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SULFATE-SENSING ELECTRODES. THE LEAD-AMALGAM/LEAD-SULFATE ELECTRODE

(IUPAC Technical Report)

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Sulfate-sensing electrodes. The lead-amalgam/lead-sulfate electrode

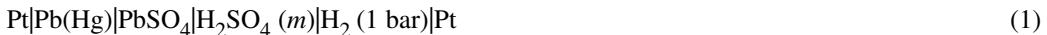
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Abstract: A new, simplified design and a convenient preparation procedure for the $\text{Pb}(\text{Hg})|\text{PbSO}_4|\text{SO}_4^{2-}$ electrode are proposed. This procedure ensures preparation of stable amalgams and reproducible electrode potentials, which make this electrode useful and attractive for both thermodynamic investigations and electroanalytical applications. For these purposes, the electrode prepared according to the proposed procedure has been exhaustively characterized both thermodynamically and as a sulfate-sensing electrode, in different sulfate solutions, including H_2SO_4 . Also, a practical standardization procedure has been proposed. The $\text{Pb}(\text{Hg})|\text{PbSO}_4|\text{SO}_4^{2-}$ electrode can be structured with a built-in concentrated Li_2SO_4 salt bridge for use as a sulfate-based reference electrode. This electrode can be operated as a reference electrode alternative to the conventional calomel or $\text{Ag}|\text{AgCl}$ reference electrodes in electroanalytical practice.

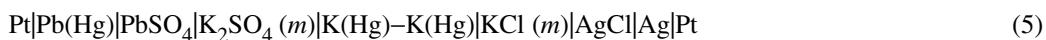
1. INTRODUCTION

It has long been recognized that sensitive and reproducible sulfate-reversible electrodes (e.g., the $\text{Pb}|\text{PbSO}_4$ or $\text{Hg}|\text{Hg}_2\text{SO}_4$ electrode) are not as readily available as chloride-reversible electrodes (e.g., a widespread $\text{Hg}|\text{Hg}_2\text{Cl}_2$ or $\text{Ag}|\text{AgCl}$ electrode) [1,2]. In this context, two major features are evident: (i) the activity solubility products of PbSO_4 and Hg_2SO_4 are larger than those of Hg_2Cl_2 and AgCl by several orders of magnitude, and (ii) in the case of the $\text{Pb}|\text{PbSO}_4$ electrode, the preparative and operational procedure had not been assessed satisfactorily until recently, so that the electrode in both $\text{Pb}|\text{PbSO}_4$ and $\text{Pb}(\text{Hg})|\text{PbSO}_4$ forms proved difficult to be used and/or unsatisfactorily reproducible. In fact, the range of the literature values of the standard potentials relevant to either electrode configuration is about 3 mV, viz. about an order of magnitude larger than that of the conventional $\text{Ag}|\text{AgCl}$ electrode. Out of these two configurations of the $\text{Pb}|\text{PbSO}_4$ electrode, the lead-amalgam-based one now proves to be reliable, because the Pb^0 -containing phase is more reproducible [2], provided that the Pb mole fraction in the amalgam varies between 0.018 and 0.66. In fact, under these experimental conditions, a two-phase system emerges at equilibrium. At this equilibrium, a liquid amalgam phase of constant composition and an intermetallic compound Pb_2Hg [3,4] are in contact. It was found that purity with respect to traces of air and spurious oxide are major factors determining accuracy and reproducibility of the measured potentials.

Before the critical redetermination performed by Fusi and Mussini [1], the literature values of the key standard potential $E^0\{\text{Pb}(\text{Hg})|\text{PbSO}_4|\text{SO}_4^{2-}\}$ of the lead-amalgam|lead-sulfate| SO_4^{2-} electrode, were mostly grouped around two distinctly different values, i.e., the higher (viz., less negative) one being close to -0.3500 V and the lower one (viz., more negative) at about -0.3526 V. The latter value is very close to the true, recently redetermined value of $-0.352\ 72 \pm 0.000\ 02$ V at $25\ ^\circ\text{C}$. This value resulted from a critical re-examination of the literature data [1] for the potentials of the following (single or double) reversible cells:



(where M = H⁺, Li⁺, Na⁺, and K⁺);



combined with new extensive and comparative potential difference measurements of the cells (1) and (2) [1]. For that purpose, a new design has been implemented and exhaustively tested for the lead-amalgam|lead-sulfate|SO₄²⁻ electrode [1] (Fig. 1).

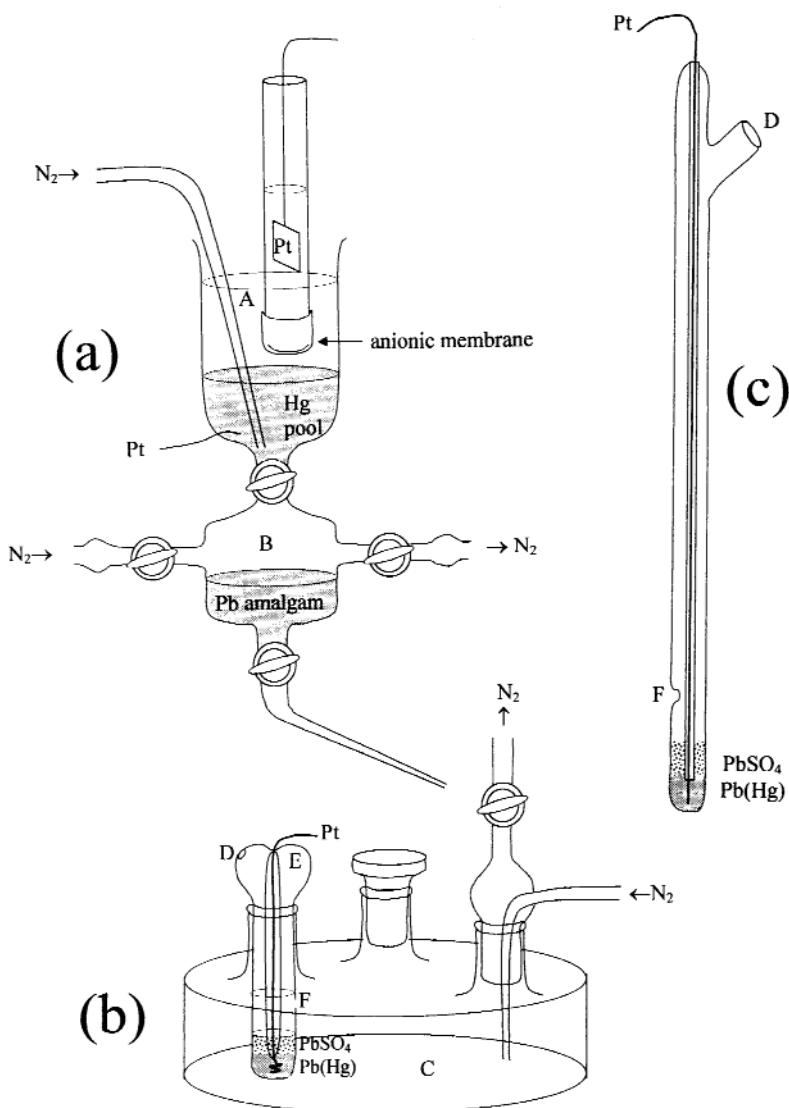
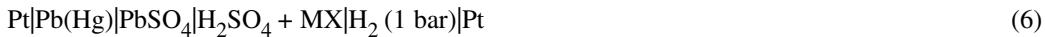


Fig. 1 (a) Scheme of apparatus for electrolytic preparation of lead amalgam; (b) laboratory assembly of a two-phase lead-amalgam|lead-sulfate electrode; (c) a compact assembly of the lead-amalgam|lead-sulfate electrode designed for small cells; (reproduced from [1] with permission).

Considering high reliability, precision, and performance of the lead-amalgam|lead-sulfate SO_4^{2-} electrode, one can now perform accurate studies of the thermodynamics of mixed electrolytes of the $\text{H}_2\text{SO}_4 + \text{MX}$ or $\text{M}_2\text{SO}_4 + \text{MX}$ types (where M = alkali metal cation, and X = Cl, Br, I) through potential difference measurements of the cells:

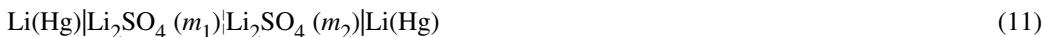


In fact, the same mixed electrolytes could not be treated if the lead-amalgam|lead-sulfate electrode in these cells were replaced by the parallel $\text{Hg}|\text{Hg}_2\text{SO}_4$ electrode, owing to the irreversible Hg_2Cl_2 precipitation.

In order to test the applicability of the $\text{Pt}|\text{Pb(Hg)}|\text{PbSO}_4$ electrode in electroanalytical chemistry, namely, as if it were operated in the ion-selective electrode (ISE) mode, supplementary extensive potential difference measurements have been carried out for two additional, irreversible cells [1]:



As shown by the cell schemes (8) and (9), operation of the $\text{Pt}|\text{Pb(Hg)}|\text{PbSO}_4$ electrode in the ISE mode requires availability of selected effective salt bridges, in order to minimize the intervening liquid junction potentials. A calomel electrode with a built-in saturated KCl bridge is appropriate here. However, it is necessary to consider a possibility of using lead-amalgam|lead-sulfate SO_4^{2-} electrodes equipped with built-in sulfate-based salt bridges, in the context of the availability of proper alternative reference electrodes for general use. Indeed, Faverio and Mussini [5] quite recently characterized concentrated Li_2SO_4 salt bridges, both in aqueous and mixed aqueous-organic solvent solutions, by using concentration cells with transference. Such cells were of following types:



It appeared that, among the unsymmetrical-valence binary salts of the SO_4^{2-} anion, only Li_2SO_4 satisfies the condition for a correct salt bridge functioning (theoretically $t_+/\text{z}_+ = t_-/\text{z}_-$) [6]. This finding suggests that a Li_2SO_4 salt bridge can be built in the lead-amalgam|lead-sulfate SO_4^{2-} electrode, analogously to the conventional calomel electrode equipped with a built-in KCl bridge, for electroanalytical use.

2. RECOMMENDED PROCEDURE OF THE $\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}$ ELECTRODE PREPARATION

The two-phase lead-amalgam electrodes can be prepared by deposition of lead on mercury cathode from aqueous $0.8 \text{ mol}\cdot\text{dm}^{-3}$ $\text{Pb}(\text{NO}_3)_2$ under a $0.02 \text{ A}\cdot\text{cm}^{-2}$ current density for 5 h, in the cathode compartment A of the cell shown schematically in Fig. 1a. The working solution is deaerated, and the mercury pool is stirred by a chromatography-grade N_2 purge. The anode is a platinum foil, and the anolyte is aqueous $6 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 . The anode compartment is a glass tube (1 cm diameter, 14 cm long) delimited by an anionic membrane ensuring the galvanic continuity with the cathode compartment. The membrane is fastened by a perforated plastic screw plug with two thin silicone rubber gaskets, which ensure watertightness. The cell operating under these conditions yields amalgams of about 0.025 atomic fraction of lead. The attainment of this condition can be tested by determining polarographically the residual content of Pb^{2+} in solutions. This test can be performed by using differential pulse polarography (DPP), through appropriate calibration curves constructed with aqueous $0.5 \text{ mol}\cdot\text{dm}^{-3}$ KNO_3 used as supporting electrolyte. The yield of lead amalgamation is close to 80 %. Then, this amalgam is trans-

ferred, still under cathodic polarization in order to avoid oxidation, into compartment B (Fig. 1a) (dearated by N₂ purge) for overnight storage at 60 °C, in order to ensure homogenization, as the amalgam turns monophasic at this temperature. Subsequently, for assembling a batch of Pb amalgam electrodes, small amounts of this monophasic Pb amalgam are transferred under N₂ counterflow into each working electrode (compartment E, Fig. 1b) and allowed to equilibrate at 25 °C, to become biphasic.

Above this amalgam pool, a layer of appropriate thickness of PbSO₄, previously equilibrated with a deaerated working electrolyte solution (aqueous H₂SO₄ or Me₂SO₄), is placed. The resulting compact, thick PbSO₄ layer ensures good mechanical stability and protects the amalgam from contact with air. The loading inlet hole D in Fig. 1b is then closed with a stopper, still under N₂ counterflow to prevent air ingress. (A remarkably more compact version of this electrode, specially designed for dimensionally critical cells, is shown in Fig. 1c.) The two-phase lead-amalgam|lead(II)-sulfate electrodes are prepared in pairs in the ad hoc C compartment (Fig. 1b) filled with the same electrolyte solution previously deaerated by N₂, in order to check their bias potential. Their mutual galvanic contact is provided by hole F.

The so-prepared lead-amalgam|lead(II)-sulfate electrode can be conveniently coupled with some another electrode. In the present cases, a mercury(II) sulfate, or even an electrode much more complicated to handle, like a flowing amalgam electrode or the hydrogen electrode, can be coupled in order to implement the required cells. Particular care must be taken to prevent exposure of the prepared electrodes to air, and in deaerating the storage compartments B.

3. THERMODYNAMIC AND ELECTROANALYTICAL CHARACTERIZATION OF THE Pb(Hg)|PbSO₄|SO₄²⁻ ELECTRODE

For accurate thermodynamic characterization of the lead-amalgam|lead(II)-sulfate electrode, Fusi and Mussini [1] followed the procedure recommended by Bates et al. [7]. This procedure was developed for cases where marked discrepancies ΔE° exist between standard potentials of electrodes determined by different schools, but there is general agreement on the required activity coefficient data. This procedure was successfully implemented earlier for the conventional silver/silver-chloride electrode [7], for which differences ΔE° in the reported standard potentials do not exceed 0.3 mV, but accurate activity coefficients for the dilute HCl solutions are available. For the present electrode, the range of the ΔE° values is about ten times as large.

Therefore, the direct determination of the key quantity, $E^\circ\{\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}\}$, was performed by measuring in quadruplicate the potential, at 25 °C, of the cell (1), expressed by the Nernstian equation, formulated as:

$$E_1 = (k/2)\lg(4m^3\gamma_\pm^3)_{\text{H}_2\text{SO}_4} - E^\circ\{\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}\} \quad (12)$$

where $k = (\ln 10)RT/F$. The selected H₂SO₄ molality was 0.1 mol·kg⁻¹, for which the mean-molal activity coefficient is $\gamma_\pm = 0.244$, determined unambiguously from three independent and exhaustive investigations [8–10]. The resulting standard potential is $E^\circ\{\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}\} = -0.352\ 72 \pm 0.000\ 02$ V at 25 °C, and it is the best, recommended value. Note, that this value is consistent with the value of $-0.353\ 06 \pm 0.000\ 60$ V [derived from inspection, cross checking, and recalculation of the literature data for the potential differences of cells (1) to (5)], considering the respective uncertainties. Using the value $E^\circ_{13} = E^\circ\{\text{Pb}^{2+}|\text{Pb(Hg)}\} - E^\circ\{\text{Pb}^{2+}|\text{Pb}\} = 0.005\ 851$ V at 25 °C, redetermined by Bates et al. [11] for the cell (13):

$$\text{Pb}|\text{Pb}^{2+}|\text{Pb(Hg)}, \quad (13)$$

one obtains $E^\circ\{\text{Pb}|\text{PbSO}_4|\text{SO}_4^{2-}\} = -0.358\ 57 \pm 0.000\ 02$ V for the companion lead|lead(II)-sulfate electrode. This datum might be useful for thermodynamic considerations but the latter electrode configuration is useless and impractical for electroanalytical applications.

The $\text{Pb}(\text{Hg})|\text{PbSO}_4|\text{SO}_4^{2-}$ electrode was characterized electroanalytically by performing systematic potential measurements of the cells (10) and (11). Obviously, a great interest in the lead-amalgam|lead(II)-sulfate electrode as a sulfate sensor for electroanalytical applications makes it desirable to control its response in various sulfate solutions. Accordingly, the potential difference, E_8 , of the cell (8) was measured. In the cell (8) this electrode, coupled with an appropriate reference electrode, is used in the ISE mode over a wide range of SO_4^{2-} activity [1]. As shown in plot A in Fig. 2, this potential difference is linear with a slope satisfactorily close to the theoretical Nernstian value $k/2$ and, as expected, the E_8 vs. $-\lg(a_{\text{SO}_4^{2-}})$ plot tends to inflect by becoming parallel to the abscissa on approaching the detection limit. The latter quantity is of the order of 10^{-4} mol·kg⁻¹, as estimated from the solubility product of PbSO_4 . The analogous linear plots for E_9 of the cell (9), where the lead sulfate electrode is replaced by a mercury(I) sulfate electrode, are parallel to those of E_8 but begin to inflect at higher SO_4^{2-} concentrations. This is because the detection limit in this case is of the order of 10^{-3} mol·kg⁻¹, in keeping with the solubility product of Hg_2SO_4 .

This analysis requires defining properly the individual ion activity, $a_{\text{SO}_4^{2-}} = m_{\text{SO}_4^{2-}} \gamma_{\text{SO}_4^{2-}}$ and the convention $\gamma_{\text{SO}_4^{2-}} = (\gamma_{\pm})^2 \text{Me}_2\text{SO}_4$ was adopted for the relevant single-ion activity coefficient. This convention is coherent with the key thermodynamic equation, $\gamma_{\text{Me}+}^2 \gamma_{\text{SO}_4^{2-}} = (\gamma_{\pm})^3 \text{Me}_2\text{SO}_4$. In the case of K_2SO_4 , the linear response is impaired at concentrations higher than ca. 0.5 mol·kg⁻¹ due to formation of the double salt $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$ [12]. The slope values determined for the Li_2SO_4 , Na_2SO_4 , and K_2SO_4 solutions were 0.0297, 0.0294, and 0.0294 V, respectively when using cell (8), and 0.0296, 0.0307 V for Na_2SO_4 and K_2SO_4 , respectively, when using cell (9). All these values are in satisfactory agreement with the theoretical slope 0.0296 V.

The obtained results show that the lead-amalgam|lead-sulfate electrode is a useful and precise electroanalytical tool as a SO_4^{2-} sensor. However, its potential role as a SO_4^{2-} -based reference electrode, analogous to the conventional Cl^- -based reference electrodes (i.e., calomel, $\text{Ag}|\text{AgCl}$, $\text{Tl}|\text{TlCl}$, equipped with built-in saturated KCl salt bridges), must be emphasized in view of reference electrodes having built-in salt bridges. Obviously, a prerequisite is the availability of appropriate SO_4^{2-} -based salt bridges. This unsymmetrical salt bridge does exist: it is a concentrated Li_2SO_4 solution, as it has been recently proven by Faverio and Mussini [5]. As it was pointed out earlier by Mussini [6], any binary ($z_+ : z_-$)-valent salt used for minimizing liquid junction potentials must be “equirtransfent”. That is, it must satisfy the condition $t_+/z_+ = t_-/|z_-|$ as closely as possible, where the t 's are the relevant ionic trans-

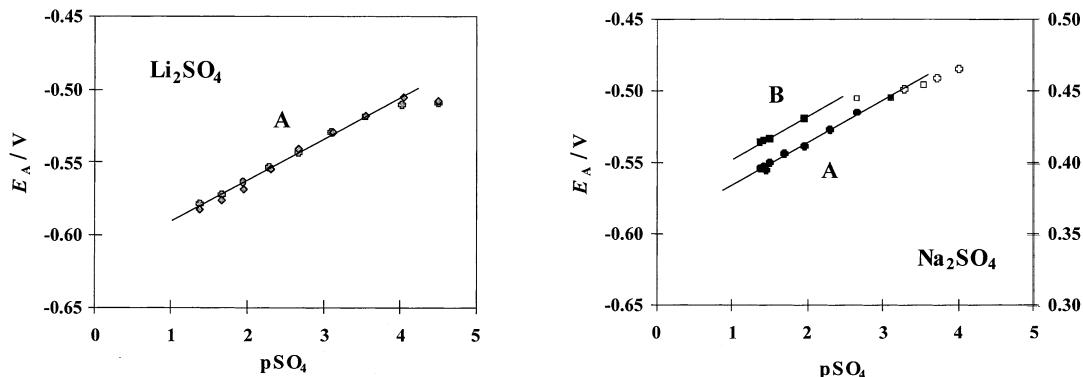


Fig. 2 Comparisons of the E vs. $-\lg(a_{\text{SO}_4^{2-}}) = \text{pSO}_4$ plots for the lead-amalgam|lead-sulfate electrode [plot A, potential differences E_8 measured for cell (8)] and the mercury|mercury-sulfate electrode [plot B, potential differences E_9 measured for cell (9)], in different aqueous M_2SO_4 solutions at different activities of sulfate anions, $a_{\text{SO}_4^{2-}}$, at 25 °C.

ference numbers. It means that this condition would be theoretically . Experimentally, it was found that an equitransference level which is as satisfactory as is that of KCl in the conventional calomel electrode. None of the other alkali metal sulfates satisfies the above condition. Using a Li_2SO_4 salt bridge of $m = 2 \text{ mol}\cdot\text{kg}^{-1}$ (whose ionic strength is $6 \text{ mol}\cdot\text{kg}^{-1}$, i.e., higher than that of the saturated KCl), Faverio, Mussini, and Mussini [5] found that the working potential of the mercury|mercurous-sulfate reference electrode is 0.6327 V at 25°C , and that of the lead-amalgam|lead-sulfate treated here is -0.3327 V .

It was recently found [5] that Li_2SO_4 is a good salt bridge also in aqueous-organic solvent mixtures, e.g., acetonitrile-water mixtures [5]. It is, therefore important, to extend the characterization and standardization of the lead-amalgam|lead-sulfate electrode to these mixed solvents.

Finally, some consideration is needed about the other PbSO_4 -based electrode, i.e., the lead-dioxide|lead-sulfate electrode. It must be noted that its technology affords satisfactory mass production of lead batteries but the problems of its electrochemical reproducibility and of the pertinent critical standard potentials are still far from being solved, in spite of the excellent study by Beck et al. [13], who determined $E^\circ = 1.6870 \text{ V}$ at 25°C . There remain still significant discrepancies with the parallel calorimetric data [2]. The key problem is that neither the electrolytic nor the chemical method of PbO_2 preparation hitherto proved completely satisfactory to yield reproducible electrode potentials. Clearly, a lot of research work is still needed, and the lead-dioxide lead-sulfate electrode is not yet at a serviceable state to electrochemists and electroanalytical chemists.

4. CONCLUSIONS

1. A new, simplified procedure for preparation and operation of the two-phase lead-amalgam|lead(II)-sulfate electrode is now offered to electrochemists and electroanalysts.
2. The recommended value of the standard potential of this electrode in aqueous solution is $E^\circ\{\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}\} = -0.352\ 72 \pm 0.000\ 02 \text{ V}$ as determined from cell (1) which constitutes the basis of the most convenient and reliable standardization procedure. Cross-checking and recalculating potential data of various interrelated cells described in the literature resulted in a value of $E^\circ\{\text{Pb(Hg)}|\text{PbSO}_4|\text{SO}_4^{2-}\} = -0.353\ 06 \pm 0.000\ 60 \text{ V}$, consistent with the above value.
3. For critical thermodynamic work, an absolute, indirect way of standardizing this electrode is recommended. Because the difference ($E - E^\circ$) is the quantity sought for most determinations, it is desirable that both E and E° are obtained by working with identically prepared electrode pairs. Such a type of standardization is based on direct comparison with the hydrogen electrode through measurements of the cell potential difference E_1 at 25°C of cell (1) for aqueous H_2SO_4 solutions of molalities selected in the range from 0.1 to $1 \text{ mol}\cdot\text{kg}^{-1}$, for which there is excellent agreement between three recently and independently revised sets of mean molal activity coefficients, γ_\pm .
4. The linear E vs. $-\lg(a_{\text{SO}_4^{2-}})$ electrode response, expected for aqueous solutions of Li_2SO_4 , Na_2SO_4 , or K_2SO_4 (based on the convention $\gamma_{\text{SO}_4^{2-}} = \gamma_\pm^2$ for the single- SO_4^{2-} -ion activity coefficient), satisfactorily verifies the expected $k/2$ Nernstian slope.
5. The lead-amalgam|lead-sulfate electrode can be equipped with a built-in Li_2SO_4 ($2 \text{ mol}\cdot\text{kg}^{-1}$) salt bridge to result in the reference electrode $\text{Pb(Hg)}|\text{PbSO}_4|\text{Li}_2\text{SO}_4$ ($2 \text{ mol}\cdot\text{kg}^{-1}$). The standard potential of this electrode is $E^\circ = -0.3327 \text{ V}$ at 25°C . This electrode is recommended as an alternative to the widespread Cl^- -based reference electrodes, if the latter are incompatible with a test solution.
6. Li_2SO_4 has favorable properties as a salt bridge also in some mixed aqueous-organic solvents, e.g., acetonitrile-water mixtures, and its combination with the lead-amalgam|lead-sulfate electrode in such solvents is an interesting perspective, for which further accumulation of data is awaited.

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