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Oxidation of hydrosulphide ions on gold
Part II: Characterization of gold/aqueous hydrosulphide solution interface

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The results of studies to characterize the gold/aqueous hydrosulphide solution interface are presented in this paper. The interface was characterized with impedance spectroscopy, contact angle and cathodic charge transfer measurements. The studies complement the cyclic voltammetry investigations presented in Part I. A detailed mechanism of the oxidation and reduction of sulphur species at gold electrodes has been suggested on the basis of this investigation. The results show that the surface becomes hydrophobic under the conditions when polysulphide ions or elemental sulphur are present at the interface.

1. Introduction

The pertinent literature on the oxidation of sulphide ions was reviewed in Part I together with results of cyclic voltammetry studies. The results of the surface characterization studies are reported in this paper. The methods used to characterize the surface are: impedance spectroscopy, contact angle and cathodic charge transfer measurements.

2. Experimental details

The basic electrochemical instrumentation was the same as described in Part I [1]. A lock-in amplifier, Model 5706 (EG & G Princeton Research Instruments) was added for impedance measurements, together with Model 368-1 impedance software to conduct the experiments. A typical impedance experiment consisted of the measurement of the magnitude and phase angle as a function of frequency. An a.c. signal of 10 mV amplitude and frequency range of 0.001 to 20 kHz was used. The electrode was preconditioned at the desired DC potential for a period of about three hours unless otherwise stated. Such a pretreatment was essential for obtaining a stable spectrum.

Contact angle measurements were made for a captive bubble intermittently placed at the electrode surface during or after various electrochemical treatments. The measurement device was manufactured by Ramé Hart, Inc. The working electrode was positioned with the exposed horizontal surface facing downwards so that a purified nitrogen bubble could be placed on the electrode with a capillary glass tube attached to a Gilmont microsyringe. Contact angle measurements were made during cyclic voltammetry and in potentiostatic and galvanostatic modes.

All measurements were carried out in 0.1 M sodium tetraborate solutions of pH 9.3 that had been deoxygenated by bubbling purified nitrogen overnight. The Na_2S stock solution was then added to obtain the desired concentration. During the entire experiment, a flow of nitrogen at the surface of the solution was maintained.

3. Results

3.1. *Impedance spectroscopy*

The impedance of the gold/hydrosulphide solution interface was measured as a function of frequency. From these values the charge transfer resistance (R_p), capacitance (C), and depression angle (α) were determined by the procedures described in the literature [2]. Typical results of the impedance measurements are plotted in the form of phase angle and magnitude – Bode plots shown in Figs 1a and 1b, and Nyquist plots, shown in Fig. 1c.

The charge transfer resistance (R_p) is given as a function of the DC potential in Fig. 2. Each data point corresponds to an independent measurement on a separately preconditioned electrode. Charge transfer measurements made during the preconditioning period did not reveal any useful information. At the end of the preconditioning period, the impedance measurement was carried out at the same DC potential.

To discuss the effect of DC potential on impedance five potential regions are considered which are marked as Regions a to e in Fig. 2. In Region a, $-0.6 < E < -0.4$ V, it was observed that the value of R_p was small and virtually potential independent. This region coincided with the underpotential region for sulphur deposition discussed in Part I [1]. The depression angle

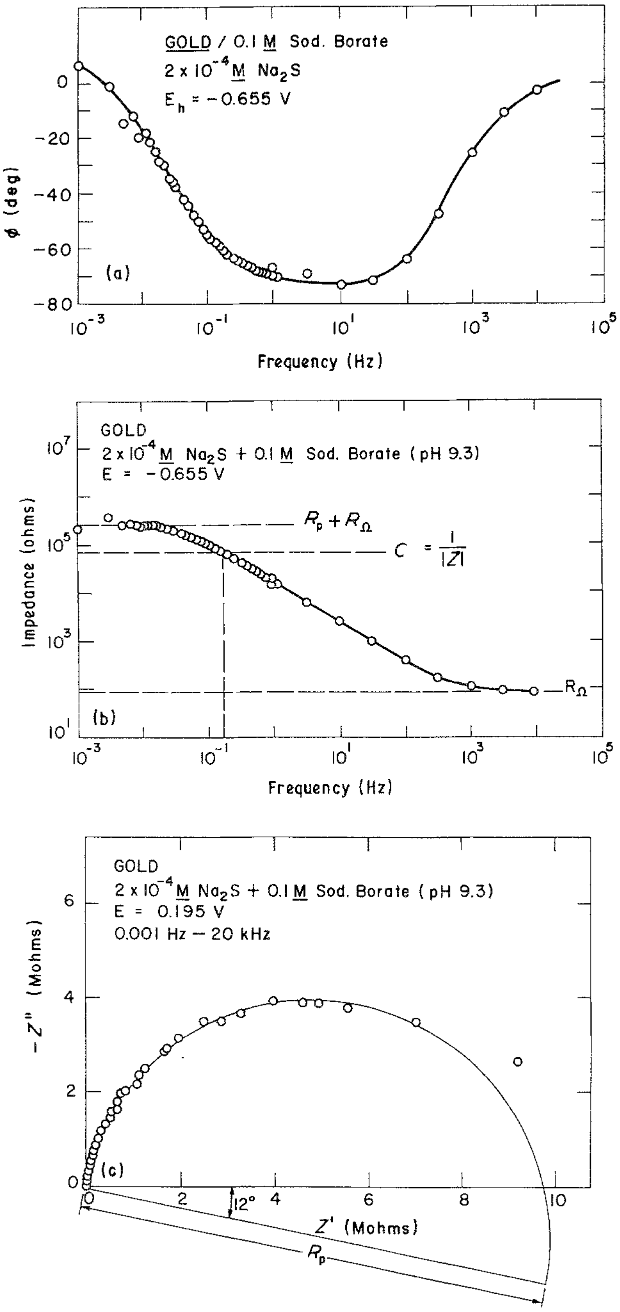

Fig. 1. Representative impedance spectra of the gold/sulphide solution interface in the frequency range 0.001–20 kHz, (a) and (b) show phase angle (ϕ) and magnitude ($|Z|$) of the impedance, respectively, as a function of frequency; spectra obtained at a DC potential of −0.655 V. (c) Nyquist plot of imaginary component of impedance ($-Z''$) against real component of impedance (Z'); spectra obtained at a DC potential of 0.195 V.

α was fairly large in this region as can be seen in Fig. 3. From the depression angle, which has been associated with surface roughness [3–6], one may conclude that the surface roughness is large in this potential range. The surface coverage of 0.5, reported later in this chapter, supports these findings. The low surface coverage could indicate that the sulphur film grows laterally producing inhomogeneities on the electrode surface, which is in accordance with the high depression angle value of 15°.

For $-0.4 < E < -0.15$ V, R_p increased as the potential was increased and is referred to as Region b. In this region the increase in R_p was associated with the increase in surface coverage to about one close-packed monolayer of chemisorbed sulphur (surface coverage data is presented in a subsequent section), which gave rise to passivity. The depression angle decreased in this potential range to about 5°. The passivation of the gold electrode could have been due to the fact that the chemisorbed sulphur layer, Au|S$_x$ grew as a 2-dimensional monolayer. These results are in agreement with the low energy electron diffraction studies [7] which have shown that at low surface coverage, (Region a), the chemisorbed sulphur atoms are usually not ordered, but at intermediate coverages (Region b) they form a 2D-layer.

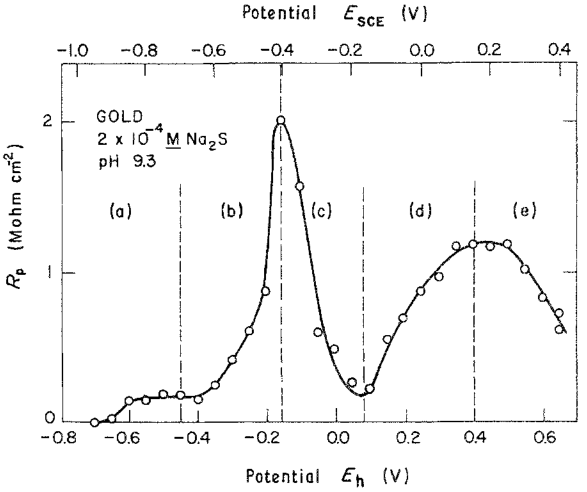

Fig. 2. Charge transfer resistance, R_p, as a function of applied DC potential for the gold/sulphide solution interface. Amplitude of AC signal = 10 mV; frequency range = 0.001–20 kHz.

The decrease in R_p in Region c ($-0.1 < E < 0.1$) is associated with formation of polysulphides which led to a decrease in passivity of the gold electrode. The gold surface became hydrophobic in this potential region as inferred from an increase in contact angle. The results are discussed in a later section. These results are in agreement with those from cyclic voltammetry which suggested the formation of polysulphides in Region c and their reduction at potentials more negative than those of Region c. The α angle data indicated that the surface continues to behave like a smooth surface in this potential region. As can

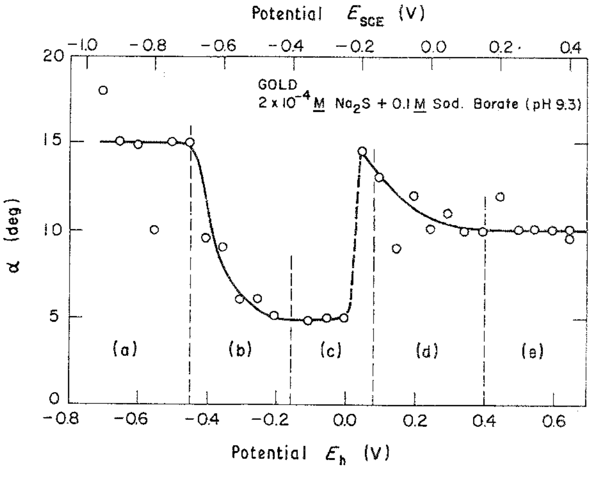

Fig. 3. Depression angle, α, as a function of applied DC potential for the gold/sulphide solution interface.

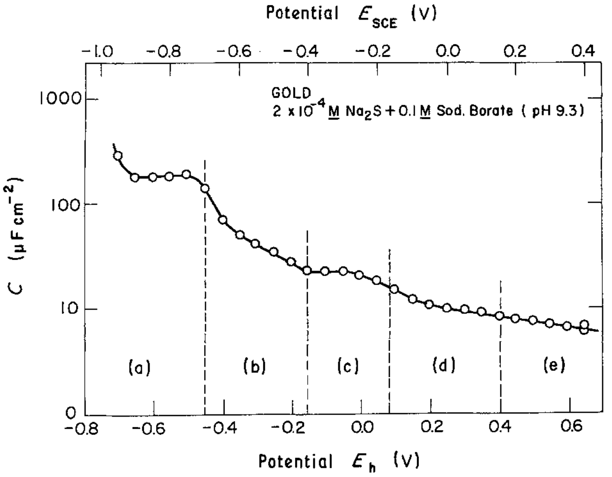

Fig. 4. Capacitance, C, as a function of applied DC potential for the gold/sulphide solution interface.

be seen in Fig. 3, the depression angle remained constant at about 5° in the polysulphide region. In Fig. 2, an increase in R_p is observed for $0.01 < E < 0.4$ V, which could be attributed to the formation and deposition of multilayers of elemental sulphur through polysulphide oxidation. As can be seen in Fig. 3, the value of α increased again at potentials > 0.0 V, most likely due to the deposition of multilayers of sulphur. A dissolution reaction occurred at potentials more positive than 0.4 V (Region e) with the resultant decrease in the value of R_p. In this range of potentials, partial oxidation of elemental sulphur occurs to form sulphoxy species such as $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, $S_2O_6^{2-}$.

Double layer capacitance measurements provide valuable information on electrode processes, such as adsorption, desorption and film formation [8]. The capacitance (C) versus DC potential results, shown in Fig. 4, suggested that below -0.65 V the increase in capacitance was due to hydrogen adsorption. This observation is supported not only by the formation of hydrogen micro-bubbles on the gold electrode, but also by the appearance of an inductive loop in the Nyquist plot at about -0.7 V. The drop of R_p to zero could be explained by hydrogen evolution which accounts for the entire current passing across the gold/sulphide solution interface. A typical capacitance value of about 185 μF cm^{-2} was obtained in the region (-0.65 V $\leqslant E \leqslant -0.5$ V), where it is assumed that HS^- ions are specifically adsorbed onto the electrode surface. A constant capacitance value below $E = -0.45$ V in this region seems to support this hypothesis. Similarly, in the potential range of -0.15 and -0.05 V, where the formation of a polysulphide layer is proposed, the magnitude of the capacitance was ~ 22 μF cm^{-2}. In these two potential ranges the capacitance was independent of potential. The decrease in capacitance at about -0.05 V suggested that the polysulphide layer thickness increased with increasing potential up to ~ 0.1 V. As the potential was made more positive than 0.1 V, the capacitance decreased as the gold surface became covered with multilayers of elemental sulphur, which is known to be non-conducting. These results are supported by the insulating character of the adsorbed sulphur proposed by Wierse *et al.* [9] from differential capacity measurements.

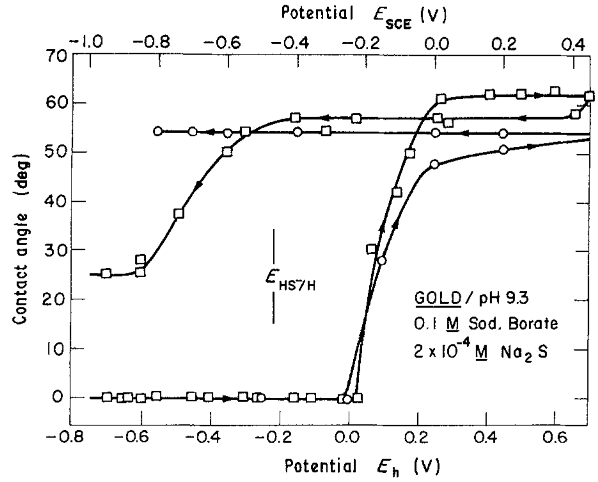

Fig. 5. Contact angle measurements during a potential sweep in which potential was applied at 2 mV s^{-1} from -0.7 V, swept to 0.7 V reversed and ended at -0.7 V. □ Present work, ○ Walker *et al.* [10] who used a scan rate of 1.5 mV s^{-1} and 0.01 M NaHS.

3.2. *Contact angle*

The results of contact angle measurements under potential sweep and potentiostatic modes are presented in Figs. 5 and 6, respectively. A sweep rate of 2 mV s^{-1} was used during contact angle measurements. In comparison Walker *et al.* [10] used a sweep rate of 1.5 mV s^{-1}, but used the same bubble during the entire scan. The circles in Fig. 5 represent the data obtained by Walker *et al.* [10]. With the exception of the results at low potentials in the cathodic scan, the data are in general agreement. As can be seen in Fig. 5, the gold

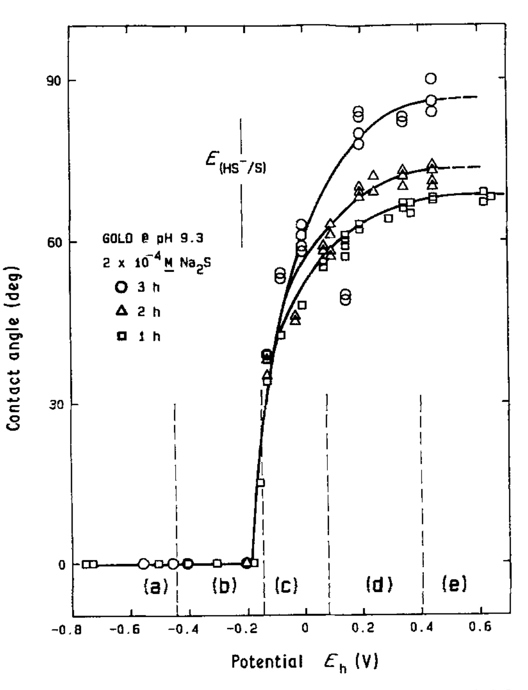

Fig. 6. Contact angle as a function of applied DC potential for the gold/sulphide solution interface. Preconditioning time = 1 (□), 2 (△) and 3 (○) hours.

electrode was hydrophilic at potentials below 0.0 V. The specific adsorption of HS^- ions on the electrode below −0.5 V could well explain the hydrophilic gold surface found during these measurements. However, a non zero value of contact angle above −0.5 V was expected if chemisorbed sulphur is hydrophobic. These results suggest that the presence of a sub-monolayer of sulphur atoms is not enough to impart hydrophobicity to the gold surface. As the potential swept to more positive potentials, $E > 0.0$ V, the electrode became hydrophobic reaching a contact angle of 62° in the potential region where multilayers of sulphur were deposited. Moreover, it was observed that the contact angle decreased from 62° to 57° at the beginning of the cathodic reduction in the negative-going scan. The contact angle remained at 57° in the negative-going scan up to about −0.35 V, the potential at which sulphur was reduced to polysulphide ions, as observed by cyclic voltammetry [1]. Furthermore, it was observed that in the potential region where polysulphide ions were reduced to hydrosulphide ions, a contact angle value of 25° was obtained. These results could be attributed to incomplete reduction of elemental sulphur. Walker *et al.* [10] did not observe a decrease in contact angle even in the region where hydrosulphide ions were formed. These investigators held the nitrogen bubble against the electrode with a glass capillary during the cathodic scan which probably interfered with the reduction of elemental sulphur.

The contact angle data presented in Fig. 6 were obtained under potentiostatic mode for three different preconditioning times, namely, 1, 2, and 3 hours. A sharp increase in contact angle was observed at about −0.2 V. The initial increase in contact angle coincided with the reversible potential of the HS^-/S^0 couple. The increase in contact angle occurred at potentials at which the sulphur coverage approaches a monolayer. As can be seen from Figs 5 and 6, no contact angle was observed in the region where $\theta \leqslant 1$. These results suggest that the surface coverage must exceed a monolayer for the gold surface to become hydrophobic. Microflotation tests conducted on sulphur-coated sulphide minerals show high flotation recovery when a substantial amount of sulphur is present [11].

A gradual increase in hydrophobicity occurred as the potential was raised above −0.15 V, where the increase in hydrophobicity of gold was considered to be due to S_x^{2-} species formed between −0.15 and 0.08 V (Region c in Fig. 2). At more positive potentials, that is $E > 0.1$ V, the contact angle reached a value of approximately 67° (for one hour preconditioning) and tended to level off in Region d, where multilayers of elemental sulphur were formed. The presence of multilayers of sulphur was confirmed by measurement of the reduction charge during a negative-going potential scan; the results are discussed in the next section. As observed in Fig. 6, a constant contact angle was observed in the region in which sulphur is oxidized to sulphoxy species, marked as Region e in Fig. 2. The hydrophobicity of the gold electrode in this region could be attributed to the partial oxidation of sulphur, since the oxidation of sulphur to oxyanions is known to be slow [12, 13]. When the electrode was conditioned for different periods of time, for example, 2 and 3 hours, similar changes in contact angle with DC potential were observed. Larger contact angles were obtained when the gold electrode was conditioned for longer times. Contact angle values determined potentiostatically were slightly higher than those obtained under cyclic voltammetry conditions, most likely due to differences in the time scales involved.

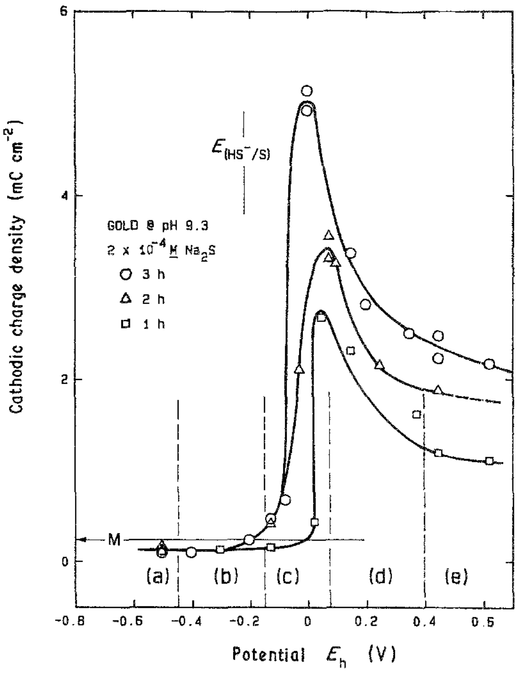

Fig. 7. Cathodic charge determination as a function of applied DC potential for the gold/sulphide solution interface. Preconditioning time = 1 (□), 2 (△) and 3 (○) hours.

3.3. *Cathodic charge determination*

Voltammetry may be used to estimate the amount of species adsorbed on the electrode surface by cathodic desorption. Fig. 7 shows the charge density as a function of potential determined in the negative-going linear potential scan for the three different preconditioning times for which the contact angle data were given in Fig. 6. The charge density equivalent to a monolayer coverage of chemisorbed sulphur is marked by line M. The surface coverage was determined by the method of Hamilton and Woods [14]. (One monolayer of adsorbed sulphur is equivalent to 0.23 mC cm^{-2}.) The cathodic desorption measurements at a scan rate of 2 mV s^{-1} were carried out immediately after the contact angle measurements were made. The charge passed in reducing the species was obtained by integrating the cathodic reduction peak on the voltammetric curve. The point where current starts to rise was used as the base-line for integration of the peak.

As shown in Fig. 7, below −0.4 V (Region a) sulphur was adsorbed on the electrode surface at the sub-monolayer level. Surface coverage in this region was estimated to be about 0.5. As the potential of deposition was extended into Region b ($-0.45 \leqslant F \leqslant$

-0.15 V), the layer of the chemisorbed sulphur grew to about one monolayer. In contrast, Hamilton and Woods [14] estimated a value of $\theta \sim 0.4$ at -0.25 V (Region b). The discrepancy between these two results could be due to the different scan rate used. The application of 20 mV s^{-1} by those authors might not have given enough time for all the species to be reduced. Up to 0.1 V in Region c the charge increases and then decreased with increasing potential in Region d. The sharp increase in cathodic charge density in Region c coincided with the increase in contact angle (Fig. 7) and with the formation of polysulphide intermediates. Based on thermodynamic considerations and cyclic voltammetry studies, polysulphide species S_x^{2-} are suggested to be mainly responsible for the hydrophobicity of the gold electrode. At more anodic potentials, for example Region d, the charge density neither increased nor leveled off as expected, but instead it decreased. This behaviour suggests that polysulphide ions are more readily reducible, probably to HS^- ions, than the elemental sulphur. This behaviour is consistent with the cyclic voltammetry results discussed in Part I [1] which showed that elemental sulphur reactions are generally slow.

4. Summary and conclusions

On the basis of this investigation, the following steps are proposed for the mechanism of oxidation of sulphide ions at a gold electrode in an aqueous solution containing 2×10^{-4} M Na_2S and 0.1 M sodium tetraborate (pH 9.3).

4.1. *Oxidation*

Step 1 Underpotential deposition (UPD) of S^0 to form a hydrophilic surface

$$\mathrm{Au} + \mathrm{HS}^- = \mathrm{Au}|\mathrm{HS}^- \qquad (1)$$

$$\mathrm{Au}|\mathrm{HS}^- = \mathrm{Au}|\mathrm{S}^0 + \mathrm{H}^+ + 2e \qquad (2)$$

Underpotential deposition of sulphide ions occurs to form atomic sulphur in the potential range of -0.60 to -0.45 V. The chemisorption of sulphur is a reversible process and it takes place at potentials about 0.30 V more negative than the reversible potential of the HS^-/S^0 redox couple. The atomic sulphur coverage is below a monolayer (coverage equivalent to ~ 0.5 of a close-packed array of sulphur atoms) and the gold surface is hydrophilic in character.

Step 2 Formation of a 2-dimensional, hydrophilic passivating layer

$$\mathrm{Au}|\mathrm{S}^0 + (\mathrm{x}-1)\mathrm{HS}^- = \mathrm{Au}|\mathrm{S_x} + (\mathrm{x}-1)\mathrm{H}^+ + 2(\mathrm{x}-1)e^- \qquad (3)$$

In the potential range of -0.45 to -0.15 V a monolayer of atomic sulphur is formed. It is proposed that the nature of the surface changes in this potential region involving bond formation between the adsorbed sulphur atoms. Passivation of gold occurs in this region due to formation of a 2-dimensional layer which might be written as $Au|S_x$. The surface remains hydrophilic in this potential range, perhaps because the quantity of sulphur present is not enough to impart hydrophobicity.

Step 3 Formation of a polysulphide which is hydrophobic

$$\mathrm{Au}|\mathrm{S_x} + \mathrm{HS}^- = \mathrm{Au}|\mathrm{S}_{\mathrm{x}+1}^{2-} + \mathrm{H}^+ \qquad (4)$$

The atomic sulphur layer reacts with sulphide ions in solution to form polysulphides in the potential range of -0.15 to $+0.08$ V according to Reaction 4. The presence of polysulphide multilayers was inferred by cathodic desorption and cyclic voltammetry measurements. On the basis of this investigation, it is considered that Reaction 4 is reversible. The formation of polysulphides, according to the above reaction, renders the gold surface hydrophobic. Multilayers of equivalent sulphur are present at the surface in this range of potentials.

Step 4 Deposition of elemental S^0 to form a hydrophobic surface

$$\mathrm{Au}|\mathrm{S_x^{2-}} = \mathrm{Au} + \mathrm{xS}^0 + 2e^- \qquad (5)$$

In the potential range, of $+0.08$ to $+0.4$ V, polysulphide ions oxidize to form multilayers of elemental sulphur which might be represented as the stable 8-ring allotrope form, S_8. The deposition of multilayers of elemental sulphur was confirmed by cathodic desorption measurements. The surface is hydrophobic in this range of potentials.

Step 5 Oxidation of elemental S^0

$$\mathrm{xS}^0 + \mathrm{yOH}^- = \mathrm{S_xO_y^{2-}} + \mathrm{yH}^+ + 2(\mathrm{y}-1)e^- \qquad (6)$$

Although elemental sulphur oxidized to sulphoxy ions at higher potentials ($0.4 \leqslant E \leqslant 0.6$ V), a decrease in contact angle was not observed. These results imply that a layer of sulphur is always present under oxidizing conditions because of the slow rate of sulphur oxidation.

4.2. *Reduction*

The reduction of elemental sulphur also involves a series of steps:

Step 1 Formation and decomposition of an activated complex

$$\mathrm{Au}|\mathrm{S_8} + \mathrm{HS}^- + e^- = [\mathrm{AuS_9^{2-}}]^* + \mathrm{H}^+ \qquad (7)$$

$$[\mathrm{AuS_9^{2-}}]^* = \mathrm{Au}|\mathrm{S_7} + \mathrm{S_2^{2-}} \qquad (8)$$

$$\mathrm{S_2^{2-}} + 2\mathrm{H}^+ + 2e^- = 2\mathrm{HS}^- \qquad (9)$$

It is observed that the reduction of elemental sulphur occurs through a 1-electron transfer process. Formation of an activated complex as an intermediate,

$[AuS_9^{2-}]^*$, is postulated. Further reduction of S_2^{2-} species occurs at about -0.5 V.

Step 2 Reduction of polysulphides to HS^-

$$Au|S_x^{2-} + H^+ + 2e^- = Au + S_{x-1}^{2-} + HS^- \qquad (10)$$

$$S_2^{2-} + 2H^+ + 2e^- = 2HS^- \qquad (11)$$

The reduction of polysulphides occurs through a 2-electron transfer reaction at the electrode surface. The reduction of these species occurs at less reducing potentials than that of elemental sulphur, confirming the observations by previous investigators that elemental sulphur is difficult to react once formed [15].

Acknowledgements

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