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A SILVER/SILVER SULPHIDE SELECTIVE ELECTRODE PREPARED BY MEANS OF CHEMICAL TREATMENT OF SILVER WIRE

D.Dobčnik, I.Gros and M.Kolar

Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia

Summary. The preparation and usability of a sulphide ion selective electrode, prepared by means of chemical pretreatment of silver wire with an ammonium perdisulphate solution, and the sulphidization in an alkaline sulphide solution are described. The electrode is suitable for direct potentiometric measuring of sulphide in alkaline solutions of concentrations down to 1×10^{-6} mol/L. The 45 min required for each chemical treatment are enough for the preparation of the described electrode.

INTRODUCTION

Ag/Ag₂S electrodes are prepared by means of anodic polarization of a silver rod in a solution of sodium sulphide [1], by dipping the platinum spiral, coated with porous silver, into a solution of hydrogen sulphide [2], by sulphidizing the silver wire with sulphur vapor in nitrogenous atmosphere [3] as well as by sulphidizing with copper-alloyed silver wire in a saturated alkaline solution of sodium sulphide [4]. The authors state that even after six days of chemical treatment no black sulphide layer was observed on the surface of a pure silver wire (99.99%) which suggests that the silver sulphide layer is probably produced through an anodic reaction of a localized corrosion process [4].

The preparation conditions and the performance of a small size Ag/Ag₂S selective electrode are described. The analytical behaviour of this electrode, produced by chemical treatment of a silver wire, is described in terms of potential-concentration curves, electrode selectivity and titration procedures.

A series of electrodes have been prepared and investigated. Their response and selectivity to Ag⁺ and S²⁻ were measured and compared with those of a commercial Orion silver/sulphide electrode. Several titrations were performed to evaluate the performances of the electrode. The investigated electrode was found as a good substitute for the commercial silver/sulphide electrode in a wide variety of practical analytical systems. A simple preparation by means of chemical pre-treatment of a silver wire with an ammonium perdisulphate solution and sulphidization in alkaline sulphide solution were performed. The electrode has proven to be suitable for direct potentiometric measuring of sulphide in alkali solutions of concentrations down to 1x10⁻⁶ mol/l. The 45-min required for chemical treatments are enough for the preparation of the described electrodes.

EXPERIMENTAL

Reagents

All the chemicals used were of the analytical grade and all the solutions were prepared in doubly distilled water.

A SAOB [5] solution was prepared by dissolving 2 moles of NaOH, 0.2 moles of ascorbic acid and 0.2 moles of Na₂EDTA in water and diluting them to a final volume of 1000 mL.

Standard silver solutions were prepared from a stock solution (0.1 mol Ag⁺/L) by sequential dilution with 0.1 mol/L KNO₃.

A stock solution of Na₂S was prepared by dissolving the reagent grade Na₂Sx9H₂O in 25%(v/v) SAOB [5]. It was standardized iodometrically by titration with a Na₂S₂O₃ solution. Standard solutions were prepared from a stock solution by sequential dilution with 25%(v/v) SAOB.

Preparation of electrodes

The pure silver wire (99.99% Ag) between 0.8 and 1.0 mm in diameter was connected with a copper wire and adhered into a glass tube with epoxy resin. The free Ag-wire should be 10 to 15 mm long. The wire is furtheron treated in HNO_3 (1+1) for approximately 10 s and thoroughly washed with doubly distilled water; then was immersed into a 0.1 mol/L solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 15 min. After being washed with the doubly distilled water, the electrode was sulphidized in a 0.1 mol/L alkaline solution of Na_2S for 30 min. Finally the electrode was thoroughly washed with doubly distilled water.

Apparatus

All potentiometric measurments on sulphide electrodes were performed with a digital mV/pH meter ISKRA MA 5730. The ISKRA saturated calomel electrode (SCE) with 0.1 mol/L KNO_3 salt bridge was used as a standard reference elektrode.

Comparative measurments were made with ORION 94-16 sulphide electrode.

All measurments were carried out at 298 ± 0.1 K.

RESULTS AND DISCUSSION

Surface analysis

The depth-profile diagram obtained by the Auger electron spectrometer (PHI SAM model 545 A) shows a quantitative elemental composition of atomic layers on the surface of the silver wire. As can be seen from Fig.1, the stoichometric composition of Ag_2S is found only in the first atomic layers on the surface of the silver wire. The broadening of the concentration profile is typical of the rough surface of the chemically etched metal surface [6, 7].

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Figure 1. The AES composition-depth profile of a sulphidized silver wire obtained by sputtering with 1 keV Ar^+ ions at a 47° incidence angle and a raster size of 10 mm x 10 mm.

Potentiometric behaviour

Response of the silver/silver sulphide wire electrode to Ag^+ and S^{2-} ions

The equilibrium potentials observed during the serial dilution of 0.1 mol/L silver nitrate in the measuring cell were plotted against $\log C_{\text{Ag}^+}$. A linear response with a slope of 58.8 mV per concentration decade (59.1 mV/decade for a theoretical Nernstian response) was obtained in the concentration range from 10^{-1} to less than 10^{-5} mol/L, followed by a non linear region at lower concentrations (Fig. 2). The same procedure was used for the sulphide ion response plot in an alkaline SAOB solution containing ascorbic acid. A linear response for E vs. $\log C_{\text{S}^{2-}}$ over the range from 0.1 to nearly 10^{-6} mol/L with the slope of 28.1 mV per concentration decade (29.55 mV/decade theoretical) was recorded as shown in Figure 3. A deviation from linear behaviour was observed in the concentration range from 10^{-6} to 10^{-7} mol/L.

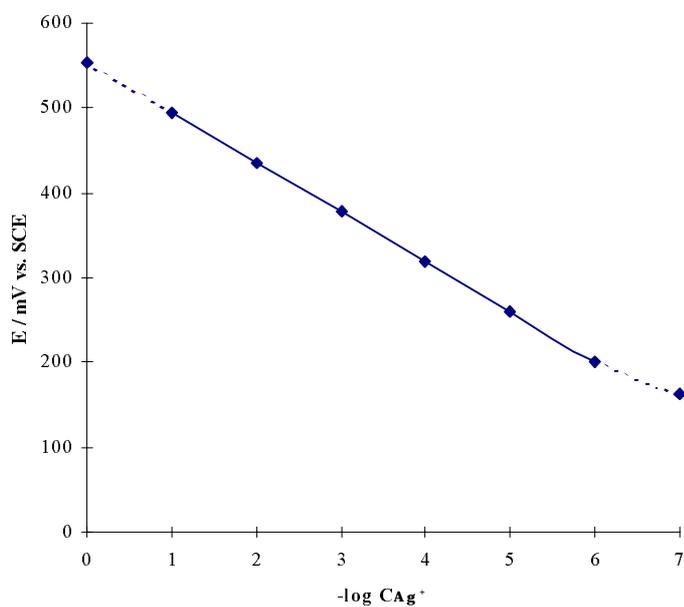


Figure 2. Response of the silver / silver sulphide electrode to the silver ion concentrations in 0.1 mol/L KNO_3

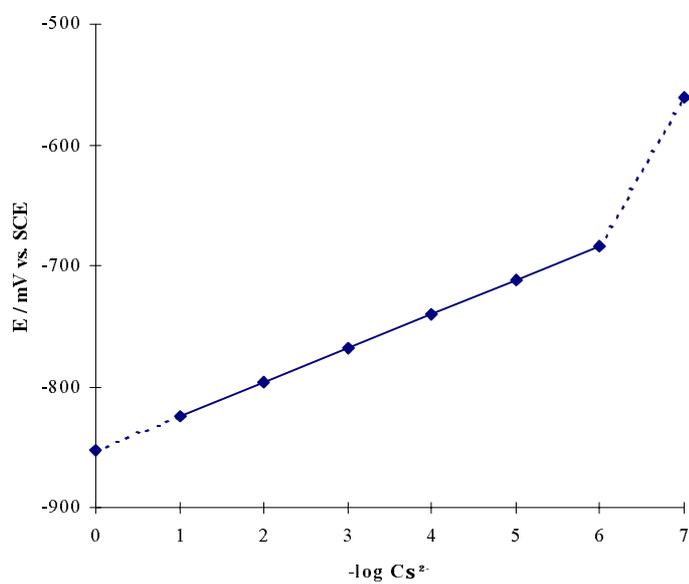


Figure 3. Response of the silver / silver sulphide electrode to the sulphide ion concentrations in 25% (v/v) SAOB

The extrapolated intercepts at $\log C_{\text{Ag}^+}$ and $\log C_{\text{S}^{2-}} = 0$ in Figures 2 and 3 give us the values $K_{\text{Ag}^+} = 553.7$ mV and $K_{\text{S}^{2-}} = -852.8$ mV vs. SCE. Using this data and considering the potential of SCE (242.0 mV) two expressions that correlate the potential and the concentration of measuring ion can be written:

$$E_{\text{S}^{2-}} = -610.8 - 28.1 \log C_{\text{S}^{2-}}$$

$$E_{\text{Ag}^+} = +795.7 + 58.8 \log C_{\text{Ag}^+}$$

The effects of several anions, namely Cl^- , Br^- , SCN^- , I^- , NO_3^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ on the sulphide potential response of the electrode were tested by using the mixed solution technique [8] with a constant level of sulphide concentration 1×10^{-5} mol/L and increasing concentrations of anions in the range between 10^{-1} and 10^{-6} mol/L.

The anions have no influence in this concentration region on the measurement of sulphide. The results show that the investigated electrode can be used for selective analytical measurements in a wide variety of practical systems.

Potentiometric titrations

The wire electrode was also tested as an end-point indicator electrode in potentiometric titrations involving Ag^+ or S^{2-} ions. For comparison, the titrations were followed simultaneously with home made $\text{Ag}/\text{Ag}_2\text{S}$ electrodes and commercial silver/sulphide electrodes. The shape of the potentiometric titrations of Ag^+ ions and the actual potential values close to and beyond the end points were in excellent agreement.

Also, the comparison of the potentiometric titration of sulphide with Pb^{2+} in alkaline solution indicates that the titration curve and end point observed coincide to a satisfactory degree (Fig. 4, 5, 6, 7) throughout some differences in potential between both electrodes.

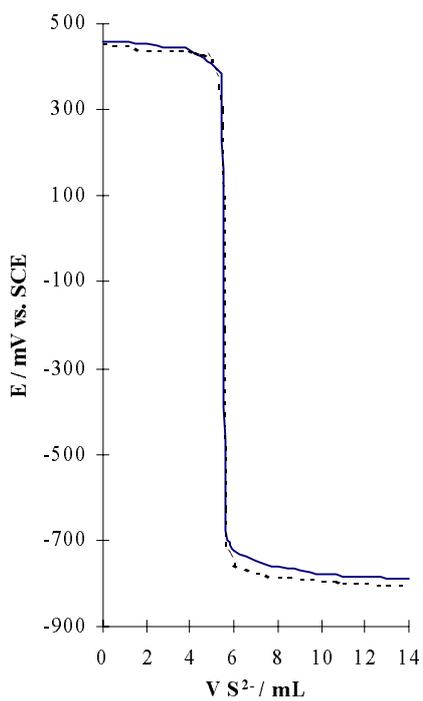


Figure 4. Ag^+ titration with 0.1 mol/L S^{2-}

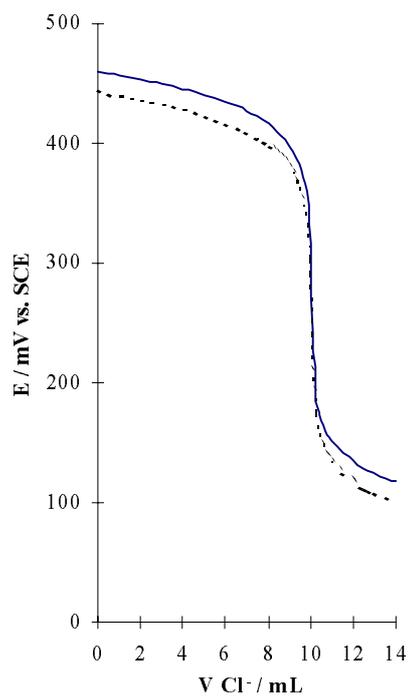


Figure 5. Ag^+ titration with 0.1 mol/L Cl^-

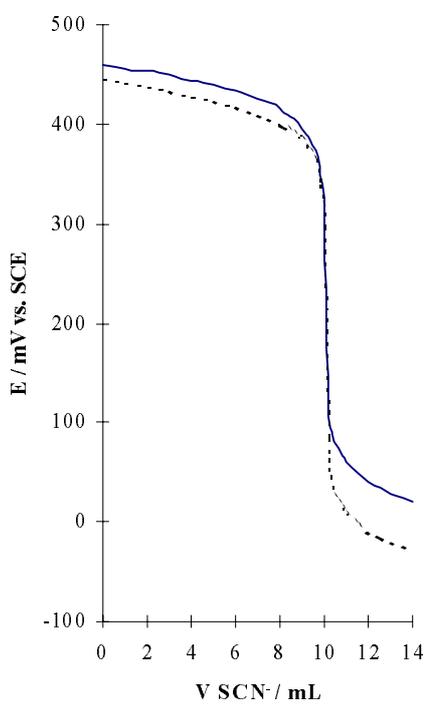


Figure 6. Ag^+ titration with 0.1 mol/L SCN^-

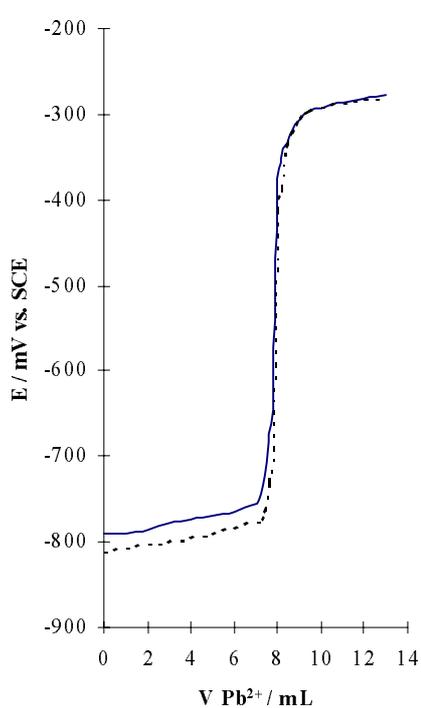


Figure 7. Sulphide titration in alkaline solution with 0.1 mol/L Pb^{2+}

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Povzetek: Opisujemo pripravo sulfidne ionoselektivne elektrode s kemijsko obdelavo srebrne žice v amonijevem peroksidisulfatu in v alkalni sulfidni raztopini. Elektroda omogoča direktne potenciometrične meritve koncentracij sulfidnih ionov v alkalnih raztopinah navzdol do 10^{-6} mol/L. Priprava elektrode je enostavna in hitra.