

A NEW LEAD/LEAD SULPHATE REFERENCE ELECTRODE FOR LEAD/ACID BATTERY RESEARCH

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Summary

A description is given of a new reference electrode made from the porous lead plate material used in the lead/acid battery. The reproducibility and stability of the equilibrium potential is achieved by keeping the state-of-charge at 0.90 ± 0.05 , and by using 4.80 M (25 °C) H_2SO_4 solution as electrolyte. The latter avoids passivation effects and minimises liquid junction potentials with the test solution. The electrode, represented as Pb(porous)/ $PbSO_4$, H_2SO_4 (4.80 M), shows a value of 0.9678 ± 0.0005 V versus an Hg/ Hg_2SO_4 electrode at 25 °C in the same solution. This potential is indefinitely stable if the electrode is reconditioned every three months by a charge-discharge cycle using conventional PbO_2 lead/acid battery plates as counter electrodes.

Introduction

Studies of positive or negative electrodes in an electrochemical cell require the use of a reference electrode. A good reference electrode should: sustain a well-defined, potential-determining reaction; have a practical potential close to the thermodynamic value for this reaction; be kinetically reversible; offer a low liquid-junction potential when coupled to the cell electrode under examination.

Reference electrodes commonly employed to investigate the behaviour of the positive and negative electrodes of lead/acid cells are of two types, namely, the Hg/ Hg_2SO_4 reference electrode and the so-called "cadmium

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reference electrode". The latter is generally used by technologists in battery manufacturing plants, while the former is preferred by research workers undertaking fundamental studies of the lead/acid system.

The characteristics of the Hg/Hg₂SO₄ reference electrode are well known [1]. Extensive use of this electrode in the lead/acid industry is prevented, however, by:

(i) the risk of contamination of batteries by mercurous ions and mercury from accidental breakage of the electrode;

(ii) the susceptibility of the electrode to develop a high polarisation resistance when subjected to vibration or mechanical shocks in the industrial environment. (Note, the adverse effect of vibration has been observed in the authors' laboratories and identified as being due to progressive coalescence of mercury that is initially dispersed in a finely-divided form in the mercurous sulphate in a good reference electrode.)

The cadmium reference electrode is simply a rod, or strip, of cadmium dipped into the H₂SO₄ electrolyte in the battery cell. This electrode is not, however, thermodynamically stable in the electrolyte and becomes corroded, with both oxygen reduction and hydrogen evolution occurring as cathodic reactions in local cells:



The relatively high solubility of CdSO₄ in the H₂SO₄ electrolyte (240 g l⁻¹ in 6 M acid [2]) ensures a continued corrosion of the cadmium as long as it is in contact with the acid. As a result, the CdSO₄ (product) accumulates in the cell electrolyte and causes unpredictable results. Finally, due to a relatively small true/apparent area ratio of the compact electrode, contamination and coverage of the electrode surface by impurities in the electrolyte is unavoidable. This leads to an uncertainty in the electrode potential by as much as ±20 mV [3].

Given that PbSO₄ is only sparingly soluble and not hydrolysed in dilute H₂SO₄, that the Pb²⁺/Pb electrode reaction is fast, and that the exchange-current density for hydrogen evolution on lead is small [4], a reference electrode of the second kind based on Pb/PbSO₄, H₂SO₄ should be of interest both from fundamental as well as applied points of view, especially for lead-acid battery research.

The development of a Pb/PbSO₄ reference electrode has been attempted before, both with, and without, the amalgamation of lead [1, 5]. Problems caused by ohmic polarisation across the poorly conducting, compact PbSO₄ film, and significant potential shifts due to the passivation of lead have, however, limited the use of this electrode system. These limitations may be ascribed mainly to the use of compact (nonporous) lead electrodes, often made worse by amalgamation which further reduces the electrode area.

A promising solution to the above difficulties is to use a highly porous lead electrode, which may be readily derived from the negative plate of

lead/acid cells, as a basis for the reference electrode. The present work shows that such a reference electrode (which is symbolically represented as Pb(porous)/PbSO₄, H₂SO₄) is stable, reproducible, and fully compatible with all aspects of lead/acid battery research.

Fundamental considerations

In the charged state, the negative plate of a lead/acid cell usually consists of a porous mass of lead (with small amounts of BaSO₄, lignin, and lamp black) distributed evenly on either side of a cast grid of lead-antimony (2 - 5 wt.%) alloy. The three additives in the porous lead active material assist in the stabilisation of the porous structure of the electrode during charge/discharge cycling, but they do not themselves take part in the potential-determining reaction at the electrode, namely:



The additives are therefore beneficial, even from the point of view of a reference electrode, provided that the electrode kinetics are fast.

Other factors of importance that should be considered in characterizing the Pb(porous)/PbSO₄, H₂SO₄ reference electrode are as follows.

(i) If the electrode is in a fully-discharged state, or nearly so (*i.e.*, state-of-charge (SOC) $\ll 1$), the lead sulphate crystals tend to grow rapidly by the 'Ostwald ripening' process, which leads to electrode passivation. The SOC of the electrode should therefore be close to unity at all times.

(ii) If the electrode is in a fully-charged state (state-of-charge = 1), there is, by definition, virtually no PbSO₄ present in the electrode or in the electrolyte. The electrode will therefore tend to behave as an ideally polarised electrode, especially in the direction of cathodic polarisation. This is not acceptable for its use as a reference electrode. It is, hence, necessary that the SOC of the electrode be less than unity.

A consideration of factors (i) and (ii) suggests that the SOC of the electrode should be close to, but not equal to, unity; a suitable value may be about 0.9, or within the range of 0.85 - 0.95 for flexible and practical operation. For a proper reference electrode, the electrode potential should, however, be independent of the actual SOC as long as the latter is neither zero nor unity. The constancy of the reference electrode potential in the proposed SOC range should therefore be verified experimentally.

(iii) In practical lead/acid cells, the specific gravity of the H₂SO₄ electrolyte varies between 1.18 and 1.28, depending on the SOC of the cell and the electrolyte temperature. If a single reference electrode is to serve the entire range of H₂SO₄ concentration in the cell, a minimal liquid-junction potential should exist between the Pb(porous)/PbSO₄ reference electrode and the test electrode when the specific gravity of the H₂SO₄ in the reference electrode compartment has a value midway in the above range, *i.e.*, 1.230 (equivalent to 4.8 M at 25 °C). The solubility of PbSO₄ in sulphuric

acid of this specific gravity is about 2.4 mg l^{-1} at 25°C [3], which is sufficiently small to ensure saturation of the electrolyte under practical conditions.

The potential of the Pb(porous)/PbSO₄, H₂SO₄ reference electrode should, however, be independent of the H₂SO₄ concentration when measured against an Hg/Hg₂SO₄ electrode in the same electrolyte. Again, this aspect requires experimental verification.

In summary, the above fundamental considerations suggest that the Pb(porous)/PbSO₄, H₂SO₄ (4.8 M) electrode at an SOC of 0.90 ± 0.05 offers promise as a reference electrode in lead/acid cells.

Experimental

Positive and negative lead/acid battery plates were obtained, in a formed and dried condition, from the production line at UB-MEC Batteries Ltd. The negative plates were cut to size ($\sim 12 \text{ cm}^2$ exposed area) to give electrodes with a nominal capacity of 0.45 A h at the 5-h rate. The electrodes were placed between excess-capacity positive electrodes and discharged to 80% depth-of-discharge and then given 20% overcharge in H₂SO₄ (4.80 M) at 25°C . After five such cycles to ensure capacity stabilization, the negative electrodes were fully charged and then carefully discharged to an SOC between 0.85 and 0.95. One of these negative electrodes was reassembled in the following test cell with a freshly prepared Hg/Hg₂SO₄ electrode of large area, the latter being calibrated against a standard hydrogen electrode; test cell: Pb(porous)/PbSO₄, H₂SO₄ (4.80 M), Hg₂SO₄/Hg.

The H₂SO₄ in the test cell was presaturated with PbSO₄ and gently stirred *in situ* for about 24 h to equilibrate with the acid in both the porous Pb electrode and the Hg/Hg₂SO₄ electrode. Without these precautions, the cell potential showed a drift of about 10 mV, or more, when the concentration of the electrolyte was changed. Such a drift is not in accord with theory, and may be avoided by the described procedure.

Measurements of the e.m.f. of test cells at $25 \pm 0.1^\circ \text{C}$ were made with an accuracy of $\pm 10 \mu\text{V}$ using a high input-impedance electrometer (Keithley) with a precision voltage back-off (Knick Potential Source). The measurements were conducted over about three months for each of the several test cells.

In order to check the kinetic reversibility of the test electrodes, steady-state, linear polarisation studies were carried out in the galvanostatic mode, using large-capacity PbO₂ counter electrodes and an Hg/Hg₂SO₄ reference electrode with a Luggin capillary aligned close to the centre of the test electrode. In order to determine the recovery rate of the equilibrium potential, open-circuit transients were manually recorded using the Keithley electrometer (as above) after a steady-state galvanostatic polarisation of the test electrode. The SOC was calculated on the basis of the capacity obtained in the previous cycle, and the final equilibrium values were taken after 10 h

at about 25 °C, the electrolyte being gently stirred and the cell kept covered to prevent evaporation of water.

It has been reported [7] that the positive plate of the lead/acid cell, *viz.*, PbO₂(porous)/PbSO₄, H₂SO₄, could also be used as a reference electrode. Therefore, a comparative study of this electrode was carried out. The positive electrode was conditioned in a similar manner, with two excess capacity negative electrodes as counter electrodes. For equilibrium potential measurements of the positive electrode at any given SOC, the following test cell was set up: PbO₂(porous)/PbSO₄, H₂SO₄ (4.80 M), Hg₂SO₄/Hg.

Results and discussion

Open-circuit potential

The equilibrium potential of the Pb(porous)/PbSO₄, H₂SO₄ electrode was found to be -0.9678 ± 0.0005 V at 25 °C against an Hg/Hg₂SO₄ electrode in the same electrolyte. This value was stable over a period of one month, after which it drifted gradually in the anodic direction by about 1 mV. After about three months, there was a further shift in the potential by a few mV in the anodic direction; this indicated the development of a passive film. At this stage, the test electrode was removed from the cell and given one charge/discharge cycle against opposing PbO₂ positive plates in a different container with H₂SO₄ of the same concentration as in the test cell. After adjusting the SOC to 0.90 ± 0.05 by a controlled discharge, the reference electrode was transferred to the test cell and its equilibrium potential monitored against an Hg/Hg₂SO₄ electrode in the same electrolyte as before. The original value of -0.9678 ± 0.0005 V was regained.

It follows, therefore, that a Pb(porous)/PbSO₄, H₂SO₄ reference electrode at an SOC of 0.90 ± 0.05 , fabricated from industrial lead/acid battery negative plates, has a reproducible and stable equilibrium potential of -0.9678 ± 0.0005 V *versus* Hg/Hg₂SO₄ in the same solution at 25 °C when reconditioned every month or so. This reconditioning can be accomplished by a simple charge/discharge cycle (as in a lead/acid cell) using industrial PbO₂ plates as counter electrodes. It is instructive to compare the observed reversible potential with the data reported [1] for the cell: (–)Pb(Hg)/PbSO₄, Na₂SO₄·10H₂O, Na₂SO₄(satd.)/Hg₂SO₄/Hg (+) that has a value of 0.96464 V at 25 °C. The (approximate) 3 mV shift in the cathodic direction for the potential of the new reference electrode cannot be associated with porous lead corrosion in contact with the electrolyte since any corrosion would have caused only an anodic shift. The difference is possibly due to the presence of sodium sulphate saturated in the electrolyte of the above cell which may affect the solubility of lead sulphate crystals. In any case, this minor difference in potential is perhaps acceptable for a Pb(porous)/PbSO₄ electrode to be used as a practical reference electrode for lead/acid battery research.

Polarisation measurements

The steady-state galvanostatic polarisation of a Pb(porous)/PbSO₄, H₂SO₄ electrode in the low polarisation region is shown in Fig. 1. The data show that there is a good linearity over at least 200 μV in both the cathodic and the anodic directions. Higher polarisations are neither necessary nor desirable, otherwise concentration gradients are likely to occur in the electrolyte within the porous electrode. The results in Fig. 1 also show that there is no polarisation hysteresis between the forward and reverse scans. The slope and position of the linear polarisation curve are also virtually unaffected (not shown in Fig. 1) with change in either the electrode SOC over the range 0.85 - 0.95 or the concentration of the electrolyte over the range 4 M - 5 M.

The exchange current density for the potential-determining reaction (3) may be estimated from Fig. 1 and the equation for steady-state linear polarisation in the absence of mass-transfer control, *i.e.*,

$$i_0 = - \frac{RT}{(\alpha + \beta) nF} \left(\frac{di}{d\eta} \right)_{\eta \rightarrow 0} \quad (4)$$

Assuming that $(\alpha + \beta)$ is close to unity (often true), the slope of the line in Fig. 1 gives, with eqn. (4):

$$i_0 \approx 10^{-3} \text{ A cm}^{-2}$$

This value for the exchange current density, which is characteristic of a 'fast' electrode reaction, may be compared with that reported [5] from a.c.

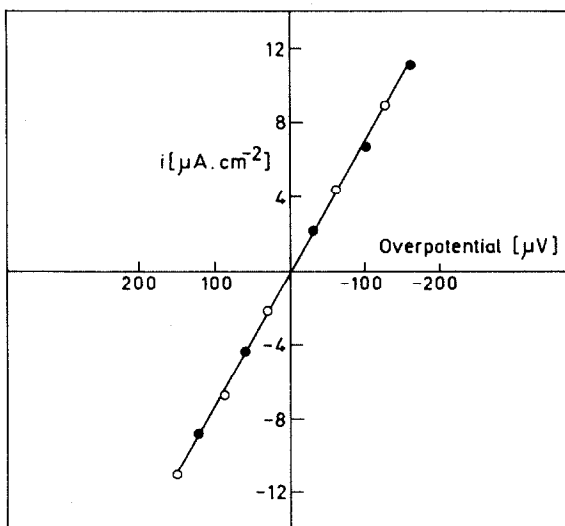


Fig. 1. Steady-state galvanostatic linear polarisation data for Pb(porous)/PbSO₄ electrode in H₂SO₄ solution. ●, Increasing polarisation starting from zero current in the cathodic (or anodic) direction; ○, decreasing polarisation from the far-end of cathodic (or anodic) polarisation. $\eta = 0$ corresponds to $-0.9678 \text{ V vs. Hg/Hg}_2\text{SO}_4$ electrode in the same solution. SOC = 0.90 ± 0.05 .

impedance data for a Pb(compact)/PbSO₄ electrode, namely, 10^{-6} - 10^{-8} A cm⁻². The 3 - 5 orders-of-magnitude higher exchange current density obtained in the present work is attributable mainly to the porous structure of the electrode.

Open-circuit potential transients

The open-circuit recovery transients of the Pb(porous)/PbSO₄, H₂SO₄ electrode subjected to a prior galvanostatic polarisation are shown in Fig. 2. It can be seen that the electrode recovers its equilibrium potential within a few minutes after cessation of a prior small polarisation. The equilibrium potential is retained for several weeks (not shown in the Figure) unlike the case with compact electrodes [6].

Effect of temperature

As calculated from Fig. 3, the equilibrium e.m.f. of the Pb(porous)/PbSO₄, H₂SO₄ (4.80 M), Hg₂SO₄/Hg cell shows only a small positive temperature coefficient of 0.16 mV °C⁻¹. Data obtained with a Pb(porous)/PbSO₄, H₂SO₄ reference electrode at any temperature may therefore be transposed, without significant error, to an Hg/Hg₂SO₄ reference electrode at the same temperature in practical systems.

Effect of state-of-charge

Figure 4 shows the variation of the equilibrium potential of a Pb(porous)/PbSO₄, H₂SO₄ reference electrode with SOC (curve 1). For comparison, similar data obtained with a PbO₂(porous)/PbSO₄, H₂SO₄ electrode

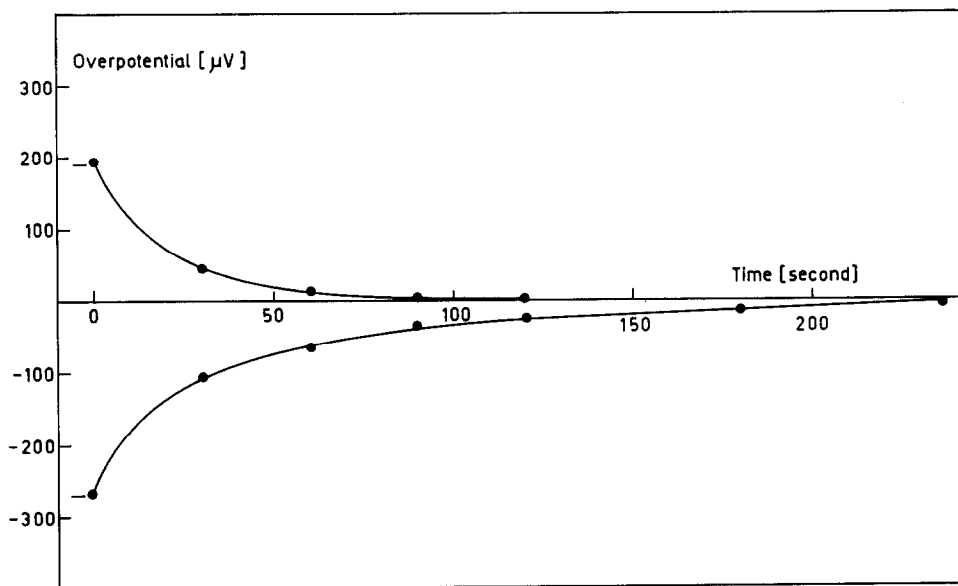


Fig. 2. Polarisation decay transients for Pb(porous)/PbSO₄, H₂SO₄ electrode on open circuit following a steady-state galvanostatic polarisation. SOC = 0.90 ± 0.05.

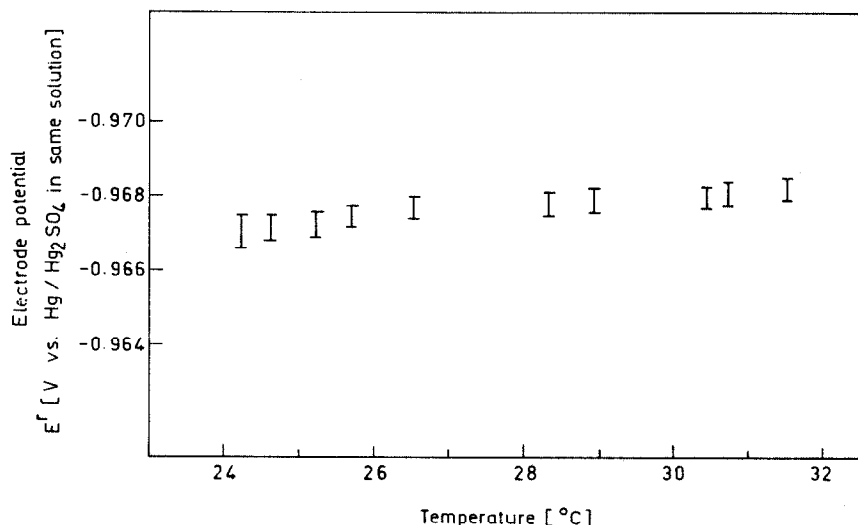


Fig. 3. Equilibrium potential (E^r) of Pb(porous)/PbSO₄, H₂SO₄ electrode at different temperatures. SOC = 0.90 ± 0.05.

is also shown (curve 2). At an SOC close to unity and zero, the equilibrium potentials are mixed potentials due to the near-absence of oxidants in the negative active material (curve 1), or reductants in the positive active material (curve 2). For either electrode, an SOC from about 0.2 to 0.95 corresponds to the respective equilibrium potential for the electrode. As the SOC approaches zero, the potential of the negative electrode shifts to more positive values than the reversible value, indicating a tendency towards passivation. For the PbO₂ electrode, on the other hand, the electrode potential moves to more negative values than the reversible potential, indicating a tendency for deactivation by sulphation.

The slopes of the equilibrium potential *versus* SOC curves are ±0.5 and 22 mV/decade for the porous Pb electrode and the porous PbO₂ electrode, respectively. This clearly shows the superiority of the Pb(porous)/PbSO₄, H₂SO₄ electrode over the PbO₂/PbSO₄, H₂SO₄ electrode as an industrial reference electrode, even though the latter has been used for this purpose in some cases. This difference in behaviour of positive and negative electrodes may be due to the different mechanisms of the two electrodes as described in the literature [8 - 10].

The effect of antimony dissolution from the electrode grid (substrate) was not evaluated separately in the present work, since the utility of production-line battery electrodes as possible reference electrodes was the main objective.

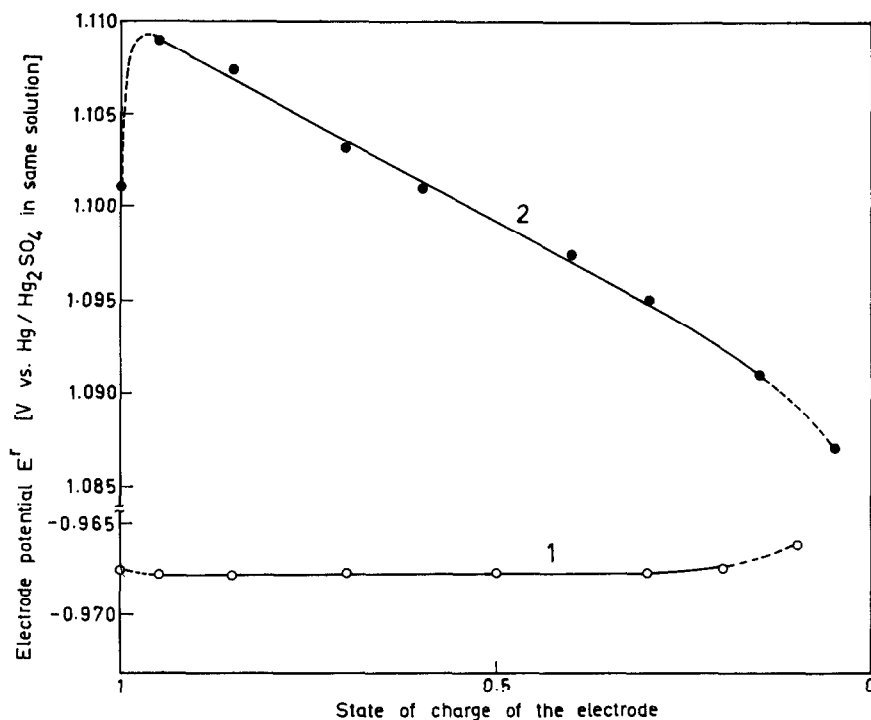


Fig. 4. Dependence of the equilibrium potential (E^r) of Pb(porous)/PbSO₄, H₂SO₄ (4.80 M) electrode (curve 1) and of PbO₂/PbSO₄, H₂SO₄ (4.80 M) electrode (curve 2) on SOC at 25 °C.

From the above observations, it is concluded that the Pb(porous)/PbSO₄, H₂SO₄ reference electrode exhibits a stable and reproducible equilibrium potential. The electrode is also kinetically reversible and quickly recovers from any (unintentional) polarisation. The electrode is easily prepared from the negative plate of commercial lead/acid batteries, and its potential is close to its thermodynamic value. The potential is independent of the SOC of the electrode, although it is desirable to keep the latter within the range of about 0.85 to 0.95 for long-term stability. There is no contamination of the battery system by foreign ions with this reference electrode.

The Pb(porous)/PbSO₄, H₂SO₄ (4.80 M) reference electrode has been successfully employed for in-plant research and development work on lead/acid batteries at UB-MEC Batteries Ltd. Operational convenience has been enhanced by immobilizing the H₂SO₄ electrolyte in the reference electrode through the addition of sodium silicate [11]. The gelled electrolyte has been found to have no significant effect on the value, or stability, of the equilibrium potential of the electrode.

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List of symbols

- i_0 Exchange current density at an electrode
 i Current density at an electrode (cathodic current positive)
 E Electrode potential
 E^r Equilibrium electrode potential
 η Electrode polarisation = $E - E^r$
 $\alpha(\beta)$ Energy transfer coefficient for the cathodic (anodic) reaction

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