *positive* plates. The bottom of the plates will undergo a *cathodic* reaction (discharge)
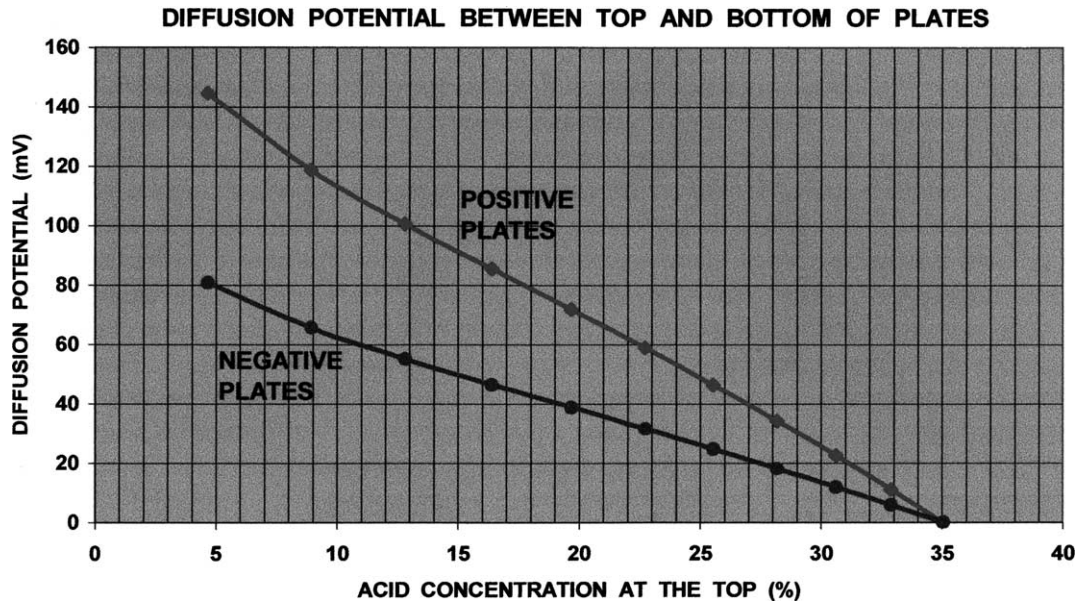
Fig. 10. Calculated diffusion potentials for two-compartment cell with $PbO_2/PbSO_4$ electrodes.

and the top of the plates an *anodic* reaction (charge). The result will be a redistribution of the state of charge. The bottom of the plates tends to be in a lower state of charge than the top. Upon recharge, more acid is then being formed at the bottom part. This mechanism thus amplifies stratification, with corresponding adverse effects on service life.

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