An investigation of the deposition and reactions of sulphur on gold electrodes

I. C. HAMILTON

Chemistry Department, Footscray Institute of Technology, PO Box 64, Footscray, Victoria 3011, Australia

R. WOODS

CSIRO Division of Mineral Chemistry, PO Box 124, Port Melbourne, Victoria 3207, Australia

The oxidation of sulphide species in solution has been investigated on a gold electrode in borate solutions of pH 6.8 and 9.2 and in 1 mol dm^{-3} NaOH. Sub-monolayer coverage by sulphur occurs at under-potentials. At more positive potentials, multilayers of sulphur can be deposited. The reaction producing sulphur, and the reverse process, involve the formation of polysulphides as intermediates. The pre-dominant polysulphide intermediate is S_2^{2-}. Oxidation of sulphide to sulphate occurs to some extent in parallel with sulphur deposition. Both reactions are inhibited by the presence of a surface layer of sulphur. At high potentials, sulphur is oxidized to sulphate.

1. Introduction

A knowledge of the electrochemical properties of sulphide minerals is valuable in understanding reactions of metallurgical importance, for example in mineral flotation and in leaching. In order to identify the products of oxidation of a range of metal sulphides, we are carrying out electrochemical investigations on electrodes prepared from these materials. Studies on galena (PbS) [1], chalcopyrite (CuFeS$_2$) [2] and pyrite (FeS$_2$) and pyrrhotite (Fe$_{1-x}$S) [3] have already been reported.

One of the species formed in the oxidation of metal sulphides is elemental sulphur. Sulphur can be identified from the characteristics of its electro-reduction and from the electrochemical behaviour of the dissolved sulphide species formed by this cathodic process.

The formation of sulphur on noble metals by anodic oxidation of hydrogen sulphide species has been the subject of a number of investigations [4–13]. Much of this work has been stimulated by observations that the presence of sulphur on the metal surface can enhance electrocatalytic activity for a number of oxidation reactions.

Of the noble metals, gold is the most convenient for studying processes such as the oxidation of dissolved sulphide species, because there is an extensive potential range over which there is no significant background current from interaction with water. However, detailed studies of the reactions of sulphide species on this metal are particularly sparse, possibly because sulphur deposited on gold does not display electrocatalytic activity [11, 13].

Allen and Hickling [4] studied the oxidation of sulphide ions in alkaline solution on a range of electrode materials. They concluded that poly-sulphide species were formed. Wierse *et al.* [11] investigated the reactions of sulphur formed by oxidation of sulphide and polysulphide ions in 1 mol dm^{-3} NaOH. These authors concluded that polysulphide ions are not produced when a layer of sulphur deposited on gold is reduced by the application of a linear potential sweep.

Van Huong *et al.* [13] found that sulphur, deposited from the gas phase on gold, is stable over a wide potential range in neutral solution. Sulphur is not thermodynamically stable in neutral or alkaline solution [14]; the thermodynamically favoured species are sulphate and hydrosulphide or

sulphide ions depending on potential and pH. The reports that sulphur is formed on gold in alkaline solutions, and that it is relatively stable to further oxidation due to kinetic limitations, are consistent with our findings on the oxidation of metal sulphides [1-3].

Wierse et al. [11] concluded from their investigations that the deposition of sulphur on gold is restricted to submonolayer quantities. Since this observation differs from that expected from our work on sulphide minerals, we have carried out a study of the sulphide–sulphur system on gold. These investigations, which show that multilayers of sulphur can be formed, are reported in this communication.

2. Experimental details

All experiments were conducted at $23°$ C in solutions prepared from analytical grade reagents and doubly distilled water. Three electrolytes were employed: (i) $0.194 \, mol \, dm^{-3} \, H_2B_4O_7 + 0.0015 \, mol \, dm^{-3} \, Na_2B_4O_7 + 0.049 \, mol \, dm^{-3} \, Na_2SO_4$ (pH 6.8); (ii) $0.05 \, mol \, dm^{-3} \, Na_2B_4O_7$ (pH 9.2); and (iii) $1 \, mol \, dm^{-3}$ NaOH. Sulphide solutions were prepared from $Na_2S \cdot 9H_2O$ dissolved in the appropriate electrolyte. Electrolyte solutions were deoxygenated with purified nitrogen prior to the addition of sulphide.

The dominant sulphide species in solution are hydrogen sulphide (H_2S) at pH 6.8, hydrosulphide ion (HS^-) at pH 9.2 and sulphide ion (S^{2-}) in $1 \, mol \, dm^{-3}$ NaOH [14].

Potentials were measured against a saturated calomel reference electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale, taking the potential of the SCE to be 0.245 V against the SHE [15]. All potentials reported are on the SHE scale. The electrode potential was controlled by a potentiostat programmed with a Utah 0151 sweep generator and serviced by a current integrator. The potentiostat and integrator were designed and constructed in these laboratories. Current–potential and charge–potential relationships were recorded simultaneously on a Yew Model 3086 XY_1Y_2 recorder.

The gold electrode was a 3.5 mm diameter disc mounted on a Beckman rotating electrode assembly. The real surface area of the gold was estimated by the method proposed by Rand and Woods [16]. This procedure involves holding the electrode for 100 s at 1.8 V in $1 \, mol \, dm^{-3} \, H_2SO_4$ under which conditions approximately a monolayer of oxygen is adsorbed. The quantity of oxygen adsorbed is then determined by stripping on a negative-going linear potential sweep. Monolayer charge corresponds to $386 \, \mu C \, cm^{-2}$ [16]. The charge found for the electrode used in the present study was $55 \, \mu C$ and hence the real surface area was $0.14 \, cm^2$. The surface roughness did not change during the series of experiments.

Gold forms complexes with sulphide ions. The soluble complex, AuS^-, is considered [17] to be involved in ore genesis by providing a transport medium for gold in vein-forming fluids. E_h–pH diagrams have been constructed [18] showing the probable stability domain of AuS^-. This domain appears within the range of potential and pH of interest in the present work.

In order to determine if gold dissolved to any extent during potential cycling, a $2.4 \, cm^2$ gold foil electrode was subjected to 800 consecutive $20 \, mV \, s^{-1}$ cycles between -0.65 and 0.3 V in $50 \, cm^3$ of pH 9.2 borate solution containing $6 \times 10^{-4} \, mol \, dm^{-3}$ sodium sulphide. The solution was agitated during cycling by bubbling nitrogen slowly through the cell. The solution, which was a pale yellow colour after this treatment, was analysed for gold using atomic absorption spectrophotometry. No gold was detected ($< 0.3 \, \mu g \, cm^{-3}$).

In all the Figures in this paper, positive currents are anodic and negative currents cathodic; current densities refer to real surface area.

3. Results and discussion

3.1. Cyclic voltammetry of the sulphide/sulphur system

Voltammograms recorded when a gold electrode was cycled in solutions containing sodium sulphide are shown in Figs. 1 to 3. In each of the electrolytes studied, namely, borate solutions of pH 6.8 and 9.2 and $1 \, mol \, dm^{-3}$ NaOH, positive-going scans commenced at a potential just above the onset of hydrogen evolution. The scans are characterized by a prewave followed by a current peak.

The prewave appears just after commencement of the sweep, at a potential which becomes $\sim 30 \, mV$ more negative with each unit increase in
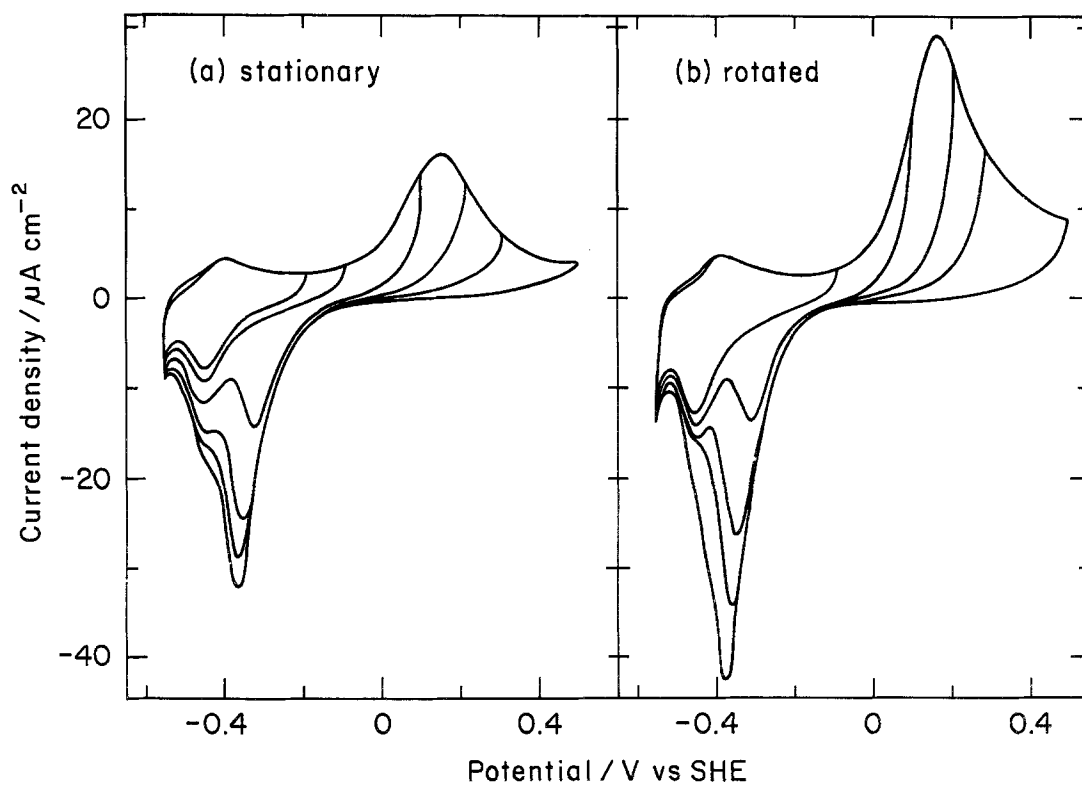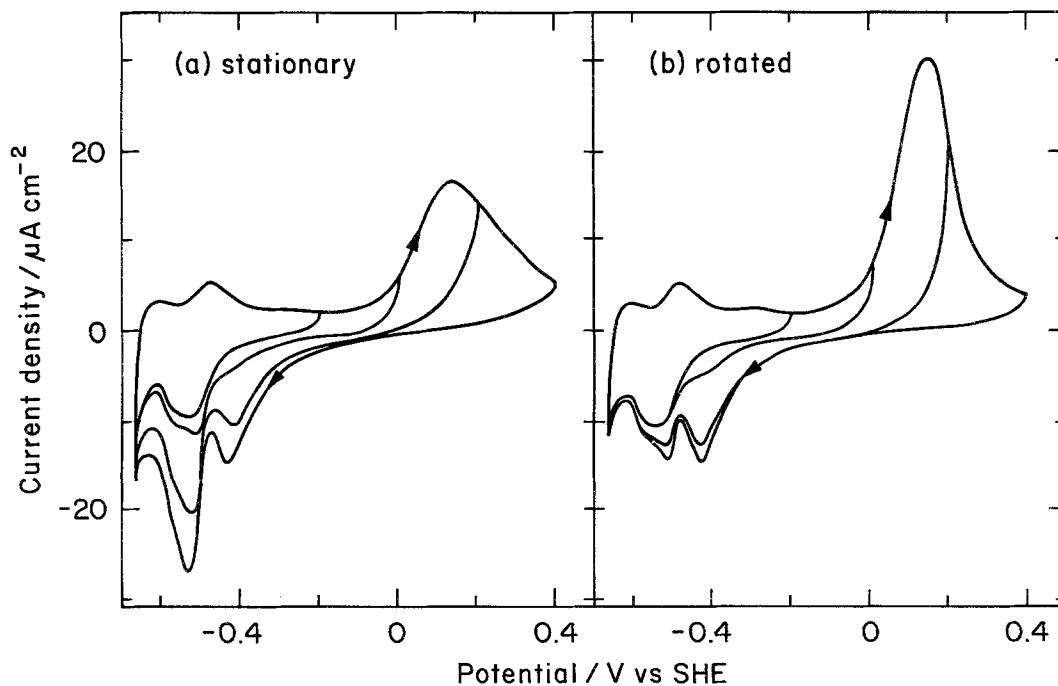
Fig. 1. Voltammograms for gold electrode in borate solution of pH 6.8 containing 1.7×10^{-4} mol dm^{-3} H$_2$S. Triangular potential cycles at 20 mV s^{-1}. The electrode was (a) stationary and (b) rotated at 10 Hz.

Fig. 2. Voltammograms for gold electrode in borate solution of pH 9.2 containing 1.6×10^{-4} mol dm^{-3} HS$^-$. Triangular potential cycles at 20 mV s^{-1}. The electrode was (a) stationary and (b) rotated at 10 Hz.
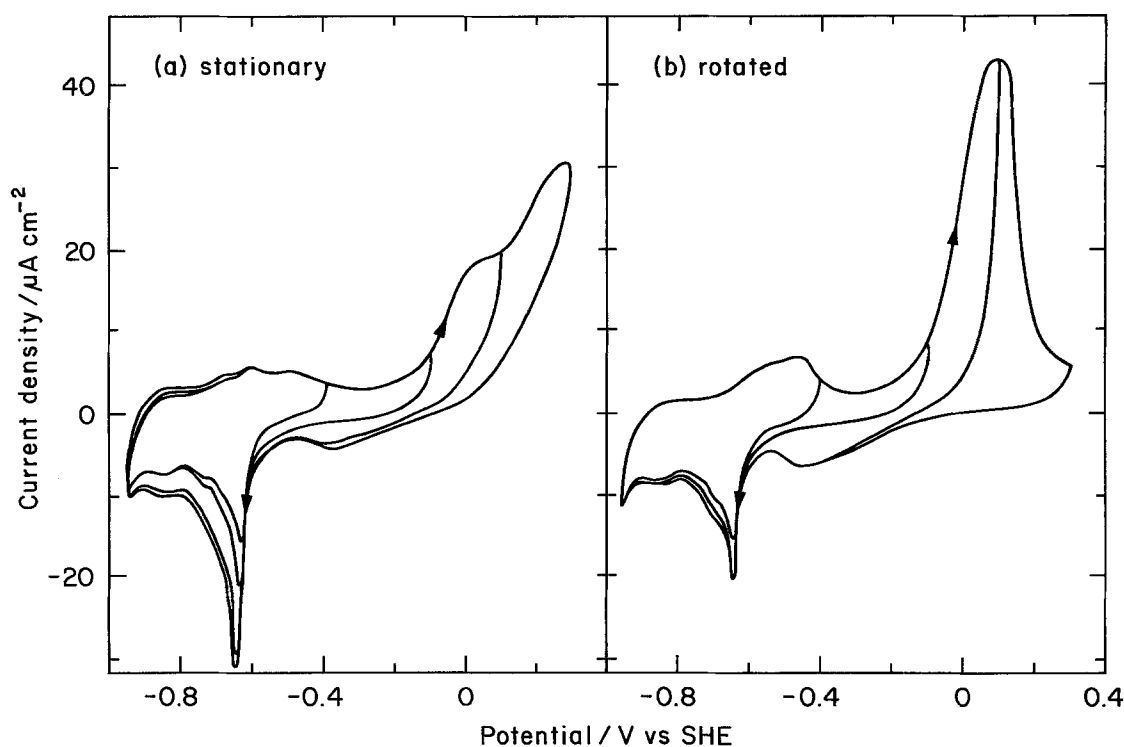
Fig. 3. Voltammograms for gold electrode in 1 mol dm^{-3} NaOH containing 1.7×10^{-4} mol dm^{-3} S^{2-}. Triangular potential cycles at 20 mV s^{-1}. The electrode was (a) stationary and (b) rotated at 10 Hz.

pH. The product of the anodic reaction which gives rise to this wave remains at the gold surface since the cathodic charge (Q_c) passed on the return scan is equal to the anodic charge (Q_a) passed on the preceding positive-going scan for both a stationary and a rotated electrode. These properties are consistent with the deposition of sulphur on the gold surface.

$$S^{2-} \rightarrow S + 2e. \qquad (1)$$

The pH dependence arises because the reacting species will be H$_2$S below pH 7, HS$^-$ between pH 7 and 12.9 and S^{2-} above pH 12.9.

The potential at which the prewave commences is considerably below the reversible potential for Reaction 1 at each pH. For example, anodic current begins to flow at -0.64 V in the pH 9.2 solution (Fig. 2); this potential is 0.42 V more negative than the reversible potential of the HS$^-$/S couple at the experimental pH and HS$^-$ concentration [14].

The underpotential deposition of sulphur indicates that there is a strong interaction between the deposited sulphur and the gold substrate. This conclusion is consistent with investigations [19]

of the adsorption of sulphur from the gas phase which demonstrated that reconstruction of the ad-layer occurs to form an adsorbed, two-dimensional sulphide.

Wierse et al. [11] defined a monolayer of sulphur on gold as one sulphur atom per surface metal atom. This definition is unrealistic since sulphur atoms are too large to be accommodated in such a packing density. Kostelitz et al. [19] found the saturation coverage of sulphur on the 1 1 1, 1 0 0 and 1 1 0 single crystal surfaces of gold to be 0.74×10^{15}, 0.73×10^{15} and $0.70 \times 10^{15} \cdot$atom cm^{-2}, respectively. The respective gold surface-atom densities on these planes are 1.25×10^{15}, 1.40×10^{15} and 1.72×10^{15} per cm^2. Thus, the sulphur monolayer is determined by the size of the sulphur atom and not the number of metal surface sites. From these results, it can be assumed that monolayer sulphur coverage on polycrystalline gold involves 0.72×10^{15} atom cm^{-2}. This is equivalent to a deposition charge of 0.23mC cm^{-2}.

Underpotential deposition of sulphur gives rise to a charge of $\sim 90 \mu$C cm^{-2} for each of the three

solutions. This is equivalent to a fractional sulphur coverage of ~ 0.4.

When the upper potential limit of the cycle is extended into the region in which the main anodic peak appears, Q_c becomes less than Q_a. For example, cycles at a stationary electrode traversing the whole potential region covered in Figs. 1 to 3, gave Q_c/Q_a ratios of 0.92, 0.84 and 0.44 at pH 6.8 and 9.2 and 1 mol dm^{-3} NaOH, respectively. The respective Q_c/Q_a ratios when the electrode was rotated at 10 Hz were 0.74, 0.55 and 0.39.

In the oxidation of sulphide minerals [1–3], Q_a can be greater than Q_c because oxidation to oxy-sulphur ions occurs in addition to the formation of sulphur and these ions are not reduced on the return scan. However, a reaction of the type,

$$S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e \qquad (2)$$
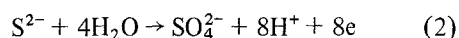
cannot account completely for the charge imbalance in the present case. The relative rates of Reactions 1 and 2, and hence Q_c/Q_a, should be independent of electrode rotation. The fact that this ratio is less when the electrode is rotated indicates that a soluble intermediate is formed during the reaction producing sulphur.

Allen and Hickling [4] suggested that the oxidation of sulphide ions in alkaline media proceeds via a series of polysulphides. Thus, the formation of sulphur could be presented as a two-step process,

$$xS^{2-} \rightarrow S_x^{2-} + (2x-2)e \qquad (3)$$

$$S_x^{2-} \rightarrow S_x + 2e. \qquad (4)$$
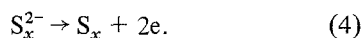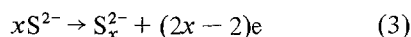
Polysulphides do not appear on the electrochemical equilibrium (E_h–pH) diagram for the sulphur–water system [14]. The only stable species in basic solutions are HS$^-$ and S^{2-} which occupy domains at low potentials and SO$_4^{2-}$ which covers the high potential region. However, reactions involving sulphate are generally slow [20] and take place at significant rates only at high overpotentials. Indeed, this is the reason sulphur is formed in the oxidation of sulphide ions.

An E_h–pH diagram covering the metastable situation in which sulphate and other oxy-sulphur anions are not considered is presented in Fig. 4. It can be seen that polysulphides, from S$_2^{2-}$ to S$_5^{2-}$, now appear. In constructing Fig. 4, only the fully dissociated polysulphide ions have been considered since the hydrogen polysulphides, the

sulphanes, are known [22] to be considerably stronger acids than H$_2$S.

Since sulphur(0) exists in polymeric form, metastable polysulphides are reasonable intermediates in the oxidative concatenation necessary to form surface sulphur from sulphide and hydrosulphide ions.

Experiments in which the electrode was rotated during only half the cycle, either the positive- or the negative-going scan, indicated that polysulphides are formed during both the anodic oxidation of sulphide and the cathodic reduction of sulphur. Fig. 5 shows voltammograms recorded in pH 9.2 solution.

Rotating the electrode during the positive-going scan increased Q_a by a factor of 1.5 compared with the value for a stationary electrode, whilst the cathodic charge observed when the resultant sulphur layers were stripped off under quiescent conditions increased only by a factor of 1.1. Thus, a soluble intermediate is formed on the positive-going scan. Fig. 5 shows that, for electrodes coated with sulphur under identical conditions, rotation during reduction on the negative-going scan significantly diminishes the observed value of Q_c. Hence, a polysulphide intermediate is also formed during the reduction process. Similar results were obtained for the other solutions investigated.

Comparison of the characteristics of sulphide oxidation with those of oxygen reduction at the same electrode indicates that mass transport plays a major role in limiting the anodic current for sulphide oxidation at a stationary electrode in pH 6.8 and 9.2 solutions with the sulphide concentrations studied here. When the electrode is rotated, the current is larger but finally limited by inhibition resulting from the deposited layer of sulphur on the gold surface.

Sulphur reduction in pH 6.8 solution gives rise to a single cathodic peak when the cycle is restricted to the underpotential region (Fig. 1). Sulphur deposited in the higher potential region is more readily reducible and gives rise to an additional peak, at less negative potentials than the other cathodic peak. Sulphur deposited at underpotentials from pH 9.2 solution also results in a single cathodic peak on reduction. However, the additional sulphur is reduced in two peaks, one in the same potential region as that for the under-
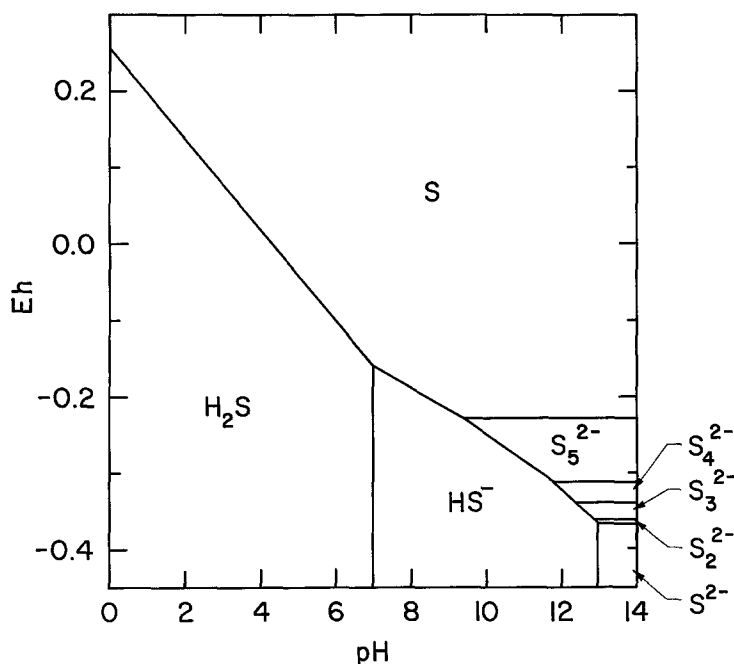
Fig. 4. E_h–pH diagram for the sulphur–water system at 25° C and 1.5×10^{-4} mol dm^{-3} dissolved species. Oxy-sulphur anions are not considered. Diagrams computer generated employing the CSIRO-NPL Thermodata system [21].

potential layer and the other appearing at less negative potentials (Fig. 2). Rotating the electrode has no effect on the latter peak but decreases the height of the former peak considerably (Fig. 5). This behaviour suggests that the first, i.e. less negative, peak arises from the reduction of sulphur to polysulphide by the reverse of Reaction 4 and the second, more negative peak corresponds to further reduction of the polysulphide intermediate to hydrosulphide ion by the reverse of Reaction 3.
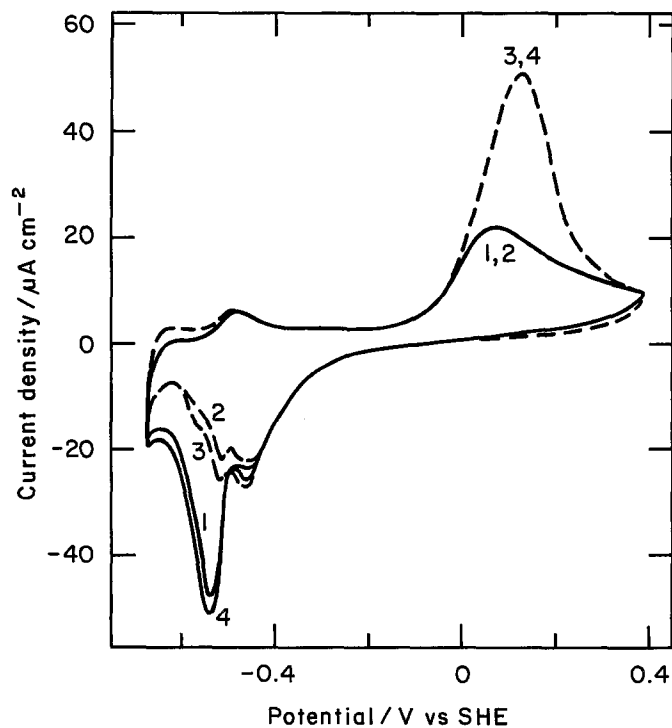

Fig. 5. Voltammograms for gold electrode in borate solution of pH 9.2 containing 1.9×10^{-4} mol dm^{-3} HS^{-}: —— electrode stationary, and – – – – electrode rotated at 10 Hz; 1, electrode stationary on both scans, 2, electrode stationary on positive-going scan and rotation commenced at -0.05 V on negative-going scan; 3, electrode rotated on both scans and 4, electrode rotated on positive-going scan and rotation terminated at -0.05 V on negative-going scan.

Since the sulphur deposited at underpotentials gives a single peak, and the charge associated with this peak is not affected by electrode rotation, reduction of this layer must either take place in a single step from sulphur to sulphide or through intermediates which remain adsorbed. It is assumed that this situation still applies when additional sulphur is present. Subtraction of the charge corresponding to reduction of the underpotential layer from the Q_c values for more substantial layers gives the charge passed in reducing the additional sulphur. Reduction of the additional sulphur at a rotated electrode produces polysulphide ions which are dispersed. At a stationary electrode, the polysulphide ions remain at the electrode and are reduced further to hydrosulphide ions.

The ratio of the cathodic charge for the additional sulphur reduced at a stationary electrode to that at a rotated electrode was found to be two under the conditions of Fig. 5. Thus the value of "x" in Reactions 3 and 4 is 2, i.e. the predominant polysulphide intermediate is S_2^{2-}.

In 1 mol dm^{-3} NaOH, reduction of the underpotential layer gives rise to a major peak at -0.65 V followed by a number of less well defined peaks at more negative potentials (Fig. 3). Stripping of the sulphur deposited in the higher potential region results in an increase in cathodic current in the potential region of the major peak plus a new peak at ~ -0.4 V. The additional peak occurs at approximately the same potential as the first cathodic peak observed at pH 9.2 which is assigned to polysulphide formation. This would suggest that the same process is operating in 1 mol dm^{-3} NaOH. However, the charge associated with the peak at ~ -0.4 V does not increase in proportion to the total cathodic charge, Q_c, but remains constant once it has grown to $90 \mu C$ cm^{-2}. This behaviour suggests that the peak arises from a surface process.

It was shown above that the composition of the intermediate polysulphide can be deduced from the relative charges passed in stripping a sulphur layer from a stationary and a rotated electrode. Analysis of these charges indicates that S_2^{2-} is the intermediate in 1 mol dm^{-3} NaOH as well as at pH 9.2.

Wierse *et al.* [11] found that voltammograms for solutions of polysulphides in 1 mol dm^{-3} NaOH were similar to those for sulphide ion. This

supports the interpretation of the voltammograms presented here in terms of reactions proceeding through polysulphide intermediates.

The above analysis indicates that little polysulphide is lost to the solution from a stationary electrode during the negative-going scan. It is reasonable to assume that a similar situation applies to the anodic process taking place on the positive-going scan. Indeed sulphur is deposited even when the electrode is rotated, suggesting that the second step in the process, the oxidation of polysulphide to sulphur, is relatively rapid. Thus, diffusion of polysulphide away from the electrode surface does not account for the large charge imbalance observed for a stationary electrode. This process only accounts for the difference between the charge imbalance for rotated and stationary electrodes.

It is apparent, therefore, that sulphate is formed on the positive-going scan by Reaction 2 in parallel with sulphur deposition. In fact, the peak current observed for a stationary electrode in 1 mol dm^{-3} NaOH is greater than expected for a diffusion-controlled 2e process. This conclusion is derived from comparisons of the currents for sulphide oxidation and oxygen reduction under the same conditions. The high anodic current is explained by a contribution from the 8e process, Reaction 2.

The charge ratio, Q_c/Q_a was found to be 1.0, 0.67 and 0.44 for a stationary electrode in 1 mol dm^{-3} NaOH when the upper potential limit of the cycle was -0.1, 0.1 and 0.3 V, respectively. Thus, sulphate formation increases rapidly with increase in potential. It is possible that the second step in the major anodic wave in Fig. 3a is due to this process.

Sulphate formation must be inhibited by sulphur deposited on the electrode surface since the anodic current decreases considerably with increase in potential in the high potential region of Fig. 3b.

3.2. Deposition of sulphur at constant potential

The rate of growth of the sulphur layer at constant potential can be determined by stepping the potential to the value of interest, holding for a fixed time, and then applying a 20 mV s^{-1} negative-going linear potential scan. The results presented in the previous section show that the cathodic
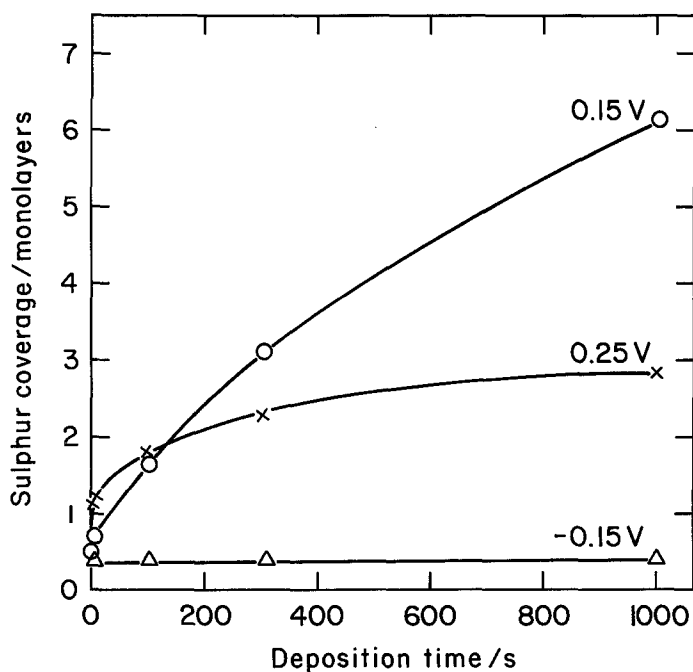
Fig. 6. The coverage of sulphur formed on stepping the potential of a gold electrode in borate solution of pH 6.8 containing 1.7×10^{-4} mol dm^{-3} H$_2$S from -0.55 V to -0.15, 0.15 or 0.25 V as a function of the deposition time.

charge, Q_c, provides a good estimate of the sulphur coverage provided the scan is carried out under quiescent conditions. Figs. 6 to 8 present sulphur coverages determined in this way as a function of deposition time.

At the lowest potentials in Figs. 6 and 7, the coverage does not increase with time but remains at the sub-monolayer level. When the electrode is held at higher potentials, i.e. in the region of the major anodic peak in Figs. 1 to 3, the deposit grows with time to multilayer levels.

The rate of growth of the sulphur deposit is slow once the initial monolayer has been formed. This is most likely due to the insulating nature of the layer [11].
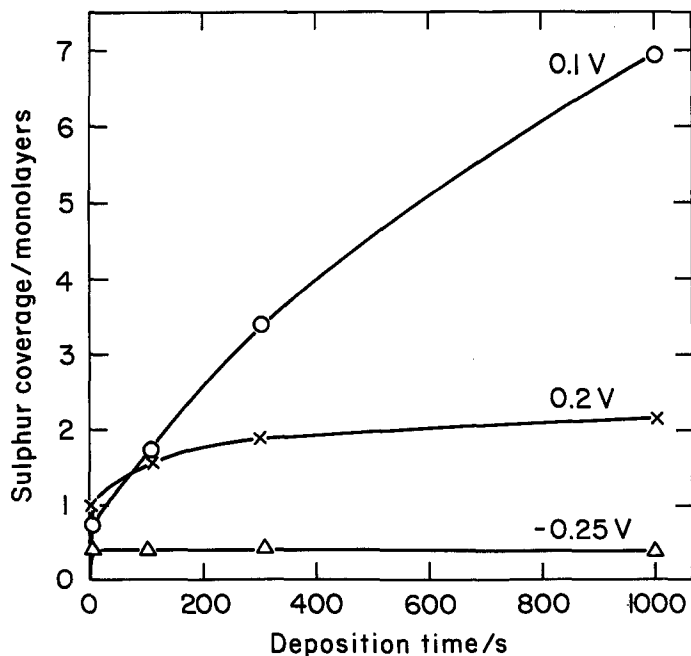
The rate of sulphur deposition increases with

Fig. 7. The coverage of sulphur formed on stepping the potential of a gold electrode in borate solution of pH 9.2 containing 1.5×10^{-4} mol dm^{-3} HS$^-$ from -0.67 V to -0.25, 0.1 or 0.2 V as a function of deposition time.
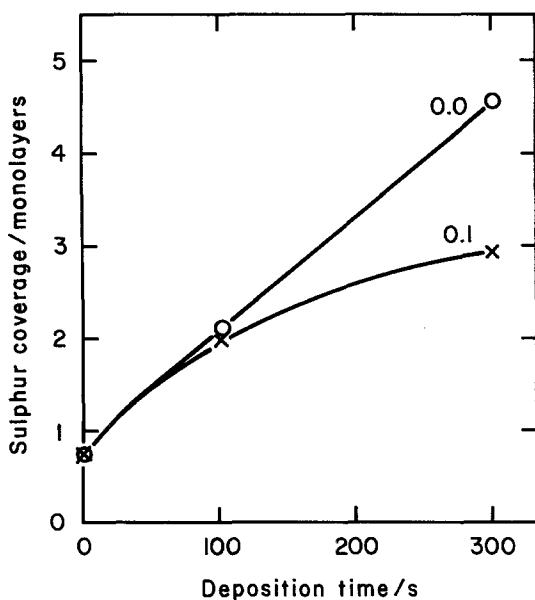
Fig. 8. The coverage of sulphur formed on stepping the potential of a gold electrode in 1 mol dm^{-3} NaOH containing $1.7 \times 10^{-4} \text{ mol dm}^{-3} \text{ S}^{2-}$ from -0.9 V to 0 or 0.1 V as a function of deposition time.

increase in potential at short times, as is to be expected for an anodic process. However, the rate at longer times decreases with increase in potential in the higher potential range studied (Figs. 6 to 8). This apparently reflects a variation in the physical nature of the sulphur deposit with change in the potential of deposition.

Wierse et al. [11] carried out investigations of the deposition of sulphur in 1 mol dm^{-3} NaOH with the electrolyte continually stirred by bubbling nitrogen through the solution. In this situation, polysulphide intermediates will be dispersed and sulphur coverages greater than that of the underpotential deposit will be underestimated. We have determined Q_c for electrodes rotated at 10 Hz during both deposition and stripping of the sulphur. The maximum Q_c value observed corresponded to $\sim$ 2e per surface gold atom, which is the order of magnitude reported by Wierse et al. [11].

3.3. Oxidation of sulphur to sulphate

Wierse et al. [11] compared the charges passed in reducing a sulphur layer on a negative-going scan with that passed in oxidizing an identical layer on a positive-going scan. They found a ratio of 3 : 1 for the oxidation to reduction charges in

1 mol dm^{-3} NaOH. They assumed the reduction process involved 2e and hence the oxidation must proceed to S(VI). That is, the reaction forms sulphate rather than other oxysulphur anions.

$$S + 4H_2O \to SO_4^{2-} + 8H^+ + 6e. \qquad (5)$$
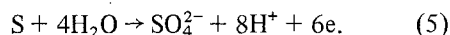
Fortunately, the potential range in which sulphur was deposited by Wierse et al. was mainly in the underpotential region and hence their assumption regarding the reduction charge was correct.

We have confirmed that Reaction 5 also applies to the oxidation of sulphur at both pH 6.8 and 9.2. For example, a stationary gold electrode in pH 9.2 borate solution containing 1.3×10^{-4} $\text{mol dm}^{-3} \text{ HS}^-$ was swept to 0.25 V at 20 mV s^{-1} and then held at that potential for 100 s. Fig. 9 shows the voltammogram obtained when the layer was reduced on a 20 mV s^{-1} sweep. The cathodic charge, Q_c, recorded was $520 \mu\text{C cm}^{-2}$. The same procedure was adopted for depositing the sulphur layer and an identical anodic charge was passed in the operation. A 200 mV s^{-1} anodic potential sweep was then applied to oxidize the sulphur layer. A rapid scan was employed in order to minimize any contribution from the diffusion of HS^- to the electrode surface. From measurements of oxygen reduction under the same quiescent conditions operating in the cell, the mass transport limited current for the oxidation of HS^- to SO_4^{2-} at the concentration employed would be $\sim 0.05 \text{ mA cm}^{-2}$. This current is negligible compared to that for oxidation of the sulphur layer in Fig. 9.

The anodic oxidation peak at 1.25 V in Fig. 9 arises from both sulphur oxidation and oxygen adsorption. The latter can be determined from the cathodic desorption peak at 0.55 V on the return scan. Thus, the net anodic charge recorded for the complete cycle from 0.25 V corresponds to sulphur oxidation. The experimental charge was 1.60 mC cm^{-2} and hence the ratio of oxidation to reduction charges is 3.08, close to the value of 3 expected for sulphate being the oxidation product. Analogous experiments in pH 6.8 solution gave a ratio of 3.10.

3.4. Cyclic voltammetry of the sulphide/sulphur/ sulphate systems

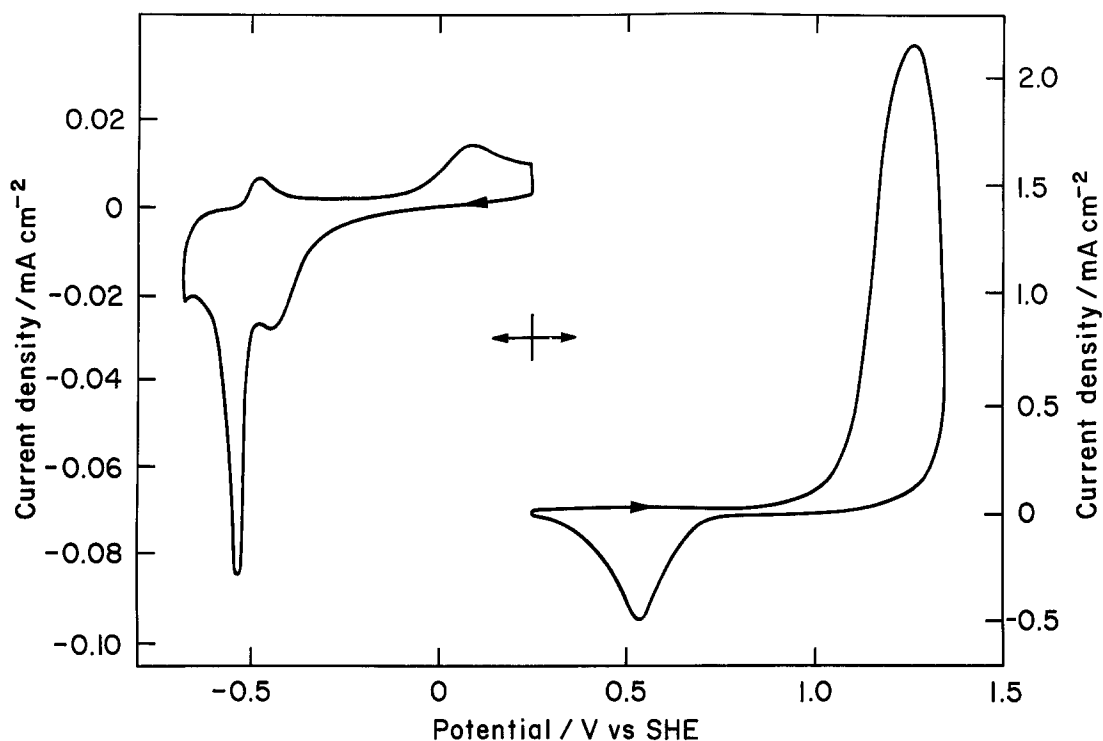Cyclic voltammograms for a stationary electrode

Fig. 9. Voltammograms for a gold electrode in borate solution of pH 9.2 containing 1.3×10^{-4} mol dm^{-3} HS$^-$. A potential sweep at 20 mV s^{-1} applied from -0.65 V to 0.25 V and the potential held at that value for 100 s before applying a triangular potential cycle (a) negative-going at 20 mV s^{-1} and (b) positive-going at 200 mV s^{-1}. Left ordinate scale refers to (a) and the right to (b).

over the complete range of available potentials between hydrogen and oxygen evolution display the oxidation and reduction peaks already described for reactions involving sulphide and sulphur. Rotating the electrode introduces additional features in the high potential region.

Fig. 10 shows voltammograms for stationary and rotated electrodes in pH 9.2 solution containing 1.4×10^{-4} mol dm^{-3} HS$^-$. For the stationary electrode, we see anodic peaks for sulphur deposition (0.1 V) and sulphur oxidation (1.25 V) and cathodic peaks for oxygen desorption (0.6 V) and reduction of sulphur adsorbed on the negative-going scan (-0.5 V).

The commencement of oxidation of adsorbed sulphur appears at more positive potentials when the electrode is rotated than when it is stationary. This behaviour arises because the sulphur layer blocks surface sites necessary for oxidation to sulphate and the layer is thicker when the electrode is rotated. The potential scans in Fig. 10 are reversed before the oxidation of the sulphur layer is complete and anodic currents due to the oxi-

dation of the remaining sulphur appear in the initial stages of the negative-going scans.

Oxidation of HS$^-$ to SO$_4^{2-}$ by Reaction 2 is favoured in the high potential region of the voltammograms but is inhibited on the positive-going scans by the presence of the layer of sulphur on the gold surface. However, once this layer has been removed, Reaction 2 can occur and this results in the anodic currents on the return scans being greater than on the preceding positive-going scans. The currents on the return scans are not completely mass transport controlled because oxygen adsorbs on the gold surface in the relevant potential region and this also inhibits Reaction 2. For rotated electrodes, the current on the return scan increases as the potential approaches 1 V. This could arise from desorption of the oxygen layer through reaction with HS$^-$ to form SO$_4^{2-}$; the oxygen desorption peak is very small for the rotated electrodes (Fig. 10). As the negative-going scan proceeds below ~ 0.9 V, the current falls again. This is due to sulphur being readsorbed by Reaction 1 and once more inhibiting Reaction 2.

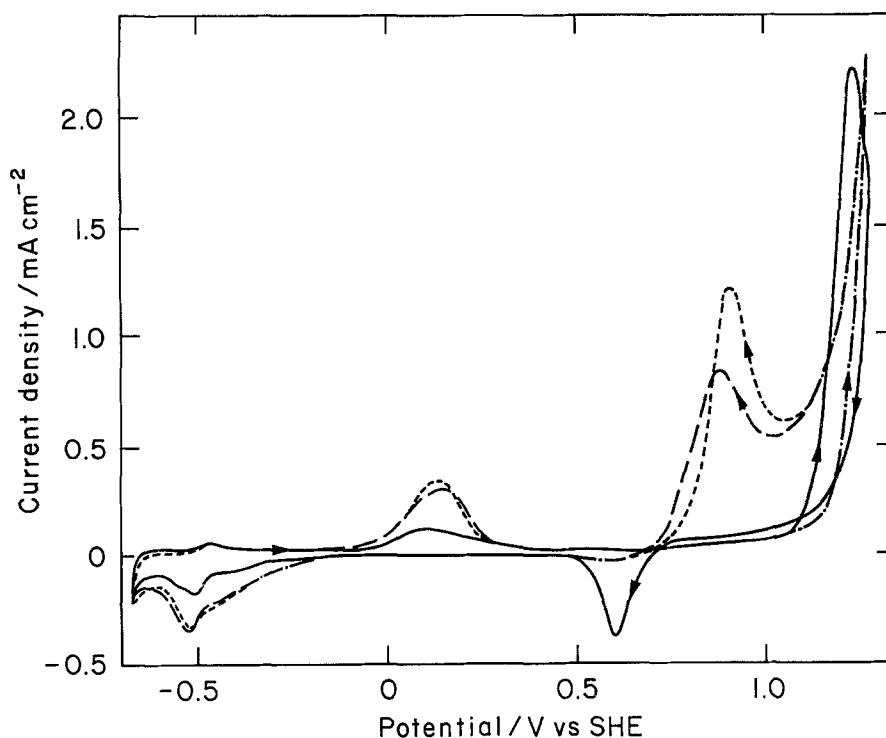Fig. 10. Cyclic voltammograms for gold electrode in borate solution of pH 9.2 containing 1.4×10^{-4} mol dm^{-3} HS^{-}. Triangular potential cycles at 20 mV s^{-1}. Electrode ——— stationary, ————— rotated at 10 Hz and .... 50 Hz.

There appears to be no potential region at which the gold surface does not become deactivated by the presence of deposited sulphur or adsorbed oxygen. Hence, at no stage is the reaction controlled completely by mass transport of HS^{-}. This is apparent from a comparison of the currents in Fig. 10 for electrodes rotated at 10 and 50 Hz. For mass transport control, the current at the higher rotation speed should be $5^{1/2}$ times that at the lower speed.

Analogous behaviour is observed on cycling a gold electrode in pH 6.8 borate solution and in 1 mol dm^{-3} NaOH containing sulphide.

Acknowledgements

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