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ELECTROCHEMISTRY OF SULPHUR IN ALKALI SOLUTIONS

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SUMMARY

Voltammetric studies were carried out on gold electrode to identify the oxidation products of elemental sulphur in alkali solutions. The oxidation of HS^- and S_2^{2-} is reversible followed by oxidation to sulphur which gets incorporated in the hydrous films on gold. Pitting occurs when the film break and the pitting susceptibility of gold increased with alkali concentration. On the sulphur covered gold surface, no oxygen reduction was observed and H_2S evolved along with hydrogen.

KEY WORDS: Sulphur electrochemistry, Voltammetry, Gold electrodes

INTRODUCTION

Towards the development of porous iron electrodes for use in Ni-Fe alkaline batteries, an activated iron electrode was developed [1]. The activation of the porous iron electrode was carried out in 6M KOH solutions containing 32gpl elemental sulphur by passing various cathodic currents. The improved performance of these electrodes prompted us to study the oxidation behaviour of sulphur in high alkali solutions. In order to identify the products of oxidation of sulphur, voltammetric studies were carried out on gold which offers an extensive potential range over which there is no interaction of gold with water. A few studies were reported on the Au/ S^{2-} and Au/ SO_2 interactions in aqueous solutions [2-4]. Place exchange mechanism with the formation of surface oxides [5,6], Au/ O^{2-} may lead to similar process on Au/ S^{2-} or breakdown of passive oxide film may take place in presence of sulphur. The paper presents the oxidation products of sulphur and their effects on gold surface.

EXPERIMENTAL DETAILS

Cyclic voltammetric experiments on pure gold were carried out in a Bio-Analytical Systems (BAS) 100A using the electrode supplied by them. The cell consists of gold electrode (0.008cm²) as working electrode, platinum wire as counter and a mercuric oxide as reference electrode, respectively. The electrolytes were solutions of different concentrations in purified KOH solutions with and without sulphur. The elemental sulphur was dissolved in KOH solutions by heating upto 60°C. The solutions (0.1M to 10M KOH, 0.1M KOH + 0.01M sulphur and 1-10M KOH + 0.1M sulphur) were prepared from analytical reagent chemicals and distilled water.

During measurements purging with purified nitrogen along with stirring was effected. Pretreatment and polishing were done in accordance with BAS manual. Voltammetric sweep rates were varied from 20 to 500 mVs⁻¹ and sometimes to 1000 mVs⁻¹.

RESULTS

1- BEHAVIOUR ON GOLD

When polarised from -1.3V to 0.9V in 0.1M KOH solution the electrochemical spectrum revealed during the positive scan an anodic peak at 492 mV followed by O₂ evolution at 750mV. Negative scan brought out a cathodic peak at 138mV followed by a shoulder at -96mV. The anodic peak potential shifted to positive potentials while cathodic peak moved to negative potentials with increase of sweep rate. The oxygen evolution potential shifted towards negative direction. Above 100mVs⁻¹ a distinct anodic peak appeared around 0.0V.

In 1.0M KOH solutions the positive scan exhibited an anodic peak at 480mV where as in the negative scan there were two cathodic peaks: at 153mV and -102mV (Fig.1).

The peak at 153mV (II) predominated at high sweep rate. The cathodic peak potential (III) was found to shift to positive direction with sweep rate. In 6.0M KOH solutions one more cathodic peak appeared at -450mV whose potential shifted towards negative direction with sweep rate. The anodic peak potential was independent of sweep rate at all concentration. The charges flowed under the peaks decreased with sweep rate.

Upon continuous cycling, oxygen evolution was found to take place at the same potentials. The charges flowed under anodic peak (Q_a) and the cathodic peak (Q_c) were independent of the scan rate, while Q_c at peak (III) decreased suggesting that peaks (I) and (II) belong to a couple.

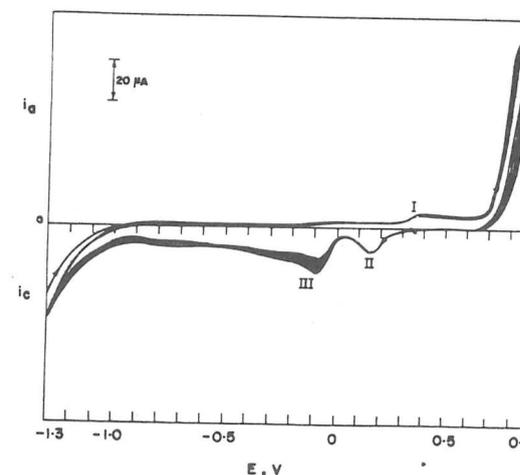


Fig 1. Cyclic voltammogram of 1.0 moldm⁻³ KOH aqueous solution on the gold electrode. E_c = -1.3 V vs. Hg/HgO; E_a = 0.9 V vs. Hg/HgO. v = 100 mVs⁻¹

The anodic peak potential varied with OH⁻ concentration with a slope of 110mV decade⁻¹ (Fig.2). The cathodic peak potential at 180mV varied with log sweep rate (Fig.3).

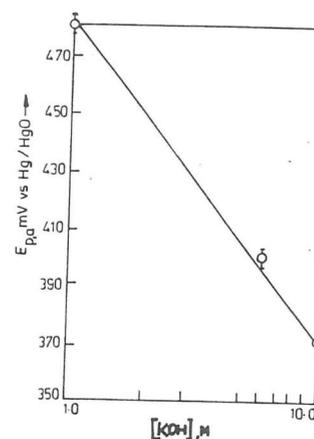


Fig 2. Plot of E_{p,a} vs. log[KOH] for gold.

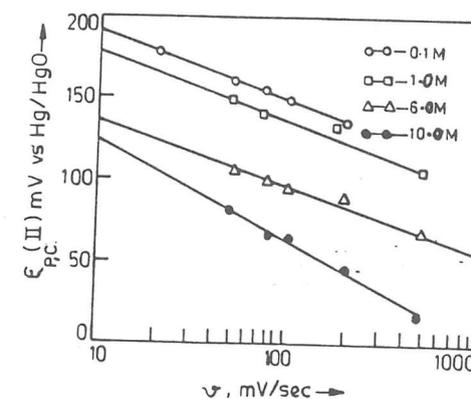


Fig.3. Plot of E_{p,c} (II) vs. log v for solutions of different KOH concentration.

Over a wide range of potentials, the oxide was not reduced on the negative scan. Hydrogen evolution was found to take place faster on an oxide surface. On subsequent sweeping hydrogen evolution took place steadily.

2- BEHAVIOUR OF SULPHUR ON GOLD

The presence of 10^{-2} M sulphur in 0.1M KOH revealed interesting features in the voltammogram (Fig.4). In the forward scan the zero current crossing potential (ZCCP) occurred at -800mV followed by an anodic peak at -109mV (I). Hysteresis in the negative scan was observed followed by three cathodic peaks at -450mV (II), -594mV (III) and at -966mV (IV).

The oxidation peak at 500mV and the cathodic peak at +138mV observed in the absence of sulphur disappeared suggesting complete modification of the surface and electrochemical reaction sequences.

The cathodic peak potential (II) was independent of the sweep rate while that of the peak (III) increased. $Q_c(II)$ increased while $Q_c(III)$ remained constant with sweep rate. The cathodic peak potential (IV) shifted towards negative potentials with sweep rate.

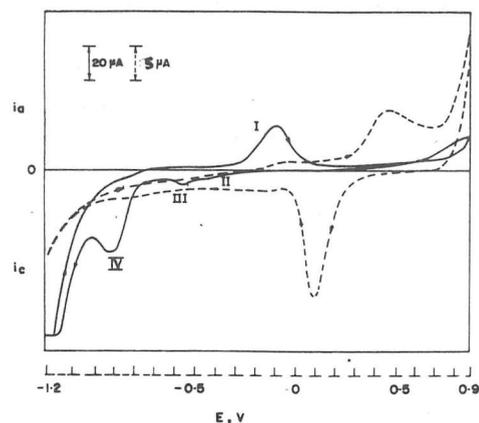


Fig 4. Cyclic voltammograms of 0.1 mol dm⁻³ KOH solutions on the gold electrode.
 - - - - without sulphur
 - - - - with 0.01 mol dm⁻³ sulphur

Increase of the KOH concentration (Fig.5) resulted in the shifting of the zero current crossing potential (ZCCP) towards negative potentials in the forward scan while the anodic peak at -400mV disappeared and became a single peak at -250mV. Beyond 500mV, during the negative scan, an inverted anodic peak appeared at higher alkali concentration. The cathodic peaks (III) and (IV)

shifted towards positive direction with increasing concentration which suggests that the OH⁻ ion favoured the reduction. At higher alkali concentration, peak potential (IV) was independent of sweep rate.

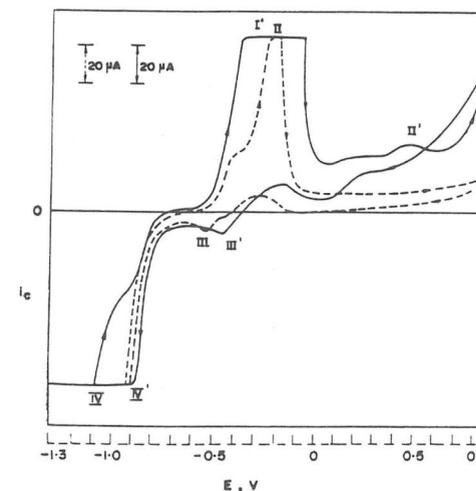


Fig 5. Cyclic voltammograms for 0.1 mol dm⁻³ sulphur solutions with different KOH concentrations. $v = 200 \text{ mVs}^{-1}$. Potentials vs. Hg/HgO.
 - - - - 1.0 mol dm⁻³ KOH
 - - - - 10.0 mol dm⁻³ KOH

Upon continuous cycling, the hydrogen evolution current decreases. The charges flowed under the peaks I, II and IV decreased while those of peaks II' and III remained constant (Fig 6).

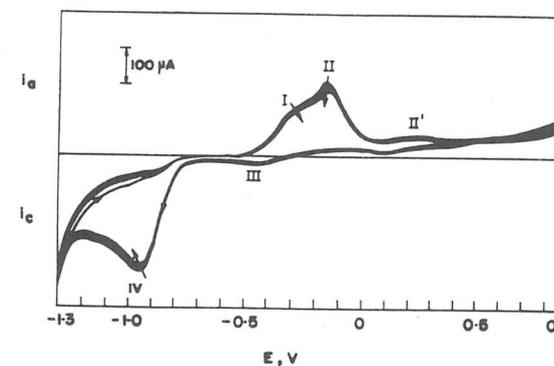


Fig 6. Cyclic voltammograms of a 10.0 mol dm⁻³ KOH + 0.1 mol dm⁻³ sulphur solution on the gold electrode. Effect of cycling $v = 100 \text{ mVs}^{-1}$. Potentials vs. Hg/HgO.

DISCUSSION

The electrochemical behaviour of gold in alkali has been studied and oxide monolayer formation was suggested before O₂ evolution [7,8]. The gold oxide is formed at potentials >530mV and oxygen evolution occurred at potentials >700mV. The currents observed are well above the double layer charging values and these charge values are well above monolayer formation. The appearance of an anodic peak whose peak potential varied with KOH concentration suggests that the discharge of OH⁻ ion takes place on gold as

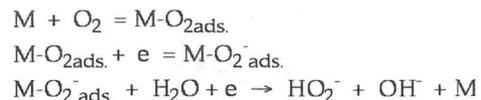


The initiation of the adsorbed hydroxide monolayer formation takes place upto the formation of Au(I) species and is followed by higher oxidation and probably further thickening of the oxygen containing layer. The existence of anionic species at the surface was earlier discussed [9]. Above 500mV, a variety of partially hydrated discrete anionic species are produced. The hydrous film is soluble in higher KOH concentration due to aurate formation.

The appearance of a cathodic peak around 156mV was due to the reduction of oxygen. The reduction of adsorbed oxygen is irreversible and the electrochemical adsorption model [10] suggests that

$$E_{p,c} = (2.3RT/\alpha_c F) \log v$$

where 2.3RT/α_cF is the cathodic Tafel slope and v is the sweep rate. In 0.1M KOH solutions, (dE_{p,c}/dlog v) gave a slope of 40mVdecade⁻¹ while in 1.0M KOH solutions 60mVdecade⁻¹ were observed. Oxygen reduction was found to occur [11] as



where M is the substrate electrode.

The independency of Q_c on the OH⁻ ion concentration and the observed Tafel slope of 40 mVdecade⁻¹ below 1.0M KOH concentration suggest that the second electron transfer was slow. At higher KOH concentrations the desorption of O₂⁻ followed by a second order homogeneous reaction in the solution phase may occur as



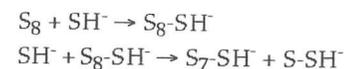
An increased Q_c over a wide range of negative potentials suggests the desorption of OH⁻ ions.

The oxidation and reduction of various species of sulphur in alkali solutions and the associated equilibrium potentials are listed (Table I, [12]).

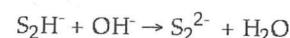
TABLE I
POSSIBLE OXIDATION-REDUCTION COUPLES INVOLVING SULPHUR AND THEIR REVERSIBLE POTENTIALS AT pH 15 (30°C)

REACTION	E (mV vs. Hg/HgO)
5H ₂ S = S ₅ ²⁻ + 10H ⁺ + 8 e	-953
2HS ⁻ = S ₂ ²⁻ + 2H ⁺ + 2 e	-512
3HS ⁻ = S ₃ ²⁻ + 3H ⁺ + 4 e	-487
5HS ⁻ = S ₅ ²⁻ + 5H ⁺ + 8 e	-470
S ²⁻ = S + 2 e	-299

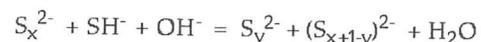
The dissolution of sulphur is initiated by the nucleophilic attack of HS⁻ on to the S₈ ring. The formed species is further attacked by HS⁻ leading to the stepwise degradation of the sulphur chain [13, 14].



and



In presence of SH⁻ and OH⁻,



to produce an equilibrium mixture of polysulphides.

The chemical analysis of the polysulphide solutions revealed S₄²⁻ and S₃²⁻ as predominant species at low pH and at very high pH, S₃²⁻ was the stable dominant species. In aprotic solvents the elemental sulphur reduction was induced by OH⁻ ion and S₃²⁻. The S₃²⁻ was the electrochemically active species at low negative and positive overpotentials [15, 16].

The appearance of an anodic peak at -400mV (more negative to the E_e of HS^-/S_2^{2-}) which varied with $\log[KOH]$ (Fig.7) suggests the formation of super sulphide anion.

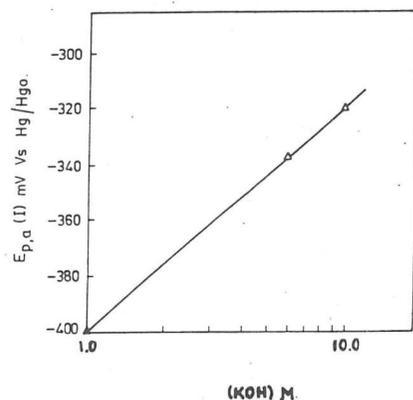
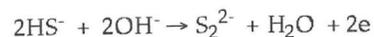


Fig 7. Plot of $E_{p,a}$ (I) vs. $\log [KOH]$ for 0.1Moldm^{-3} sulphur solutions on the gold electrode.

This was confirmed by the appearance of a cathodic peak at -350mV whose $E_{p,c}$ varied with $\log[OH^-]$ with a slope of 60mVdecade^{-1} . Increase of alkali concentration shifted the $E_{p,c}$ to more negative potentials indicating that the reduction becomes difficult. From the relative charges passed in stripping a sulphur layer from a stationary and a rotating electrode the composition of the intermediate polysulphide was deduced earlier [17]. The appearance of an anodic peak at -100mV is due to the oxidation of adsorbed S_2^{2-} and the formation of sulphur occurred at 500mV. In 0.1M KOH, the appearance of a single anodic peak is due to the underpotential deposition of sulphur [18]. The adsorption of sulphur from the gas phase demonstrated that with the increase of adsorbed sulphur atoms the formation of two dimensional sulphide takes place [19].

On a polycrystalline surface a monolayer of sulphur atoms involves $0.72 \times 10^{15} \text{atomcm}^{-2}$ [19]. This is equivalent to a charge of 0.23mCcm^{-2} . The observed anodic charges (Q_a) at +350 mV were found to be of the order of 50mCcm^{-2} in the absence of sulphur in 1M KOH solutions and of 71.25mCcm^{-2} in the presence of sulphur. The enhanced charge in the presence of sulphur may be due to the adsorption of sulphur or the enhanced formation of hydrous gold film containing sulphur.

Beyond 300mV, the polarization curves in the negative scan were different from the curve obtained in the positive scan. This suggests that a different mechanism must hold for the anodic film formation and the cathodic reduction of the films. A local exchange mechanism of the oxide growth assumed the growing of an uniform thickness. In the presence of oxidised sulphur species, the reduction of passive films can occur at random which might have been started from a weak point that will dissolve preferentially due to the local induced electric field (i.e. pitting). The pitting potential varied with sweep rate and KOH concentration.

TABLE 2
PITTING POTENTIAL OF GOLD (vs. Hg/HgO) AS A FUNCTION OF SWEEP RATE AND ALKALI CONCENTRATION

SWEEP RATE mVs^{-1}	E_{pit} (mV)		
	0.1moldm^{-3} KOH	6.0moldm^{-3} KOH	100moldm^{-3} KOH
50	500	400	320
75	520	450	300
100	600	475	280
200	620	575	280
500	750	---	---

The higher alkali concentration favoured the formation of soluble hydroxy complexes $[Au_2(OH)_8]^{2-}$ as indicated by the less noble values. The charge density under the hysteresis region which was a measure of the pitting susceptibility was found to be enhanced by the alkali concentration.

In the negative scan, the reduction of the passive film took place when the pit in the passive film reached the surface of the underlying metal. The overall process was a reversed nucleation and growth process as indicated by the inverted anodic peaks in the negative scan which was normally expected in pitting corrosion.

Oxygen reduction did not occur as observed earlier in ethanol solution [19]. On mercury the oxygen reduction in the presence of sulphur was found only for the potentials of the HgS reduction [20].

Cathodic peaks were observed on a film surface which was covered partially either with sulphur or with oxidized products of sulphur. The desorption of sulphur occurred along with reduction forming S_2^{2-} which were

converted to HS⁻ by OH⁻ ions. The appearance of the cathodic peak at round -1000mV may be due to the discharge of water yielding atomic hydrogen along with H₂S formation.

CONCLUSIONS

On gold, the oxidation of HS⁻ to S₂²⁻ is reversible and is followed by the oxidation to sulphur which gets incorporated into the hydrous film on gold. Breakdown of these films and pitting susceptibility increased with alkali concentration. On the sulphur covered gold surface, the oxygen reduction was not observed and H₂S gas evolved along with hydrogen.

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