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Passive behavior of gold in sulfuric acid medium

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Abstract: Anodic behavior of pure Au as compared to platinum (Pt) in H_2SO_4 solutions was considered by different electrochemical techniques for an appropriate insight. Cyclic voltammetry studies showed two oxidation and one film reduction peaks for Au, while one oxygen evolution reaction for Pt. Increasing H_2SO_4 concentration (from 0.5 to 1 mol/L) caused 2-fold increases in peak current density of Au. Increase in agitation promoted passive zone of Au, while it was negligible for Pt by potentiodynamic studies. Potentiostatic studies (2 h) at three anodic passive potentials in 1 mol/L H_2SO_4 showed that the admittance of Au was found to be the lowest at 1.4 V. Electrochemical noise measurements during the decay periods (16 h) after polarization showed that the thin passive film formed during potentiostatic polarization has been dissolved.

Key words: gold; passivation; sulfuric acid; electrochemical noise

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1 Introduction

Gold surface is passive in certain conditions, which is problematic for gold industry. Increase in worldwide processing of refractory and complex gold ores leads to the increase of passivation problem of gold [1]. Although many studies have been carried out on passive phenomenon of gold for many years, there is still a continued debate on this phenomenon [2]. Therefore, it is highly important to revisit pure gold corrosion studies in aqueous solutions, such as sulfuric acid reagent for better understanding of active and passive behaviors of gold.

It is stated that at low potential region (0.9−1.3 V (vs SHE)), oxygen evolution takes place on gold surface partially covered with adsorbed oxygen, while Au_2O_3 forms at high potential (1.36 V). Then gold electrodes become covered with hydrated Au_2O_3 [3,4]. Many studies have shown that Au, α-oxide (AuO, $Au(OH)_2$, Au_2O_3) and β-oxide (Au_2O_3), hydrated Au_2O_3, and complex mixtures of $Au(OH_3)$, H_2O and trapped O_2 films are formed at gold electrodes. First of all, Au_2O forms, and then converts through to Au_2O_3 prior to oxygen evolution [5]. Hydrogen evolution (Eq. (1)) and oxygen evolution (Eq. (2)) reactions can be considered for gold in solutions. In acidic medium, gold is a poor catalyst for oxygen evolution reactions since the adsorbed oxide films are poor electronic conductors [6]. Thin films adsorbed on the noble metals in oxygen saturated acid solutions are not much thicker than a monolayer [7]. According to HOARE [7], oxygen evolution occurs on gold partially covered with adsorbed oxygen in the low potential, while it occurs on Au_2O_3 at high potential. Hence, potentials at which the film starts growing and intersect are similar.

$$2H_2O+2e\leftrightarrow 2OH^-+H_2 \quad (1)$$

$$2OH^-\leftrightarrow H_2O+1/2O_2+2e \quad (2)$$

Growth of oxide film on Au depends on polarization conditions and oxide growth is not logarithmic in time. Thick oxide films which formed in minutes or hours, readily reduced in a short time indicating that activation energy of bulk-type oxide growth is much higher than that for its reduction [8].

Electrochemical formation and reduction of Au_2O_3 is a relatively slow process, since Au_2O_3 is poor conductor and poorly adherent to Au surface [9,10]. BARNARTT [3], WHITTON and DAVIES [11] concluded that film growth continues linearly at constant current. WHITTON and DAVIES [11] reported that 1.5%

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of oxidized gold in solution remains on the film surface. Dissolution and passivation occur parallel in the passive potential region (φ<1.7 V (vs SHE)), probably due to a competitive adsorption between chloride and an oxygen species. First dissolution happens then passivation takes place [3,12].

XIA and BIRSS [13] studied the oxide growth of Au in 0.1 mol/L H_2SO_4 solution and observed that α-oxide films can be formed at potentials below 2.0 V (vs SHE)) using potentiostatic test. At potentials below 1.5 V, AuO was considered as the α-oxide film while a mixture of AuO and Au_2O_3 above this potential. In addition, thickness of α-oxide film can reach up to 1.5 nm, which is equivalent to three monolayers of Au_2O_3 at high potentials or potential cycling with long test time. On the other hand, it was found that in 0.1 mol/L H_2SO_4 solutions at high potentials (between 2.1 and 2.6 V), hydrous Au β-oxide films were formed, along with the inner α-oxide [13]. From the electrochemical data at short time of growth, it can be suggested that α-oxide film is initially transformed to β-oxide film, and then thickens further with time. At the onset of β-oxide film formation, mass to charge ratio increases as the film thickens linearly with growth time. Furthermore, refractive index of this film decreases with growth time. It was suggested that the β-oxide film is initially $Au_2O_3 \cdot H_2O$, becoming $Au_2O_3 \cdot 2H_2O$ at longer growth time (thicker film) [14].

To date, most of the studies on gold electrode in sulfuric acid solutions were carried out using typical cycling voltammetry (CV) without agitation. In this work, CV as well as potentiodynamic technique at different agitation speeds was carried out. This was followed by potentiostatic studies at three different passive potentials in two concentrations of sulfuric acid (0.5 and 1 mol/L) at 25 °C. Furthermore, electrochemical noise measurement (ENM) technique was considered for gold corrosion studies during decay periods, and this was carried out after potentiostatic polarization. Also, platinum electrode was tested for comparison as a reference.

2 Experimental

2.1 Electrochemical set-up

The electrolyte with different concentrations of sulfuric acid solutions (0.5, 1 mol/L H_2SO_4) at 25 °C, was magnetically agitated during the experiments by a stirrer (4 cm in length and 1 cm in diameter). The working electrode and the counter electrode were mounted in a suitable Teflon holder and the distance between them was fixed at 2 cm. The reference electrode was Ag, AgCl/KCl_{sat} (0.202 V (vs SHE)).

For electrochemical studies, the 99.99% Au foil obtained from Sigma Aldrich as working electrode and platinum as counter electrode was used in the same electrolyte. The Au electrode was cut into small pieces of 1 cm × 1 cm, then connected with an insulated copper wire and cast in acrylic resin. The exposed surface area was 1 cm^2. Prior to experiments, all working surfaces of the electrodes were ground with SiC abrasive paper (Leco Corporation) down to 1200 grit and washed with double distilled water.

2.2 Electrochemical measurements

The measurements of the current densities of the gold electrodes were carried out by potentiodynamic measurements in H_2SO_4 solution from 250 mV below the corrosion potential (φ_{corr}=680 mV (vs SHE)) to a final potential of approximately 1.6 V above φ_{corr}, at a scan rate of 0.166 mV/s. Also, potential polarization was employed at three different potentials (1.2, 1.4 and 1.6 V) at 25 °C. The experimental setup was an EG&G PARSTAT 2263 potentiostat/galvanostat controlled by PAR PowerSuite Electrochemistry Software for potentiostat measurements.

Electrochemical noise (EN) measurements were carried out using the zero resistance ammeters (ZRA) set-up mode [15]. Two identical specimens of gold electrodes were used as the working electrode and Ag, AgCl/KCl_{sat} (0.202 V (vs SHE)) was used as reference electrode. The electrochemical current noise was measured as the galvanic coupling current between two identical working electrodes (WE) kept at the same potential in agitated (50 r/min) 0.5 mol/L sulfuric acid solution. A GAMRY model PC4/750 potentiostat linked to a personal computer was used to log potential. Current was sampled at a scan rate of 10 Hz for 102.4 s, giving a total of 1024 readings. EN experiment data treatment was done using the GAMRY ESA400 software [16,17]. The noise data were collected for 16 h immersion of the working electrodes in the solution followed by 2 h polarization after potentiodynamic at three different potentials (1.2, 1.4 and 1.6 V). Noise data were also transformed into the frequency domain using a fast Fourier transformation (FFT) algorithm and presented as power spectral density (PSD) calculated in the frequency domain from 5×10^{-2} to 5 Hz. All tests were performed in duplicates. In general, the reproducibility of the data was found to be ~5%.

For data analysis of potentiodynamic, corrosion potential (φ_{corr}), reduction current density (J), the critical passive potential (φ_{cp}), the critical passive current density (J_{cp}), the starting potential of the transpassive region (φ_{sp}) and the starting current density of the transpassive region (J_{sp}) were considered since they provide much information on active-passive behaviors.

2.3 XPS analysis procedure

Surface characterization studies were carried out using X-ray photoelectron spectroscopy (XPS). XPS results were collected using an AXIS-ULTRA instrument by Kratos (UK). The lens system is in the “hybrid” configuration, and the aperture is in the “slot” position. This assures the highest sensitivity with an analyzed spot approximately 800 μm × 400 μm, which is the size of monochromatic X-ray beam. In order to have a precise knowledge of the binding energy scale just before the analysis of the sample, pure gold electrode has been cleaned in situ by sputtering with argon ion beam (10 mA current and 2 keV energy) for about 20 min. The Af4f$_{7/2}$ line was then recorded at high resolution. As expected, the Au peak was fitted to have a BE of exactly 83.95 eV.

3 Results and discussion

3.1 Voltammetric characteristics of Au and Pt electrodes in various concentrations of sulfuric acid medium

Cyclic voltammetry can be considered to be ideal “in situ” measuring technique, since it can investigate the surface behavior of an electrode sensitively by cyclic voltammograms in non-agitated solutions [18]. Cyclic voltammetry studies on polished surfaces of the gold and platinum electrodes were carried out at a scan rate of 20 mV/s in 0.5 mol/L H_2SO_4 solution at 25 °C. The typical CV curves for the gold electrode in 0.5 mol/L sulfuric acid solutions are shown in Fig. 1. The scan potential was in the range of −0.2 to 2.2 V (vs SHE). Duplicate experiments were carried out to get the redox peaks on the surface of gold electrode in sulfuric acid solution and are shown in Fig. 1 as an example for duplicate experiment which was obtained at the consecutive time in the first two cycles.

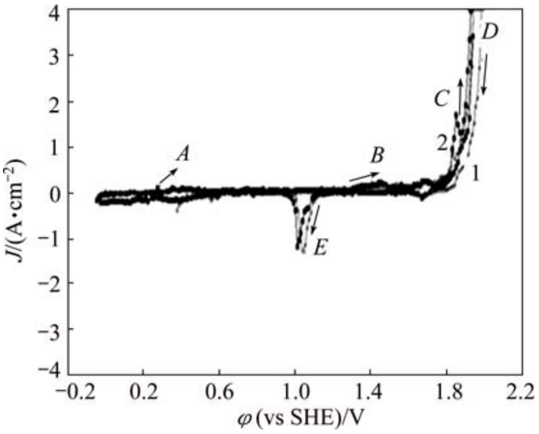

Fig. 1 Cyclic current−potential duplicate curves (1 and 2) of gold electrode in 0.5 mol/L H_2SO_4 solution with scan rate of 20 mV/s at 25 °C (dotted arrow indicates the peak and regions)

Figure 1 shows cyclic voltammogram curves of the gold electrode in 0.5 mol/L H_2SO_4. Two regions (*A* and *B*), two redox peaks (*C* and *E*) and oxygen evolution reaction (*D*) were observed on the curve varying from −0.07 to 2.0 V. The reactions corresponding to each peak are given based on the literature [5]. Region *A* (0.2−0.6 V) of the CV corresponds only to the double layer charge, while Region *B* (0.6−1.35 V) is the so-called pre-oxide region, designated here as Au(OH) [13]. Also, two oxidation peaks *C* and *D* were observed. The oxidation peak *C* at the potential of 1.85 V should correspond to reaction Eq. (3) [19]:

$$\mathrm{Au(OH)+2H_2O-2e \rightarrow Au(OH)_3+2H^+},\ \varphi^o=1.79\ \mathrm{V} \quad (3)$$

The second peak *D* appeared from ca. 1.88 V and was the highest peak among all the peaks indicating that it was due to the oxygen evolution reaction (Eq. (4)) on the Au electrode which is a good conductor:

$$\mathrm{2H_2O-4e \rightarrow O_2+4H^+},\ \varphi^o=1.23\ \mathrm{V} \quad (4)$$

The obtained potential of 1.88 V for oxygen evolution reaction should represent high overpotential since the theoretical value of φ^o should be close to 1.23 V. During the reverse sweep, one reduction peak was obtained. At the potential of ca. 1.1 V, the reduction peak φ should be as below (Eq. (5)) [19]:

$$\mathrm{Au(OH)+e \rightarrow Au+OH^-},\ \varphi^o=1.05\ \mathrm{V} \quad (5)$$

Figure 2 illustrates the typical CV curves for the gold electrode in 1 mol/L sulfuric acid solutions. It can also be observed that two regions (*A* and *B*), two redox peaks (*C* and *E*) and oxygen evolution reaction existed in Fig. 2, similar to that of Fig. 1. As seen from Fig. 2, it can be observed that the reduction peak *E* current density at 0.9 V is around 2 times that in Fig. 1. These findings suggest that the oxidation peak current *C* (Eq. (3)) is also higher than that in 0.5 mol/L (Fig. 1). This means that increase in the concentration of sulfuric acid leads to an increase of the redox peaks of Au electrode in H_2SO_4.

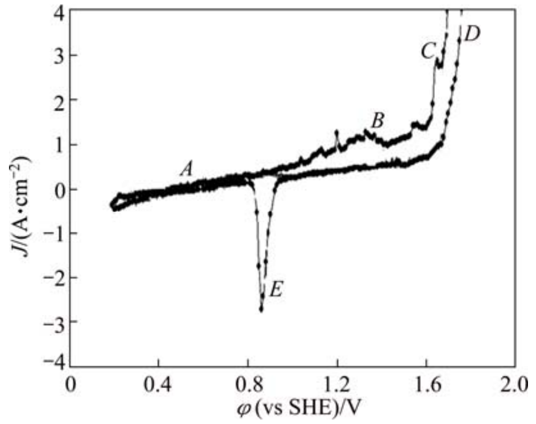

Fig. 2 Cyclic current−potential curve of gold electrode in 1 mol/L H_2SO_4 solution with scan rate of 20 mV/s at 25 °C

Figure 3 shows the typical CV curves for the platinum electrode in 0.5 mol/L sulfuric acid solutions. It was found that there was no reduction peak on the curve of the cyclic voltammogram of the platinum electrode in 0.5 mol/L H_2SO_4 at a scan rate of 20 mV/s at 25 °C (Fig. 3). However, SUGAWARA et al [20] observed the Pt-oxides peak in 0.5 mol/L sulfuric acid medium during cyclic polarization. Although there was no obvious peak of reduction reaction on CV curve, a slight film could be suggested on the surface of platinum electrode during cyclic polarization.

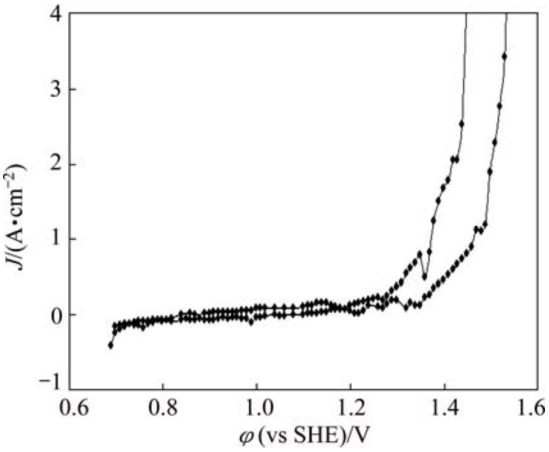

Fig. 3 Cyclic current−potential curve of platinum electrode in 0.5 mol/L H_2SO_4 solution with scan rate of 20 mV/s at 25 °C

3.2 Potentiodynamic polarization of Au and Pt electrodes

3.2.1 Au and Pt electrodes in 0.5 mol/L sulfuric acid solution

In potentiodynamic polarisation test, the gold specimens were polarized in 0.5 mol/L H_2SO_4 solution from 250 mV below the corrosion potential (φ_{corr}) to a final potential of approximately 1.6 V above φ_{corr}, at a scan rate of 0.166 mV/s [21]. The main electrochemical parameters deduced from the polarization curve for gold electrode in sulfuric acid shown in Fig. 4 are reported in Table 1. The terms φ_{corr}, J , φ_{cp}, J_{cp}, φ_{sp} and J_{sp} (Table 1) are corresponding to corrosion potential, reduction current density, the critical passive potential, the critical passive current density, the starting potential of the transpassive region and the starting current density of the transpassive region, respectively. The critical current density for passivation J_{cp} corresponds to the onset of low corrosion rates since gold passivation is not a perfect conventional one. The starting current density of the transpassive region J_{sp} corresponds arbitrarily to the highest corrosion rate before the sudden important increase in corrosion rate. Although the experiments were carried out with atmospheric oxygen, these gave the same trend as that in the absence of oxygen. All tested specimens exhibit the same curve-shape showing a passive zone with obvious break potential. It is clearly seen from Fig. 5 that the curve of platinum specimens had short passive zone as compared to that of gold electrode (Fig. 4), since platinum is easier to corrode in sulfuric acid solution. The results of Figs. 4 and 5 are presented in Table 1.

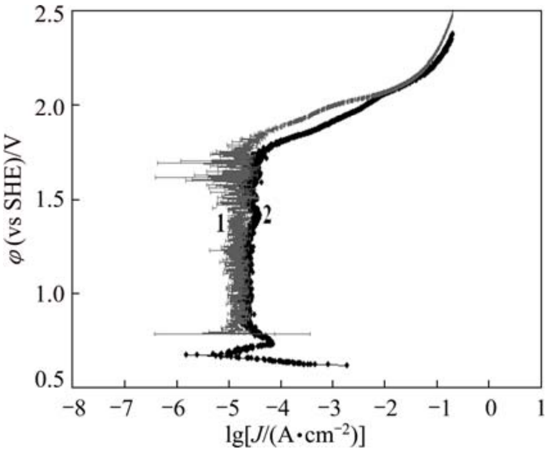

Fig. 4 Potentiodynamic duplicate curves (1 and 2) for gold electrode with scan rate of 0.166 mV/s in 0.5 mol/L H_2SO_4 solution at 25 °C, and magnetically stirred at 100 r/min

As seen from Table 1, it was found that gold electrode had much lower (~1/3) reduction corrosion current density than platinum. This suggests that the gold electrode had the better reaction resistance than platinum in sulfuric acid solution. The passive zone of gold electrode (~1000 mV) was more important than that of platinum (~808 mV), and the critical passive current density of gold (25.9 μA/cm²) was much lower than that of platinum (491 μA/cm²). This indicates that the gold electrode presents better aptitude to passivation than platinum.

3.2.2 Effect of agitation

When the gold electrode was studied by potentiodynamic measurements, the surface of gold electrode was first active, then formed a submonolayer of oxide Au(OH), and Au_2O_3. Au electrode was in passive

Table 1 Data from electrochemical studies presented in Figs. 4 and 5

Sample	φ_{corr}(vs SHE)/ mV	$J_{\text{reduction}}$/ ($\mu A\cdot cm^{-2}$)	φ_{cp}(vs SHE)/ mV	J_{cp}/ ($\mu A\cdot cm^{-2}$)	φ_{sp}(vs SHE)/ mV	J_{sp}/ ($\mu A\cdot cm^{-2}$)
Gold	680	11.4	811	25.9	1773	36.7
Platinum	270	32.5	1013	491	1821	483

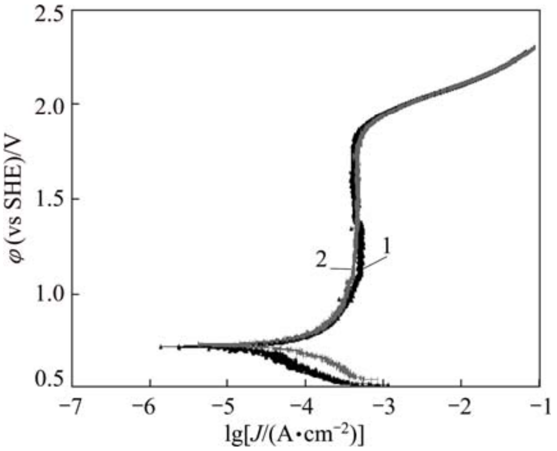

Fig. 5 Potentiodynamic duplicate curves (1 and 2) for platinum electrode at scan rate of 0.166 mV/s in 0.5 mol/L H_2SO_4 solution at 25 °C, and magnetically stirred at 100 r/min

condition. However, agitation can influence the rate of passive zone of gold electrode in sulfuric acid medium. It is worth noting that potentiodynamic studies at different agitation speeds of the magnetic stirrer were considered to investigate the effect of agitation on the passive mechanism of gold and platinum in 0.5 mol/L H_2SO_4. It is clearly seen from Fig. 6 that the agitation speed has great influence on passivation of gold in sulfuric acid solution.

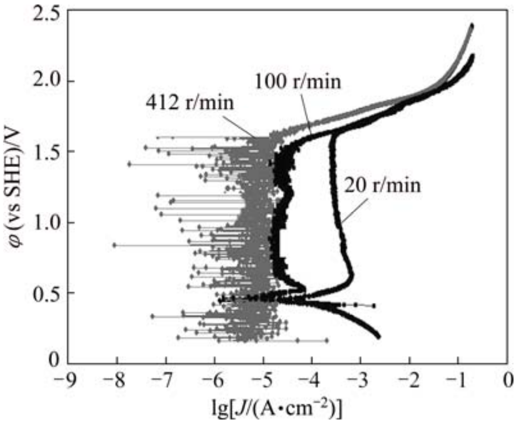

Fig. 6 Potentiodynamic curves of gold electrode at scan rate of 0.166 mV/s in 0.5 mol/L H_2SO_4 solution at 25 °C, magnetically stirred at different agitation speeds (20, 100 and 412 r/min)

At high agitation speed of 412 r/min, the most important passive zone was observed. The passive region is more important for the highest agitation (412 r/min) than that corresponding to 20 and 100 r/min. Gold electrode had the lowest passive current density 7.45 μA/cm^2 at 412 r/min as compared to 25.9 μA/cm^2 at 100 r/min, and 322 μA/cm^2 at 20 r/min. The passive current density at this rotation speed was so small and sensitive hence strong oscillatory current density was observed. This could be linked to that high agitation resulted in more hydroxide ions, atmospheric dissolved oxygen, and other oxygen carrying anions at the interface of Au/H_2SO_4 solution. More protective film of Au oxides could then be formed. Then, passive phenomenon of gold could be controlled with high rates of diffusion at imposed anodic potentials. The passive layer is unstable at the open circuit potential.

Figure 7 shows that the agitation speed has much less influence on passive phenomenon of platinum. It can be observed that the passive current density at 412 r/min was 768 μA/cm^2, somewhat lower than that of 783 μA/cm^2 at 20 r/min. The region or zone of passivation was almost the same for the two speeds. It is also interesting to find that at high agitation speed such as 412 r/min, the region of the passive zone of platinum (0.8 V) was much less important than that of gold (1.1 V) and the passive current density of platinum (768 μA/cm^2) was much higher than that of gold (7.45 μA/cm^2). At low agitation speed of 20 r/min, the passive zone of platinum (0.78 V) was also less important than that of gold (0.9 V), and the passive current density of platinum (783 μA/cm^2) was also much higher than that of gold (322 μA/cm^2). Although high agitation gave more atmospheric dissolved oxygen and oxygen carrying anions at the interface, platinum was very partially influenced by agitation in sulfuric acid solution. This means that the passive action of platinum in 0.5 mol/L H_2SO_4 solution was much less controlled by diffusion. Less dissolved oxygen and anions carrying oxygen in sulfuric acid solution caused less passive zone for gold, while it had almost no influence on platinum.

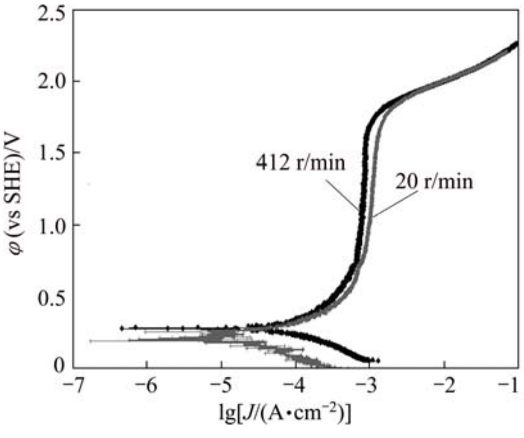

Fig. 7 Potentiodynamic curves of platinum electrode at scan rate of 0.166 mV/s in 0.5 mol/L H_2SO_4 solution at 25 °C, magnetically stirred at different agitation speeds (20 and 412 r/min)

3.2.3 Effect of sulfuric acid concentration

Potentiodynamic curve for the gold electrode at a scan rate of 0.166 mV/s in 1 mol/L H_2SO_4 solution at 25 °C and magnetically stirred at 100 r/min was presented in Fig. 8. It can be observed that a passive zone with obvious break potential existed in the potential curves. The passive zone of gold electrode in 1 mol/L H_2SO_4 solution is much longer than that in 0.5 mol/L H_2SO_4 solution.

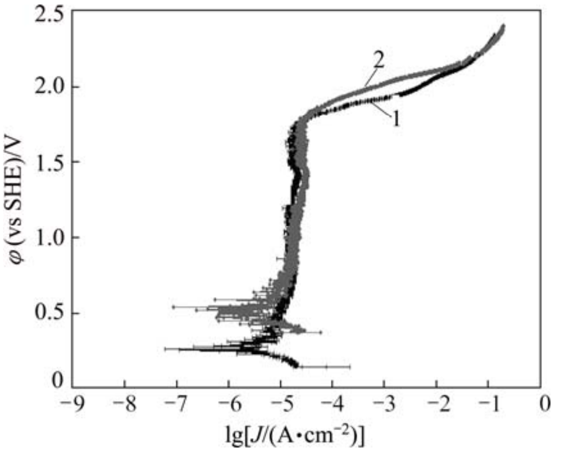

Fig. 8 Potentiodynamic duplicate curves (1 and 2) for gold electrode with scan rate of 0.166 mV/s in 1 mol/L H_2SO_4 at 25 °C, and magnetically stirred at 100 r/min

Table 2 illustrates that the reduction corrosion current density of gold electrode in 1 mol/L H_2SO_4 solution (7.95 μA/cm^2) is much lower than that in 0.5 mol/L H_2SO_4 solution (11.4 μA/cm^2) (Table 1). These findings have revealed that gold electrode in 1 mol/L H_2SO_4 solution is much easier to passivate as compared to that in 0.5 mol/L H_2SO_4 solution. It was also found that the transpassive region and/or oxygen evolution for gold electrode in 1 mol/L H_2SO_4 is higher (~1.4 V) as compared to that in 0.5 mol/L H_2SO_4 (~1.0 V), suggesting that the quality of passivation of gold electrode in 1 mol/L H_2SO_4 at 100 r/min agitation speed is better than that in 0.5 mol/L H_2SO_4 solution. In 1 mol/L H_2SO_4 solution, the passive current density was found to be 11.9 μA/cm^2, as compared to 25.9 μA/cm^2 in 0.5 mol/L H_2SO_4, but the passive region zone was almost similar.

3.3 Effect of electrode type on gold polarization

It was reported that rotating disc gold electrode could provide more reproducible results [22]. In this part, the behavior of a rotating disc gold electrode was tested as compared to that of pure gold electrode in sulfuric acid solution employing magnetic agitation. The potentiodynamic curve for the disk gold electrode (0.07 cm^2) at scan rate of 0.166 mV/s and rotation speed of 100 r/min in 0.5 mol/L H_2SO_4 solution at 25 °C was shown in Fig. 9 and the results of this potentiodynamic studies are summarized in Table 3.

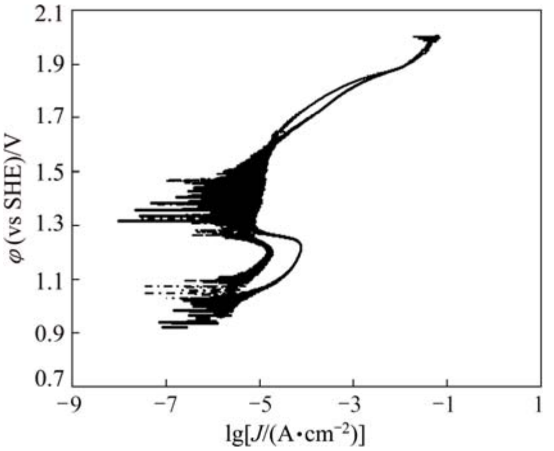

Fig. 9 Potentiodynamic duplicate curves (1 and 2) for disk gold electrode with scan rate of 0.166 mV/s, and rotation speed of 100 r/min in 0.5 mol/L H_2SO_4 solution at 25 °C

Comparison of Tables 1 and 3 shows that passive zone of the disk electrode (~300 mV) is much shorter than that of gold electrode (~1000 mV) in 0.5 mol/L H_2SO_4 solution. Considering that the reduction corrosion current density of gold disk specimen was much lower (2.57 μA/cm^2) than that of gold electrode specimen (11.4 μA/cm^2), the J_{cp} and J_{sp} are much lower (20%) for the disc electrode. This observed difference in corrosion rates and other electrochemical properties of passivation could be linked to some key parameters of the adhesion of the passive layer such as gold electrode was magnetically agitated, while the disc was submitted to a very strong rotating effect and oxygen containing ions diffusion [23]. Also, gold electrode was placed vertical, while the disc electrode surface was horizontal upside-down on the top of the electrolyte.

Table 2 Data from electrochemical studies presented in Fig. 8

Sample	φ_{corr}(vs SHE)/ mV	$J_{reduction}$/ (μA·cm^{-2})	φ_{cp}(vs SHE)/ mV	J_{cp}/ (μA·cm^{-2})	φ_{sp}(vs SHE)/ mV	J_{sp}/ (μA·cm^{-2})
Gold	203	7.95	360	11.9	1695	25.6

Table 3 Data from electrochemical studies presented in Fig. 9

Sample	φ_{corr}(vs SHE)/ mV	$J_{reduction}$/ (μA·cm^{-2})	φ_{cp}(vs SHE)/ mV	J_{cp}/ (μA·cm^{-2})	φ_{sp}(vs SHE)/ mV	J_{sp}/ (μA·cm^{-2})
Disk gold	890±37	2.57±0.1	1180±19	5.43±0.3	1485±43	7.42±0.4

3.4 Potentiostatic polarization

In potentiostatic study, a constant potential was applied between the working electrode and the reference electrode. The current density of working electrode was recorded as function of time at various potentials. In addition, potentiostatic measurements were performed to evaluate the characterization of gold electrode in 1 mol/L sulfuric acid solution since the passive film of gold electrode in 1 mol/L sulfuric acid solution was better than that in 0.5 mol/L sulfuric acid solution. In this experiment, after a potentiodynamic test at the scanning potential from −0.3 to 1.2−1.6 V (vs SHE), a potential step at one of the three potentials of 1.2, 1.4 and 1.6 V (vs SHE), respectively, was carried out since the three potential positions represent the beginning, middle and end of passive zone. As seen from Fig. 10, the corrosion rate of gold electrode in 1 mol/L H_2SO_4 solution was the lowest at 1.4 V among the three potentials, followed by that at 1.2 V and 1.6 V (the highest), respectively. The lower values of the passive current density could be due to higher thickness, less porosity, more stable composition and/or more adhesion of the surface film on gold electrode. It was found that higher film thickness resulted in lower current density on the surface of gold electrode specimen in sulfuric acid solution. It can then be stated that passive film could be formed on gold in sulfuric acid solution at certain anodic conditions.

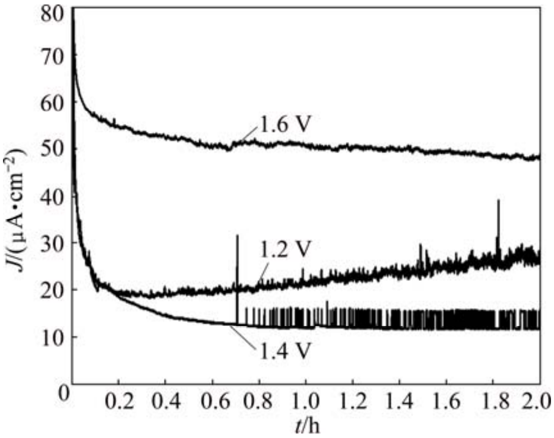

Fig. 10 Potentiostatic curves for gold electrode at potential 1.2, 1.4 and 1.6 V (vs SHE) in 1 mol/L H_2SO_4 solution at 25 °C, and magnetically stirred at 100 r/min

3.5 Electrochemical noise studies of Au

After 2 h potentiostatic polarization for 3 potentials (1.2, 1.4 and 1.6 V), following potentiodynamic scan, the ZRA measurements for electrochemical noise tests were carried out in 1 mol/L sulfuric acid solution with agitated solutions (50 r/min). It was observed that after 2, 8 and 10 h decay, the potential dropped down, suggesting that the thin passive film was dissolved in sulfuric acid.

Figure 11 illustrates that the gold electrode was in passive condition at the onset of experiment. The plateau on the surface of gold electrode was longneck of around (10±1.5) h at 1.4 V, and (7±1.3) h at 1.6 V while (3±1.2) h at 1.2 V. However, the sequence of the length or resistance of the passive film was the highest at 1.4 V, followed by 1.6 V and the lowest at 1.2 V. Duplicates were very sensible to the specimen surface preparation or roughness.

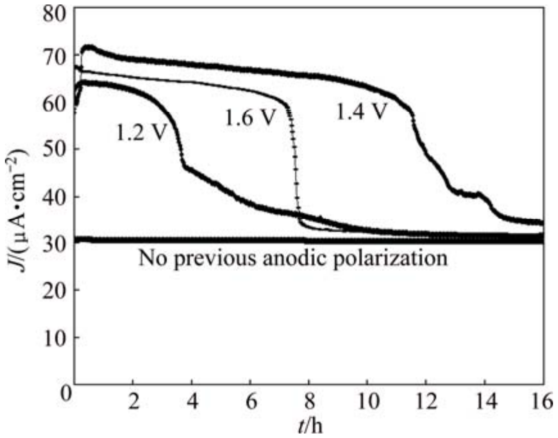

Fig. 11 Potential decay for 16 h of gold electrode after 2 h potentiostatic in sulfuric acid solution 1 mol/L H_2SO_4 at 25 °C, and magnetically stirred at 50 r/min with atmospheric condition

3.6 Admittance corrosion rate of Au during ENM studies

The statistical analysis in the time domain defines the noise resistance (R_n), which can be associated to the polarization resistance (R_p). The R_n inverse is the admittance expressed in unit of Siemens (S), which is proportional to the corrosion rate [24, 25]. After 2 h of potentiostatic polarization in sulfuric acid solution, the evolution of admittance “$1/R_n$” (mS) during 16 h of decay of gold electrode was determined in-situ every hour.

The admittance “$1/R_n$” decay curves during 16 h of gold electrode after 2 h of potentiostatic polarization in 1 mol/L H_2SO_4 solution at 1.2, 1.4 and 1.6 V (vs SHE) are shown in Fig. 12. The admittance “$1/R_n$” of gold electrode at the end of 16 h decay period was ~22.9 mS/cm^2 at 1.2 V, ~21.8 mS/cm^2 at 1.6 V and ~20.2 mS/cm^2 (lowest admittance) at 1.4 V. The admittance of gold electrode as reference without potentiostatic polarization was ~24.3 mS/cm^2 slightly higher than that of the polarized electrodes at high potentials. Also, comparison of Figs. 11 and 12, showed that the admittance of gold electrode in the passive zone (plateau) was lower than that in the active state.

It can be stated that at the end of 16 h decay, the admittance values of gold electrode were almost similar to that without passivation, suggesting that the film on the surface of gold electrode has the tendency to dissolve completely as function of time. At open circuit potentials, the admittance of the previously polarized surface becomes very close as a function of time to that of the non-polarized one. The stability and the presence of passive film were only observed under high electrode potentials in sulfuric acid solutions.

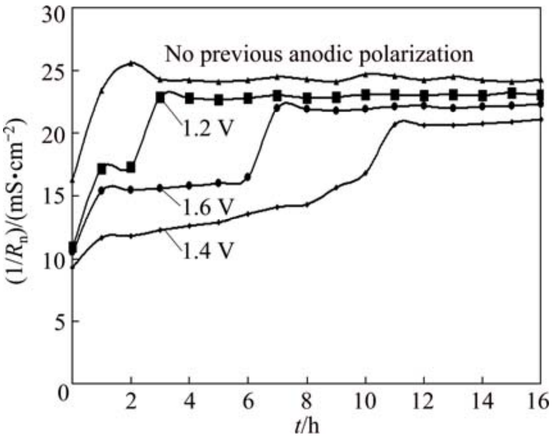

Fig. 12 Evolution of admittance “$1/R_n$” (mS) during 16 h decay of gold electrode after 2 h potentiostatic in 1 mol/L H_2SO_4 solution at 25 °C, magnetically stirred at 50 r/min, and saturated with atmospheric oxygen

3.7 XPS analysis

The photoelectron spectroscopy surface analysis for gold electrode after 2 h potentiostatic in 1 mol/L H_2SO_4 solution demonstrates that Au^{3+} and Au^+ existed on the surface of gold electrode, suggesting the formation of $Au(OH)_3$ or Au_2O_3 films on the surface of gold electrode. It is worth noting that oxide peaks were much clearer by XPS as compared to previous results in cyanide solution (Laval University report submitted to Barrick Gold Corp.). This indicates that passivation of gold surface is more stable in sulfuric acid solution. Also, Au_2O or $Au(OH)$ were produced on the surface of gold electrode during 2 h potentiostat. It is proved then that these were gold oxide and/or hydroxide film products after 2 h previous imposed polarization at 1.4 V (vs SHE), since the most important passive zone was observed at this potential for gold electrode in 1 mol/L H_2SO_4 solution. It is important to note that in this work XPS was carried out for gold electrode since platinum (Pt) is generally well known to show passive behavior in sulfuric acid solutions [26−30]. CRAIG and ANDERSON [26] reported that platinum resists sulfuric acid in all concentrations and temperatures. RACH and HEITBAUM [27] confirmed the presence of passive oxide layers on Pt electrode with XPS analysis. They reported the composition of the oxide layer as $Pt(OH)_4$ in 0.5 mol/L H_2SO_4 solutions as the main contributor to the passivation of platinum surface.

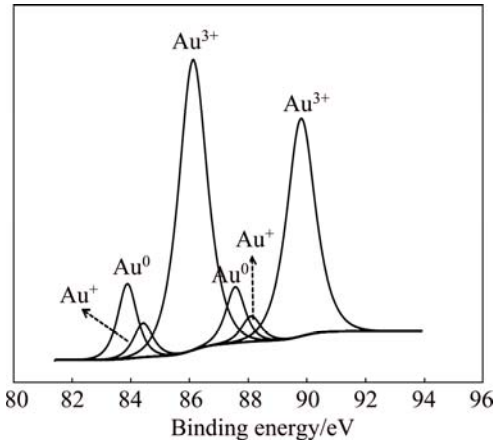

Fig. 13 X-ray photoelectron spectroscopy (XPS) surface analysis for gold electrode after 2 h potentiostatic in 1 mol/L H_2SO_4 solution at 25 °C and magnetically stirred at 100 r/min with atmospheric (Au^0: metallic gold, Au^+: gold (I) oxide, Au^{3+}: gold (III) oxide)

4 Conclusions

1) Cyclic voltammetry studies showed that the increase in the concentration of sulfuric acid from 0.5 to 1 mol/L has led to 2-fold increases in redox peak current densities of Au electrode. Also, one oxidation−reduction peak of the gold hydroxide film before oxygen evolution reaction curve was observed in 0.5 mol/L H_2SO_4, while only one oxygen evolution reaction was observed on platinum.

2) Potentiodynamic studies showed that gold electrode had better passive behavior in 1 mol/L sulfuric acid, the passive current density (11.9 $\mu A/cm^2$) was less than half of that in 0.5 mol/L, while the passive region was almost equal. Increasing magnetic agitation from 20 to 412 r/min in 0.5 mol/L acid concentration showed 1/43 current density in the passive conditions.

3) Gold has 10% bigger passive zone than that of platinum in 0.5 mol/L sulfuric acid at different agitation speeds. Moreover, at low and high agitation speeds of 20 and 412 r/min, the passive current densities of platinum showed almost the same current (775 $\mu A/cm^2$), very much higher than that of gold, which was highly controlled by agitation rate (7.45 $\mu A/cm^2$ for the highest while 322 $\mu A/cm^2$ for the lowest one).

4) The presence of monovalent and trivalent gold ions in the passive film at 1.4 V in 1 mol/L sulfuric acid solution was confirmed by X-ray photoelectron spectroscopy analysis.

5) After 2 h potentiostatic polarization in 1 mol/L sulfuric acid solution for the three potentials 1.2, 1.4 and 1.6 V, the current density of gold was found to be the lowest at 1.4 V. Moreover, after 3−10 h of decay period,

the potential dropped down to ~0.35 V (vs SHE) for all examined surfaces, corresponding to open circuit potential.

6) Electrochemical noise measurements during 16 h decay periods confirm that the thin passive film has been dissolved or disappeared almost completely. Also, after potentiostatic polarization at 3 different potentials and also after 16 h of decay period, gold showed close admittances or corrosion rates (21−23 mS/cm^2).

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金在硫酸介质中的钝化行为

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摘　要：采用不同电化学测试技术研究纯金和铂电极在硫酸溶液中的阳极行为。循环动电位法研究表明，金电极极化时会出现 2 个氧化峰和 1 个还原峰, 而铂电极只有 1 个析氧反应峰出现。将硫酸浓度从 0.5 mol/L 增加到 1 mol/L 时，金电极的峰电流密度增加 2 倍。动电位法研究表明，增加搅拌速度会提高金的钝化区域，而对铂电极无影响。2 h 的恒电位法研究表明，在 1 mol/L 硫酸溶液中，在 3 个不同的阳极电位极化下，1.4 V 时金电极的腐蚀速率最低。电化学噪音技术测试研究表明，在 16 h 的电位衰退中，在恒电位极化时所形成的钝化膜已经溶解。

关键词：金；钝化；硫酸溶液；电化学噪音

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