Conducting polymer ion sensor electrodes–III. Potentiometric sulfide ion selective electrode

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Abstract

A new potentiometric sensor electrode for sulfide based on conducting polymer films is introduced. The electrode is formed by electrochemically depositing a film of poly(3-methylthiophene) and poly(dibenzo-18-crown-6) onto an alloy substrate. Different methods were used for the electrode preparations. The alloy used has a low melting point, which allowed its use for manufacturing a microsize version of this electrode. The electrode response is stable for 3 days. The working temperature range for this electrode is between 10 and 40°C. The linear dynamic range is 1.0×10^{-7}–1.0×10^{-2} M and measures total sulfide concentration over a range of pH from 1 to 13. The polymer electrode showed high selectivity for sulfide in the presence of many common interfering anions. The electrode is useful for the measurement of total sulfide in biological environments and can be manufactured in the micron scale. Therefore, it will be useful for the measurement within biofilms. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen sulfide is created by the decomposition of metal sulfides and organic matter. Sulfur-reducing bacteria, which use sulfur as an energy source, are the primary producers of large quantities of hydrogen sulfide [1]. These bacteria change sulfates in aqueous media to hydrogen sulfide.

Another problem caused by hydrogen sulfide in the environment is its corrosive nature to metals and other materials. The effect on metals spans the gamut from tarnishing, as with silver, to deterioration by corrosion, as in the case of iron and copper [2]. It rapidly attacks many construction materials, such as concrete. Moreover, relatively high concentrations of sulfides can cause biofouling of the ion exchangers in the water softening process and to water distribution pipes.

The sulfide ion-selective electrodes are produced in different versions [3] and have been applied for measuring sulfide in various sample

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systems [4]. The liberation of hydrogen sulfide is a significant indication of flourishing and multiplying of sulfate-reducing bacteria in biofilms [1]. Commercial sulfide ion-selective electrodes have been used for studying the production of sulfide in cultures of *Desulfovibrio desulfuricans* [1] and slurries of estuarine marshland [5]. Several research groups reported the fabrication of different sulfide ion-selective electrodes for the study of microbial environments and biofilms [6–8]. The amounts of sulfide expected in these environments from aerobic and anaerobic bacteria species are in the ranges of 1.5×10^{-6}–6.0×10^{-4} M.

In situ measurement of sulfide activity was introduced by the use of the sulfide ion-selective membrane electrodes [9]. However, the determination of total sulfide can be accomplished only after the samples are buffered to high pH by a high ionic strength buffer [10]. The direct determination of total sulfide is also possible using a sulfide ion selective electrode coupled to a pH electrode [11]. The previous electrodes, cited in the literature, are limited for use in solutions with pH values < 6.0 and have some interference problems. There are a wide variety of commercially available electrodes fabricated in standard dimensions. The pH of most waters as well as treated and untreated wastewater are above pH 6.0 [12,13]. These commercial electrodes are, thus, generally limited with respect to interfering ions, with pH limits, and are relatively expensive [8].

In this work, we are continuing our attempts toward developing solid state ion selective electrodes based on polymer technology [14–18]. The sensing matrix is a conducting polymer film deposited electrochemically on an alloy substrate. We studied different parameters of preparation affecting the response behavior and lifetime of the conducting polymer sulfide selective electrode. The effect of pH and several interfering ions are also studied. The morphology of the conducting polymer film is examined using scanning electron microscopy (SEM). We suggest a possible mechanism for the response of this electrode to sulfide ion. Moreover, the advantage of using the alloy substrate with a relatively low melting point allows the fabrication of an ultramicro-version of this sensor.

2. Experimental

2.1. Reagents and solutions

Sodium fluoride, chloride, bromide, iodide, bicarbonate, acetate, citrate, thiocyanate, nitrate, nitrite, perchlorate, borate, thiosulfate, sulfate, phosphate and sulfide were of analytical grade and were purchased from Fisher Scientific. Dibenzo-18-crown-6, 3-methylthiophene, acetonitrile, tetrabutyl ammonium tetrafluoroborate and other chemicals were purchased from Aldrich, and were treated as previously described [15]. All solutions were made up with double glass-distilled and de-ionized water. Electrode calibrations were performed on 25 ml solution in 0.1 M phosphate buffer (NaH_2PO_4/Na_2HPO_4, pH 7.0) to which concentrated (1 M) Na_2S solution was incrementally added. The pH change at the neutral pH used varied between 7.0 and 7.4 for the concentration range studied, ca. 5.0×10^{-8} to 8.0×10^{-3} M sulfide, respectively. Incremental addition of the 1 M Na_2S to the solution containing the phosphate buffer where as low as 1.0–200 μl from the stock solution. The pH change was adjusted with 1 M NaOH and 1 M HNO_3 to the pH 7. In order to check whether the preparation of the conducting polymer electrode and its pretreatment steps were successful, the response of the electrode was tested when immersed in two different concentrations of Na_2S, ca. 1.0×10^{-5} and 1.0×10^{-3} M sulfide solutions (pH 7.0), respectively. Initial calibration of the conducting polymer electrode was compared simultaneously with that of an Orion Sulfide Electrode Model 94-16.

2.2. Potentiometric measurement

Potential measurements were made with an Orion model 601A ionalyzer using an Orion model 90-02 double-junction reference electrode with a 10% KNO_3 solution in its outer chamber. All measurements were conducted in the presence of 1.00×10^{-3} M KNO_3 as an ionic strength adjuster (except in the experiments where the interference and pH effects were investigated). The measurements were carried out at $25 \pm 0.5°C$ in de-aerated solutions, unless otherwise stated. We

used the injection method [19] in which a volume of concentrated solution of primary ion, smaller than the cell volume, is injected by means of a micro-pipette into the rapidly stirred test solution in which the cell assembly had been previously conditioned. The chart-recorder (and timer) is started at the instant of injection of the concentrated sample and the response time is recorded as the time after which a stable reading of ± 5 mV is reached.

2.3. Electrode fabrication

A lead glass micropipette (1.5 mm o.d, and 0.75 mm i.d.) was used as the housing body for a low melting-point alloy (44.7% Bi, 22.6% Pb, 19.1% In, 8.3% Sn and 5.3% Cd). The alloy wire was fused into a heat-pulled glass pipette. The size of the electrode tip was controlled by the speed of pipette pulling and heating temperature. This electrode can be used for the measurement within the biofilm. The tip was then polished in order to eliminate the excess glass edges and to obtain an average exposed disc area of the alloy of $\sim 0.50–0.70$ mm diameter electrode surface. The electrode surface was carefully polished and rinsed. This is followed by the electrochemical deposition of poly(3-methylthiophene).

2.4. Electropolymerization step

The electrode surface was polished using Alpha A cloth and alumina slurry. The conducting polymer films were electrochemically grown potentiostatically at 1.65 V from a solution containing 50 mM 3-methylthiophene and 100 mM tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile (AcN) for 30 s. The electrode was then transferred to a solution containing 50 mM dibenzo-18-crown-6 and 100 mM TBATFB in AcN; a constant potential of 2.0 V was then applied to the poly(3-methylthiophene) layer for 5 min. The electrode was rinsed and dried in air for the following step. The electrode was then conditioned for use in the determination of sulfide by cycling in 50–150 mM ammonium sulfide solutions. Cycling potential limits were between 0.0 and 1.6 V (unless otherwise stated). Typically, the

electrode was cycled for 10 times at a scan rate of 50 mV s^{-1}. The number and speed of scans affected the response of the electrode. The total charge accumulated during the positive cycles (0–+1.6 V) was ~ 2670 μC and the final anodic peak current was ~ 65 μA. Presumably, the polymer film is 'doped' with sulfide anion, at this stage. The electrode was then rinsed with deionized water and inserted in a diluted sulfide solution (ca. 10 mM) until a constant potential value was reached.

3. Results and discussion

3.1. Effect of electrode preparation and pretreatment method

The response of the electrode towards sulfide ions differed according to the method used for its preparation and the pretreatment step. We have examined five different methods for electrode preparation. The methods used in this study are:
1. the base alloy is mechanically polished as described above, and then immersed in 2 M $(NH_4)_2S$ solution for different time intervals (ca. 1–15 min),
2. the base alloy is immersed in the $(NH_4)_2S$ solution and subjected to electrochemical oxidation at different positive potentials,
3. the base alloy is coated with silver by electrochemical deposition, and then treated with $(NH_4)_2S$,
4. the base alloy is coated with poly(dibenzo-18-crown-6) [17], and
5. the base alloy is coated with poly(3-methylthiophene) and a thin layer of poly(dibenzo-18-crown-6) and treated with $(NH_4)_2S$ as described above.

Figs. 1–4 show the effect of the preparation schemes on the response of the electrode towards sulfide. Fig. 1 shows the response of an $(NH_4)_2S$-treated alloy electrode in the concentration range $5.0 \times 10^{-8}–5.0 \times 10^{-3}$ M sulfide. A linear response was only observed between 5.0×10^{-4} and 5.0×10^{-3} M. This electrode showed a relatively high standard variation for twenty measurements and its lifetime was short, ca. 15 min. Reactivat-
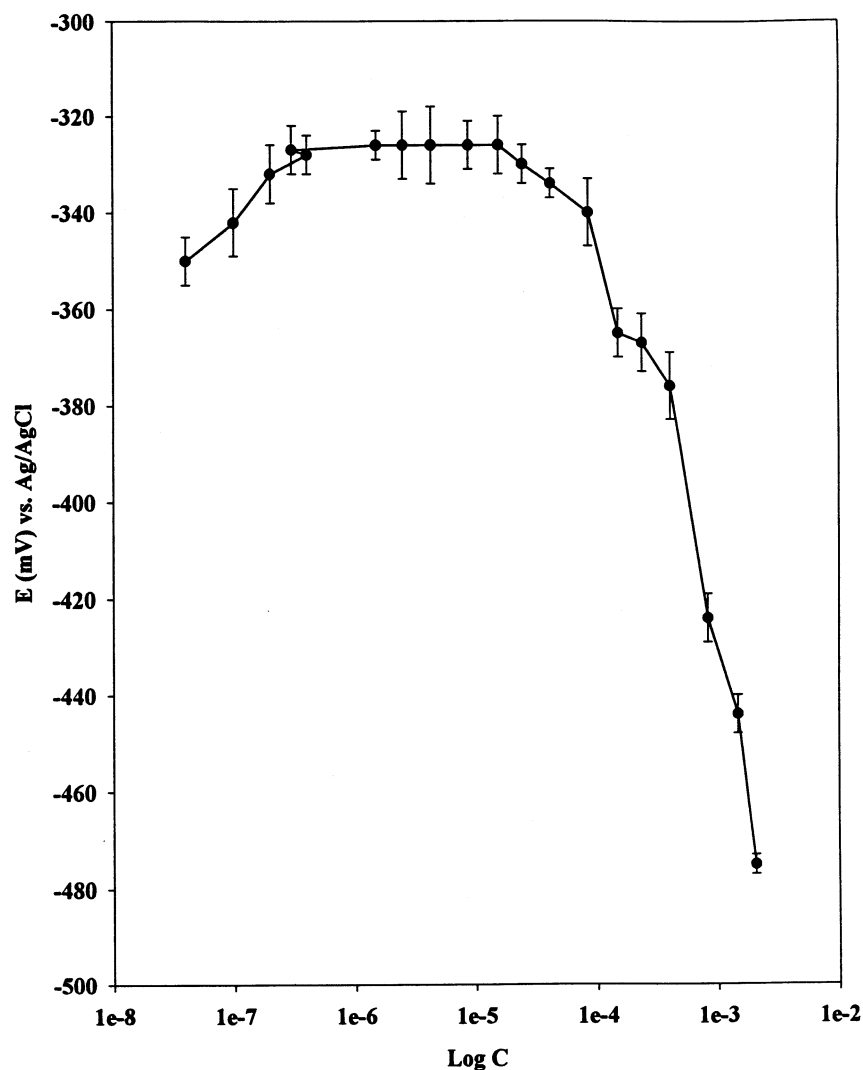
Fig. 1. Potentiometric response of $(NH_4)_2S$ treated alloy electrode to sulfide. The electrode was prepared by immersing the alloy in 2 M $(NH_4)_2S$ solution for 10 min.

ing the surface was, therefore, necessary between successive measurements.

Fig. 2 shows the potentiometric response for an electrochemically treated alloy in $(NH_4)_2S$. In this case, the electrode is subjected to repeated cycles between 0.2 and 1.5 V, with a scan rate of 100 mV s^{-1}. It was observed that the electrode response changed somewhat upon varying the limits of the potential intervals for cycling and the number of cycles, during the preparation step of the elec-

trode. The data in Fig. 2 for an electrode cycled 10 times between a 0.2 and 1.5 V potential limit is a typical example. It shows that:

1. The calibration curve exhibits two distinctly different linear portions in the concentration ranges of 5.0×10^{-8}–5.0×10^{-6} M and 5.0×10^{-6}–5.0×10^{-3} M, respectively, and
2. The standard deviation of the potential response at low concentrations of sulfide is relatively high compared to the electrode response at higher concentrations.
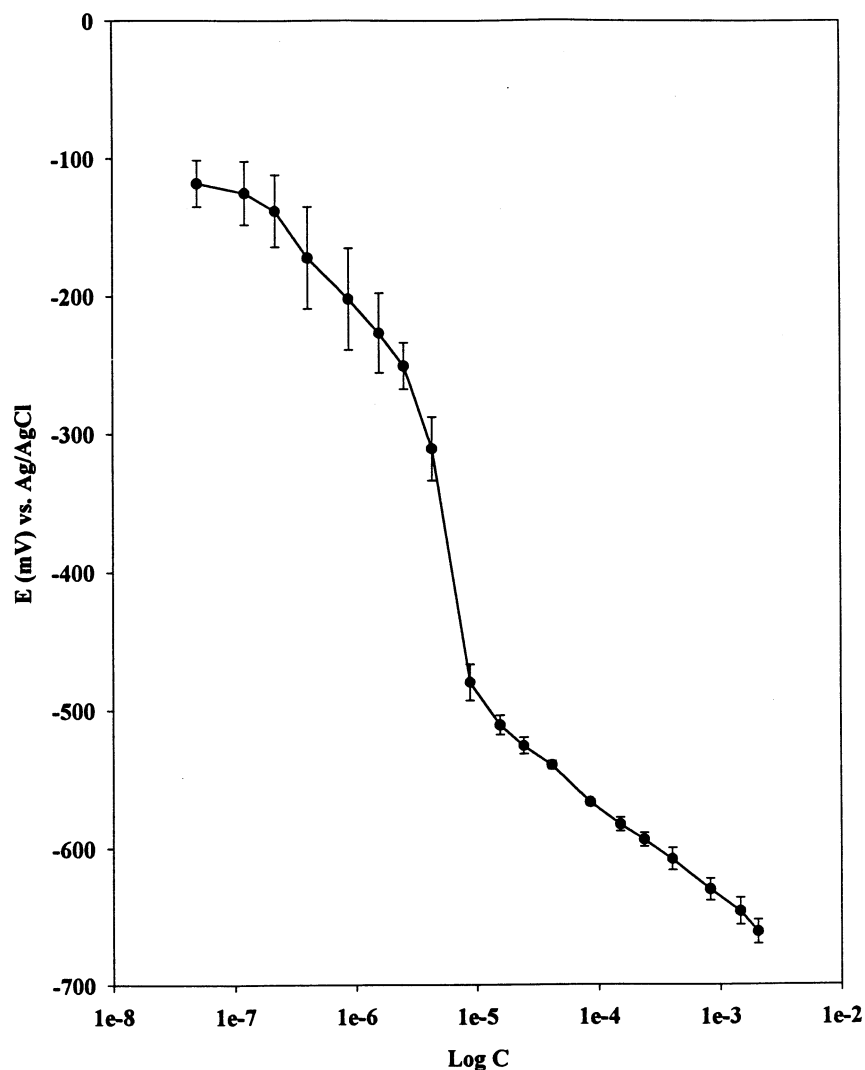
Fig. 2. Potentiometric response of $(NH_4)_2S$ electrochemically treated alloy electrode. The electrode was prepared by immersing the alloy in 2 M $(NH_4)_2S$ and subjected to constant potential of 1.4 V for 2 min.

This behavior is may be the result of the mixed composition of the base alloy that, upon exposure to $(NH_4)_2S$, forms different corresponding metal sulfides. Moreover, SEM examination of the surface of the alloy after melting and insertion into the capillary pipette shows that the surface is highly irregular with possible structure differences at the interface after the heating process (cf. Fig. 5). However, it is hard to rationalize this as the reason for the discontinuity in the two response regions, nor the high variation in the response of

the electrode at low concentrations of sulfide. Also, the stability of the electrode response for extended times, even at relatively high concentrations of sulfide, was poor. This can be explained in terms of a poor adherence of the metal sulfide layer at the surface of the electrode.

The data given in Fig. 3 show the potentiometric response of a silver-modified alloy substrate. The silver was first electrochemically deposited at the surface of the alloy. The surface was then washed with water, dried and treated with
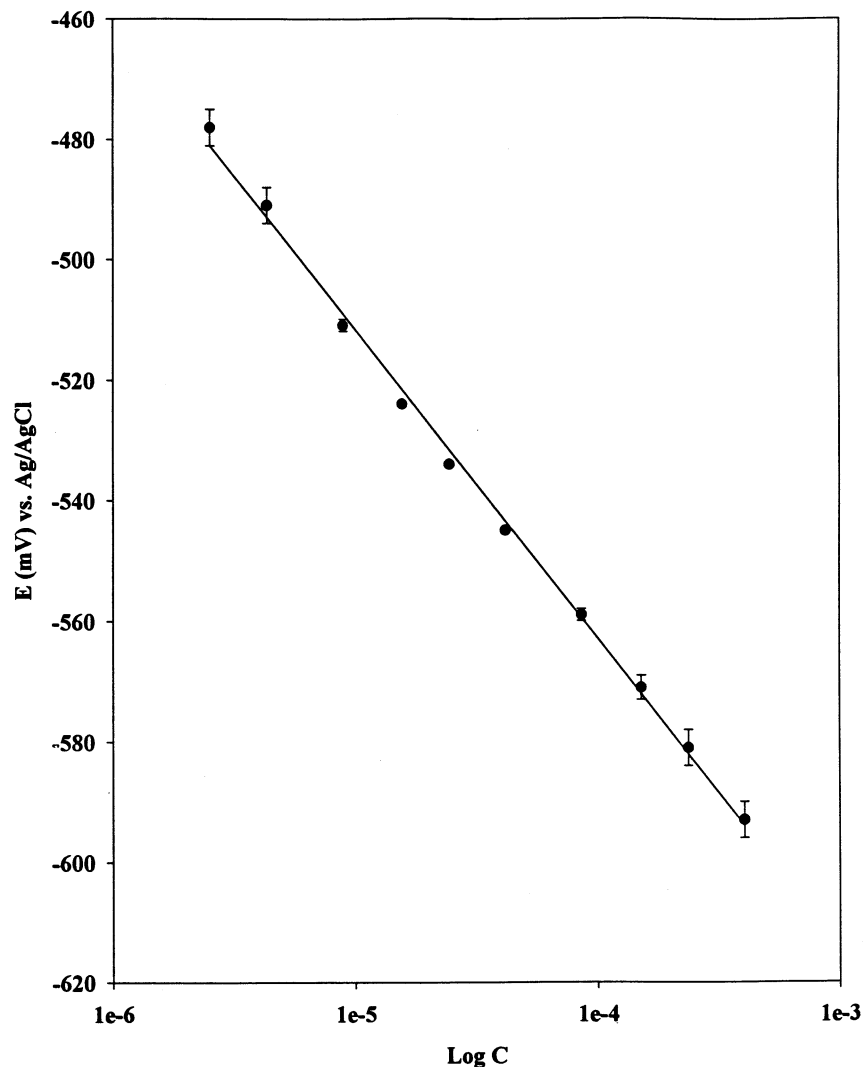
Fig. 3. Potentiometric response of Ag-coated alloy treated with $(NH_4)_2S$. The electrode was prepared by electrochemically depositing silver over the alloy substrate and then immersed in 2 M $(NH_4)_2S$ for 5 min.

$(NH_4)_2S$. The electrode showed a linear response in the range 5.0×10^{-6}–8.0×10^{-4} M sulfide. However, the response of the electrode changed considerably after 24 h of use. We noticed, upon examination with optical microscopy, that the morphology and color of the electrode surface had changed markedly. It appears that the adherence of the silver sulfide layer to the alloy substrate is weak or it dissolves over the period of 1 day.

Procedure (iv), which was previously described by Ma et al. [20], consisted of electropolymerizing dibenzo-18-crown-6 directly on the surface of a platinum electrode. The potentiometric response of this alloy electrode after the electrodeposition of the crown was unstable and irreproducible. Thus, changing the nature of the substrate from platinum to the alloy affected considerably the electrode behavior. However, the reason for using the alloy substrate rather than platinum is its relatively low melting point and the ease of con-
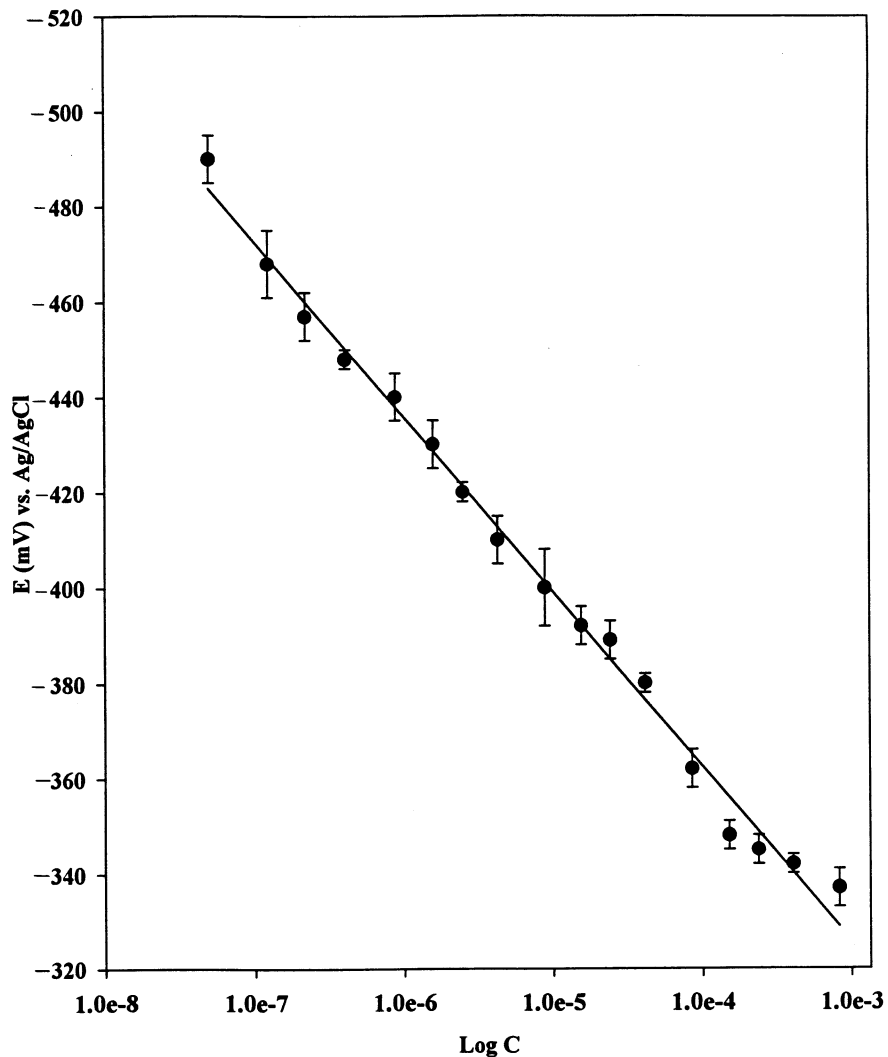
Fig. 4. Potentiometric response of conducting polymer sulfide electrode treated with $(NH_4)_2S$. The electrode was prepared as described in procedure (v) of Section 3.

structing a sulfide selective microelectrode and even ultramicroelectrode [8]. Pt and Ag could also be used to fabricate the microelectrode. However, a vertical puller, which has special heating specifications was needed for this purpose. Therefore, we used the alloy, which met the available horizontal puller heating conditions and requirements.

The response of electrodes prepared by depositing a layer of poly(3-methylthiophene), fol-lowed by the electropolymerization of the dibenzo-18-crown-6, and then electrode treate-ment in $(NH_4)_2S$, as described in Section 3, pro-cedure (v), is shown in Fig. 4. The slope for the calibration curve shown in Fig. 4 is -35.7 mV decade^{-1}, with a correlation coefficient of 0.992. The calibration curve has a linear response range between 5.0×10^{-8} and 1.0×10^{-3} M. This will allow its application for measurements in biofilms and other environmentally hazardous systems.

3.2. Optimization of the conducting polymer preparation conditions

The response of the conducting polymer sulfide electrode varied with the conditions of the electropolymerization steps. Fig. 6 shows the effect of changing the electropolymerization times for the deposition of poly(3-methylthiophene) and poly-(dibenzo-18-crown-6). The performance of the electrode was based on the Nernstian slope obtained and the lifetime of the electrode. The following conclusions are observed from the data obtained:

1. A relatively low slope is observed for the crown films formed at 5–15 min as compared to those deposited between 15 and 30 min,

2. The expected theoretical Nernstian slope is 29.5 mV decade^{-1}. Poly(3-methylthiophene) films deposited for 25 s (as indicated on the x-axis of Fig. 6) and crown films then deposited, for 20 or 30 min, gave the closest slopes to theoretical. The slopes calculated for these electrodes are in the range of -27.4 to -33.4 mV decade^{-1},

3. The pH-studies (Section 4 below) suggest that the polymer electrode responds to the total concentration of sulfide. A suggested mecha-
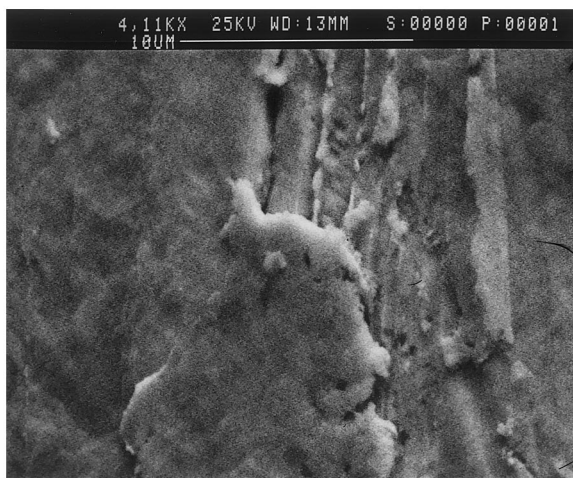

Fig. 5. Scanning electron micrograph of the alloy substrate after heating and insertion in the micropipette.

nism is illustrated in Fig. 7. The polymer film electrode is formed under oxidative conditions. In this case, the resulting oxidized polymer is doped by the counter-anions used as a supporting electrolyte during the polymerization step (TFB$^-$). The final applied potential to the polymer film in the synthesis step determines the level of doping of the film. The treatment of this polymer film in (NH$_4$)$_2$S resulted in the exchange of the preparation-step dopant (TFB$^-$) with that of the treatment-step, S^{2-} and/or HS$^-$. The number of positive 'sites' at which the exchange might take place, which in turn determines the concentration level and nature of the sulfide species within the film, is a function of several factors such as: the thickness of the polymer film, the potential used for polymerization, the level of initial doping with the TFB$^-$, the method of treatment with (NH$_4$)$_2$S, and the poly(3-methylthiophene) to poly(dibenzon-18-crown-6) ratio. The level of doping within the polymer film affects these factors as recently described [21].

4. We were not able to polymerize directly the crown ether onto the base alloy surface. On the other hand, we were able to polymerize the crown over the poly(3-methylthiophene) surface. Therefore, the poly(3-methylthiophene) is considered as the working substrate for the poly(crown ether). The role of poly(crown ether) films in solid state ion sensors was described by Ma et al. [20]. It was suggested [20] that the response mechanism of this electrode is due to the formation of hydrogen bonds and mononegative charged anions between poly-(crown ether) and guest molecules on the electrode surface. A similar hydrogen bond model is suggested in the present study. In this respect, ion-exchange or diffusion between the membrane phases and the solution phase leads to an unbalanced charge distribution. Thus, monovalent or divalent ionic species, HS$^-$ or S^{2-}, in this case, is adsorbed within the membrane. This process should predominantly take place by an ion-exchange process in order to account for the observed response. Kliza and Meyerhoff [22] proposed possible potentiometric anion response mechanisms of poly(por-
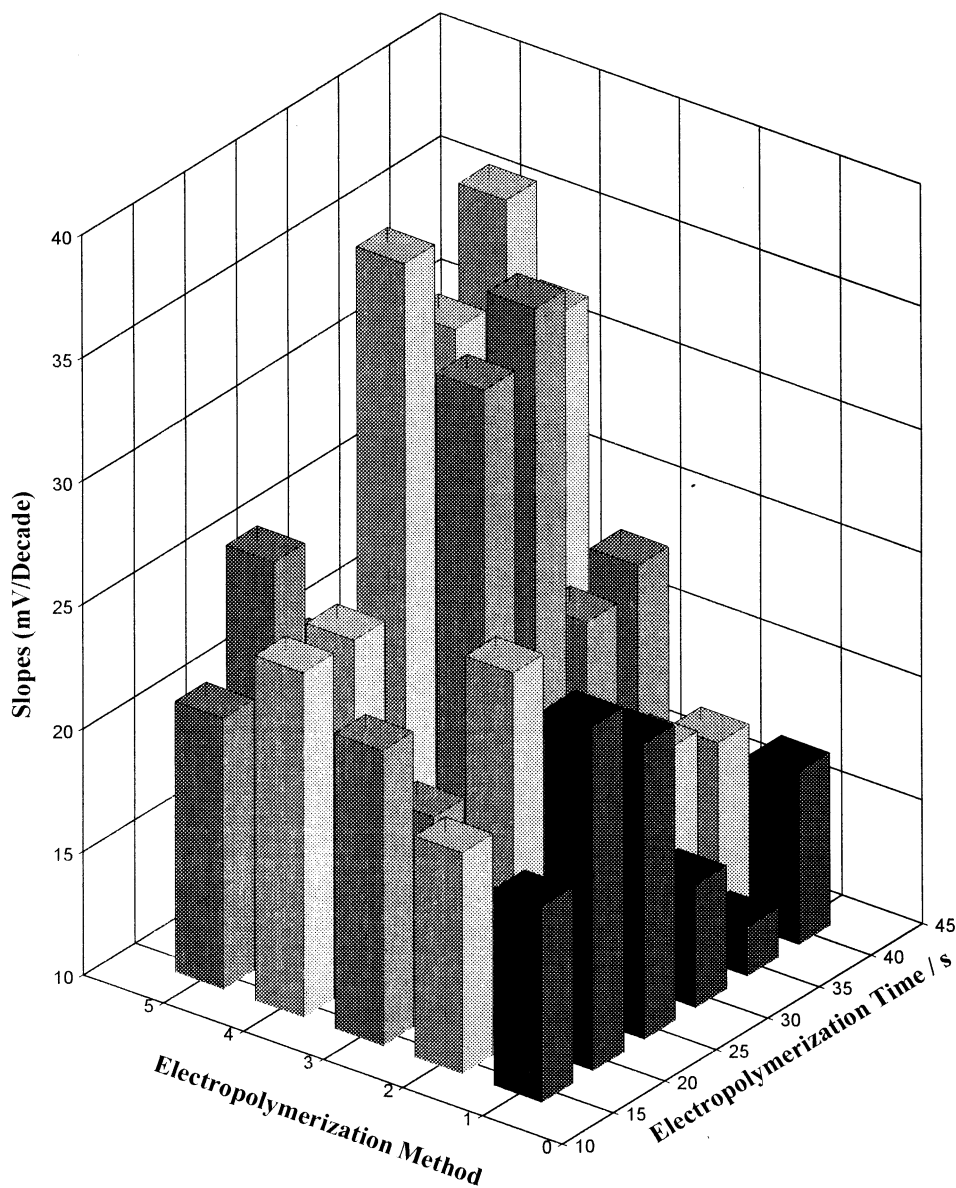
Fig. 6. Effect of varying the electropolymerization conditions of the conducting polymer sulfide electrode on the potentiometric response. Bars indicate the deposition time for crown ether (a) 5, (b) 10, (c) 15, (d) 20 and (e) 30 min.

phyrin) derivatives electrodes. Among the suggested mechanisms was a 'redox response' due to redox reaction within the conducting polymer and ion-exchange process with the anion-doped polymer backbone.

3.3. Selectivity coefficients

The electrode behavior can be represented by an equation first used by Nicolsky [23] for the glass electrode showing a mixed response to hy-
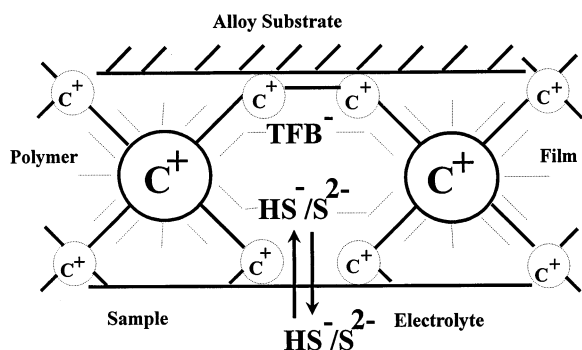
Fig. 7. Response mechanism of the conducting polymer sulfide electrode. C's represent the organic polymer film formed from the polymerization of poly(3-methylthiophene) and poly(-dibenzo-18-crown-6) in the oxidized state.

drogen and sodium ions, which can be adopted for the study of the interference effects on the conducting polymer sulfide sensor electrode:

$$E = \text{const.} \pm k \log(C_i + k_{ij}C_j)$$

and for the case of other interferents and sulfide ions as:

$$E = \pm \frac{RT}{zF} \ln\left[a_i + \sum_j K_{ij}^{\text{Pot}} a_j \right] + \text{const.}$$

where i and j are two similarly charged ions, K_{ij} is the selectivity coefficient, and K_{ij}^{Pot} is the ratio of the solubility products and activity coefficients. The selectivity coefficient of the electrode formed by procedure (v) was evaluated by the 'fixed interference method' described by Srinivasan and Rechnitz [24]. In this method, a fixed interferent concentration of 1.0×10^{-2} M was used. The results for common interfering anions are summa-

Table 1
Selectivity coefficients of the conducting polymer sulfide electrode

Anion	$\log K$	Anion	$\log K$
F^-	-5.78	SCN^-	-4.21
Cl^-	-5.12	NO_3^-	-3.84
Br^-	-4.61	NO_2^-	-3.55
I^-	-3.83	ClO_4^-	-4.05
HCO_3^{2-}	-3.55	$B_4O_7^{2-}$	-5.33
$C_2H_3O_2^-$	-4.87	$S_2O_3^{2-}$	-3.31
$(OH)(CO_2H)CH_2CO_2^{2-}$	-5.32	SO_4^{2-}	-4.18

Table 2
Technical parameters of the polymer sulfide selective electrode

| Parameter	Value
Linear concentration range (M)	1.0×10^{-7} to 1.0×10^{-1}
pH range	4–10
Detection limit (M)	2.00×10^{-9}
Temperature range (°C)	10–40
Resistance[a] (Ohm $\times 10^{-6}$)	<1
Internal reference	Solide
Reproducibility[b] (mV)	2%
Response time[c] (s)	<60
Size (o.d, i.d) (mm)	1.5, 0.70
Check point[d] (mV)	-420

[a] The ohmic resistance of the electrode after forming the polymer onto the alloy.
[b] Twenty successive preparations and measurements.
[c] Depends on the thickness of the polymer film.
[d] Measured for a freshly prepared electrode in 5.0 x 10^{-6} M sulfide.

rized in Table 1. It shows that for the large majority of anions, the selectivity coefficients are of the order of 5.0×10^{-4} or smaller. This electrode can be used successfully for the measurement of sulfide in the presence of high concentrations of sulfate ions, where the following equilibria hold:

$$2S + 3O_2 + 2H_2O = 2H_2SO_4$$

and,

$$SO_4^{2-} + 4H_2 = S^{2-} + 4H_2O$$
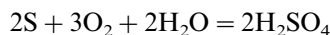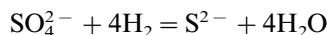
in the presence of aerobic and anaerobic bacteria, respectively.

A summary of the performance parameters for the sulfide conducting polymer electrode is given in Table 2. The data shows relatively low detection limit, fast response and a wide linear dynamic range.

3.4. pH effect

The total sulfide concentration in solution can be expressed by the following:

$$S_T = [S^{2-}]\left(1 + \frac{a_{H^+}^2}{K_1' K_2'} + \frac{a_{H^+}}{K_2'}\right)$$
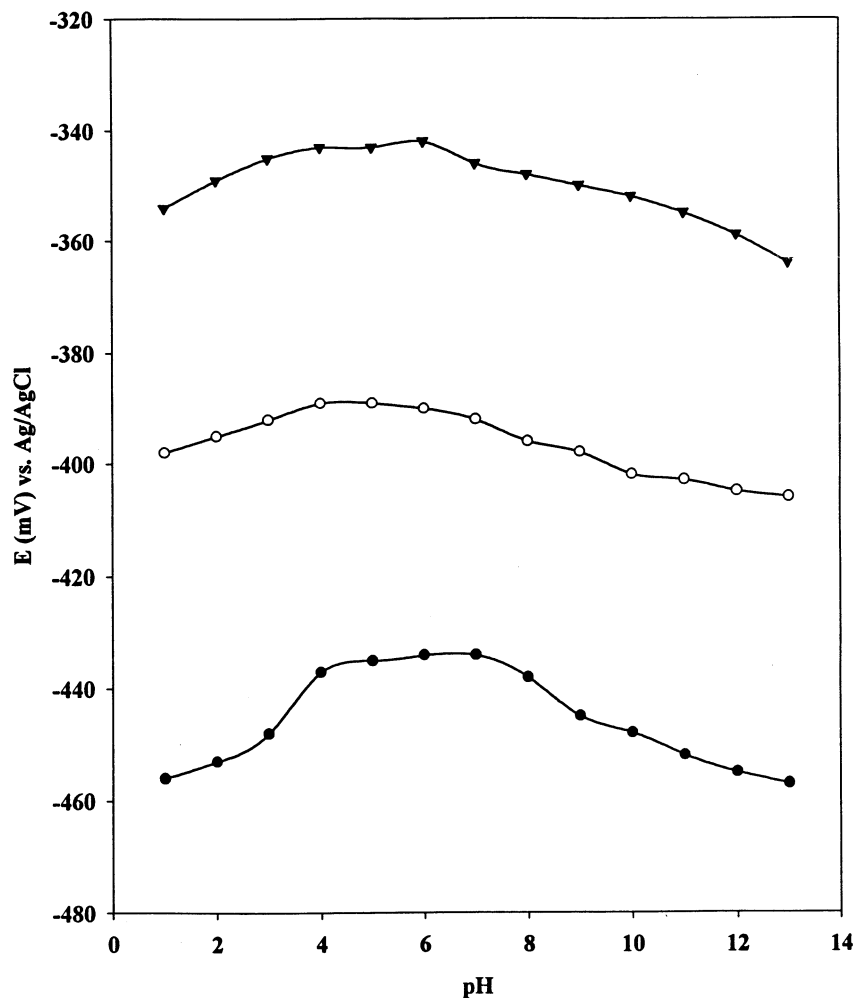
and

Fig. 8. Effect of varying the pH on the potentiometric response of the polymer sulfide electrode. (▲) 4.0×10^{-4} M, (○) 2.5×10^{-5} M, (●) 1.6×10^{-6} M sulfide.

$$S_T = [S^{2-}][HS^-] + [H_2S]K_1^{'} = \frac{a_{H^+}[HS]}{[H_2S]}K_1^{'}$$

$$= \frac{a_{H^+}[S^{2-}]}{[HS^-]}$$

S_T denotes the total sulfide in solution, and $K_1^{'}$ and $K_2^{'}$ are the apparent equilibrium constants, which are expressed in both activity and concentration terms [25]. The effect of changing the pH was examined over the range of 1.0–13.0 for 4.0×10^{-4} to 1.5×10^{-6} M sulfide concentrations. The data shown in Fig. 8 shows unexpectedly that the electrode prepared according to scheme (v) has a relatively constant response over a wide range of pH, except at low sulfide concentration. Most of the commercially available sulfide electrodes responses are strongly affected by the change of the pH and essentially respond to S^{2-} ions [26]. At pH > 7 or so, measurements with commercial electrodes must be used simultaneously with a pH electrode to obtain total sulfide concentration. The obtained slope values are not close to those theoretically reported for a dianion which should suggest that the electrode would respond to the total sulfide concentration. Thus, we can not explain why the electrode has almost same response at pH < 7.

3.5. Response time; temperature effects; life time and morphology

The response time of the sulfide polymer electrode is a function of the film thickness. Thin films give a response time of < 60 s, while thicker films (~ 2000 Å or higher) have a response time of 120 s or higher. The response is, therefore, partly controlled by the rate of diffusion of the active species within the polymer film. The working temperature range was determined from the calibration curves of the electrode measured at different temperatures. The values obtained from the slopes of the calibration curves were compared to the expected theoretical values reported earlier [27,28]. The working temperature of this electrode was found to be 10–40°C. As the response of the electrode is affected by the amount of sulfide present within the film, loss of sulfide with time is important. The electrode can be used for successive measurements for a period of ten hours without regeneration. By storing the electrode overnight in a solution containing 1.0×10^{-4} M sulfide, it can be used continuously for 3 days, after which significant degradation was then observed. The readiness of oxidation of the sulfide ions trapped within the polymer film to the corresponding sulfate ions should affect the performance and lifetime of the sensor electrode. For instance, a limited lifetime of 10 h was observed with this electrode when stored in air.

Scanning electron micrographs of the surface of the alloy substrate and the polymer-covered alloy are given in Figs. 5 and 9, respectively. Fig. 5 shows the surface of the alloy substrate after heating and insertion in the capillary glass tube. The irregularity of the surface is a key factor with respect to adherence in the deposition of successive layers. However, the polymer film response was not affected by the roughness of the alloy surface. Fig. 9, on the other hand, shows the surface of the polymer layer after treatment with the $(NH_4)_2S$. The morphology of the polymer film deposited on the alloy surface is not significantly different from that deposited on platinum [29].
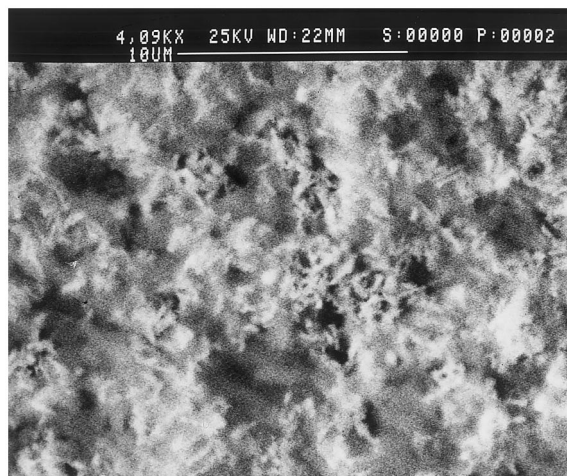

Fig. 9. Scanning electron micrograph of the alloy substrate covered with treated polymer layer (according to method V).

4. Conclusions

We prepared a sulfide selective electrode based on conducting polymer electrochemically deposited on an alloy substrate. The electrode showed high selectivity towards many common interfering anions. The optimum preparation conditions were based on electrochemically depositing a poly(3-methylthiophene) layer followed by electrodepositing a poly(dibenzo-18-crown-6) film. The film thickness and method of preparation affected the response and performance of the electrode. The electrode response was stable and reproducible for 3 days, after which the regeneration of the polymer film was necessary. The electrode can be fabricated in the micrometer dimensions [8].

Acknowledgements

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