Electrochemistry

THE EFFECT OF THALLIUM (I) SALTS ON THE ELECTROCHEMICAL PROPERTIES OF GOLD

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SUMMARY: In recent years, extensive research is being carried out concerning oxide layers on noble metal surfaces because of their importance in fuel-cells. In this study the effect of the small amounts of thallium acetate and thallium nitrate on the electrochemical properties of gold has been investigated. For this purpose, using cyclic volt-metric method current-potential curves were obtained. The electrode used in this work was a gold wire, reference and counter electrodes were calomel and platinum electrodes. Before each experiment electrode was oxidized and then reduced in 1N H_2SO_4 and reference curve was obtained in this medium. In the same concentration of thallium acetate and thallium nitrate, the anodic current observed in a medium with acetate was smaller than that observed with nitrate.

Key Words: Gold electrode, thallium adatoms, anodic charges, cathodic charges.

INTRODUCTION

It has been shown that there is a good correlation between the electrocatalytic phenomena and the nature of electrode material. The electronic band character of the surface differs quite a lot due to the deposition of the foreign metal atoms. These layers are formed due to the strong interaction between the depositing metal atoms and the atoms of the electrode metal rather than the equilibrium potential of the metal atoms. An extensive research is being carried out on these types of formations. It is believed that they can be partly charged adsorbed atoms.

On the other hand, it has been shown that Bi^{3+}, Pb^{2+} and Cd^{2+} cations interact with the oxide layers of Au and Pt electrodes (1, 2). These cations are adsorbed at the positive potentials and they affect the oxide formation and reduction mechanism.

These oxide layers on noble metal surfaces are of great importance on evolution of chlorine and oxygen, and on the mechanisms of electrode reactions in fuel cells.

In this study the effect of the small amount of thallium acetate (TIAc) and thallium nitrate ($TINO_3$) on electrochemical properties of gold has been investigated.

MATERIALS AND METHODS

In these experiments cyclic volt-metric method was used. The details of the apparatus used for obtaining current-potential curves was given in our previous study (3). The working electrode used, was a gold wire (diameter: 1 mm, approximate length: 3 cm, purity: 99,999%) obtained from Johnson Matthey Ltd. It was immersed in the middle of the cell which has three arms. In other arms, Tacussel S 09405 calomel electrode as a reference electrode and Pt electrode as a counter electrode were immersed. All potentials given in this work were referred to saturated calomel electrode (SCE). All solutions were prepared by using double distilled water. Before each experiment nitrogen was bubbled through the solution for 20 mins and throughout the experiment.

For obtaining reproducible results the electrode was oxidized at 1400 mV for 10 mins and it was reduced at 50 mV for 10 mins. Pretreatment was repeated before each experiment until reference curve was obtained in 1N H_2SO_4 (Figure 1). Charges were calculated from the area below i-E curves with the aid of a planimeter by accepting that the equation, $q=\int idt=\int dE/v$ holds for the measurements. Each experiment was at least repeated for three times and reproducible curves were obtained.

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RESULTS AND DISCUSSION

When the electrochemical properties of Pt, Au, Rh and Ir etc. noble metal electrodes in acidic and alkali medium were investigated, it has been seen that the surface of these metals have been covered by chemisorbed oxide and adsorbed hydrogen films. Only for Au hydrogen adsorption and desorption peaks have not been observed (5).

On Pt and Au, the first chemisorbed oxide or hydroxide film formation takes place at zero charge potential and either between the anions which were formerly adsorbed or by dislocating these ions. These anions affect the formation of an irreversible structure. The effect of SO_4^{2-} and $C10_4$- ions was investigated with a single crystal Au electrode (7–10).

The electrochemical behavior of Au electrode in 1N H_2SO_4, citric acid and acetic acid has already been investigated (3, 4). In the present study, the effect of $TINO_3$ and TIAc, which was added in small amounts to the acidic medium, on the current-potential curves of Au in 1N H_2SO_4 was investigated (Figures 1–3).

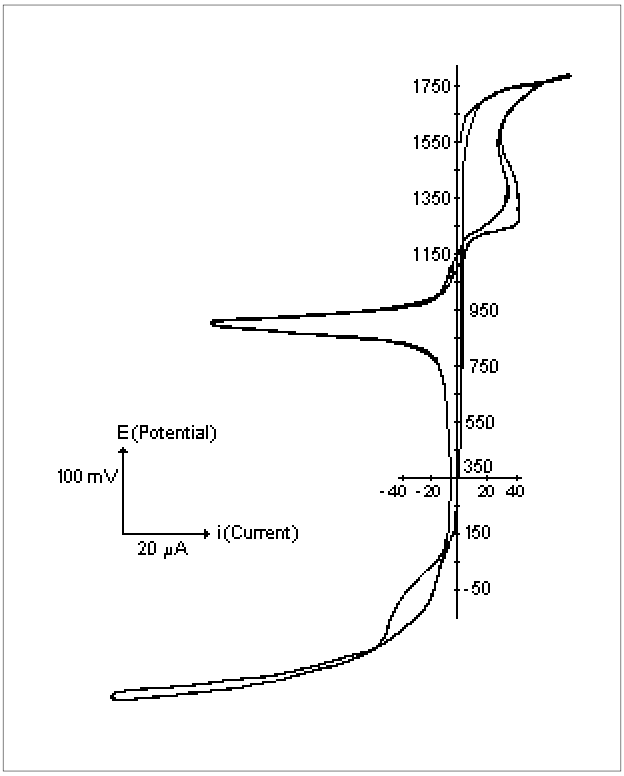
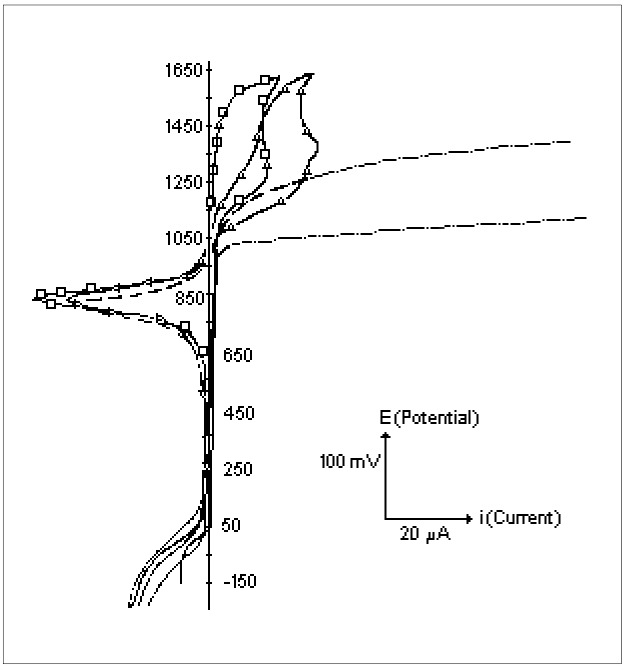


Figure 1: The i-E curves of Au electrode in 1N H_2SO_4 (—) and 1N H_2SO_4 + 10^{-5} M $TINO_3$ (- - -). Sweep rate v=50 mV/s.

Figure 2: The i-E curves of Au electrode in 1N H_2SO_4 + x M TIAc (□)10^{-6} M, (Δ) 10^{-4} M, (–|–) 10^{-3} M TIAc. Sweep rate v = 50 mV/s.



Addition of TI(I) to the medium makes the potential in which the anodic current begins to pass, more negative. In the curve obtained in 1N $H_2SO_4 + 10^{-3}$ M TIAc (Figure 2), it is seen that anodic current begins to pass at a value very near to 1000 mV, which is an equilibrium potential for TI(I) → TI(III). In Au-oxide formation region, the plateau current increases depending upon TI(I) concentration; but in cathodic region, although there has been a small change on the cathodic current in a medium containing $TINO_3$, just a small deviation dependent on the TIAc concentration has been seen in a medium containing TIAc which is of the same concentration of $TINO_3$.

These data show that in anodic region $TI(I) \rightarrow TI(III) + 2e^-$ reaction occurs together with chemisorbed AuO formation. In contrast to the case of Pt, TI(I) and TI(III) do not affect the formation surface film (6). The decrease of the cathodic current depending on the TI(I) concentration in a medium containing TIAc, is possibly due to the acetate ions. Since, as seen from the curves (Figure 3) obtained in a medium containing the same concentration of either TIAc or $TINO_3$, the anodic current observed in a medium with acetate is smaller than that observed with nitrate. In our previous work, the effect of acetate ion on

Figure 3: The i-E curves of Au electrode in 1N H_2SO_4 + 10^{-5} M $TlNO_3$ (—) and 1N H_2SO_4 + 10^{-5} M TlAc (- - -). Sweep rate v = 50 mV/s.

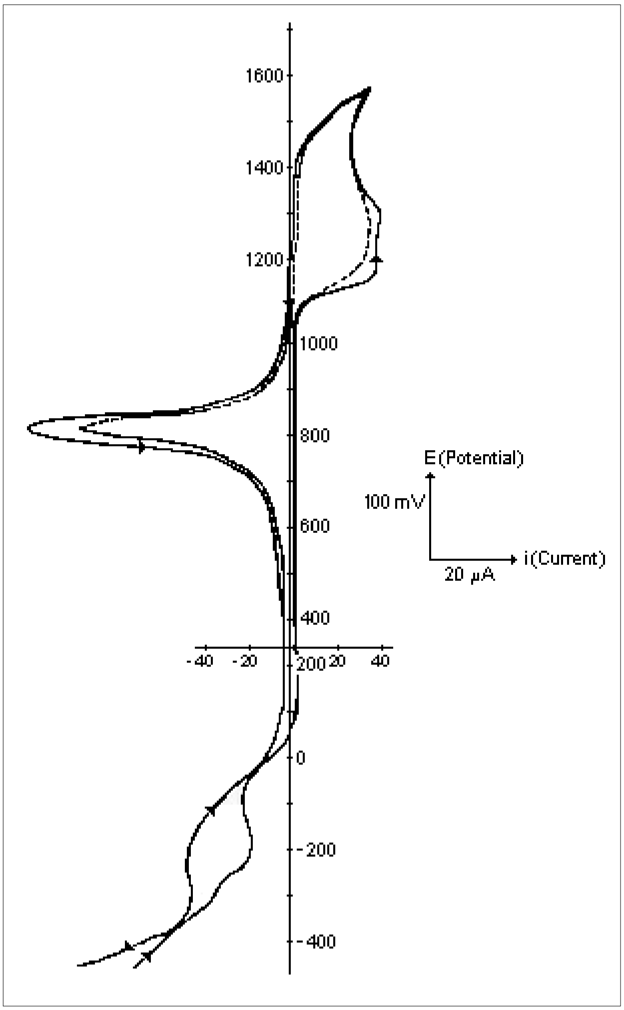
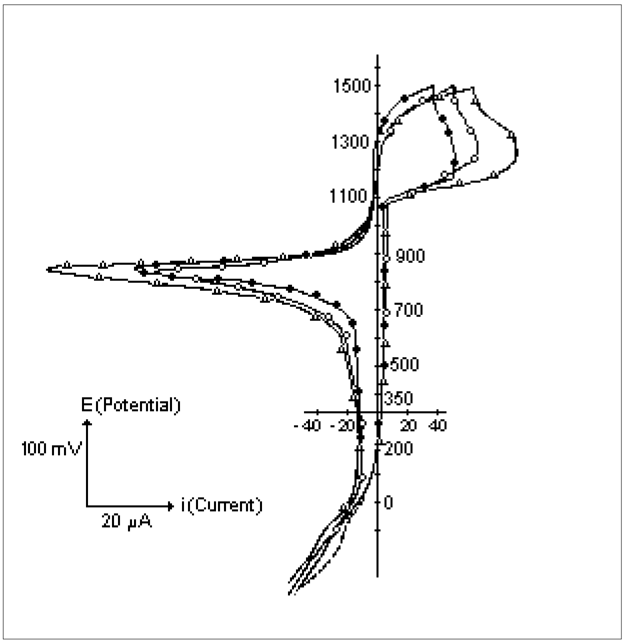


Figure 4: The i-E curves of Au electrode for the same period of waiting (10 minutes) and for the same E_λ potential (1500 mV). (●) 1N H_2SO_4 (without waiting), (o) 10^{-4} M TlAc, (Δ) 10^{-4} M $TlNO_3$. Sweep rate v = 100 mV/s.



the structure of gold oxide was investigated (3). In the presence of organic anions, the amount of charge to form a chemisorbed film on Au surface until evolution potential for O_2 is less than that to deposit a monolayer oxide film.

According to the literature the deposition of Tl on Au occurs in -0.8 V–(-1.0 V) region following hydrogen evolution. Then hydrogen transforms Tl(I) into Tl(0). Multilayer Tl dissolves at -0.6 V, there is adsorbed Tl(I) on surface among -0.2 V and +0.7 V and this Tl(I) is desorbed completely at +0.7 V(11).

For investigating the effect of adsorbed Tl(I) on electrochemical behavior of Au, the electrode which was kept at -1.0 V in various periods of waiting in 1N H_2SO_4 +10^{-4} M TlAc and 1N H_2SO_4 + 10^{-4} M $TlNO_3$, was immersed in a cell which contained 1N H_2SO_4, and the current-potential curves were obtained in the region of H_2 and O_2 evolution (Figure 4). Anodic charges are larger than that in 1N H_2SO_4, Both anodic and cathodic charge obtained with a Au electrode on which Tl was deposited in a medium containing nitrate was found larger than that obtained with a clean Au electrode. These findings can be explained in three different ways:

1. Under nitrogen atmosphere, in order to reach the stable equilibrium potential for the electrode (+400 mV in Figure 4), Tl which is precipitated during the period of waiting must be desorbed. If some Tl is left adsorbed on the surface, it is transformed into $Tl(III)_{ad}$ together with chemisorbed film of Au or transformed into $Tl(I)_{ad}$ during anodic or cathodic sweeps. In other words, it is quite impossible to remove Tl(I) which is formed by the transformation $Tl(0)_{ad}$ $Tl(I)_{ad}$ from the surface.

2. Probably, during the deposition of Tl, Au-Tl alloy forms, however, since the roughness factor of the surface will increase during the desorption of this Tl, anodic and cathodic charges increase in 1N H_2SO_4.

3. Tl which is deposited on surface, can also be dispersed into 1N H_2SO_4 as Tl(I) ions and this is consis-

Figure 5a: Cathodic charges (Q_c) versus anodic potential limit (E_λ) for different values of periods of waiting in TlAc and $TlNO_3$. Sweep rate v = 100 mV/s. For TlAc: (o) 4 mins, (Δ) 10 mins, (□) 20 mins, (∗) 60 mins. For $TlNO_3$: (●) 4 mins, (▲) 10 mins, (■) 20 mins.

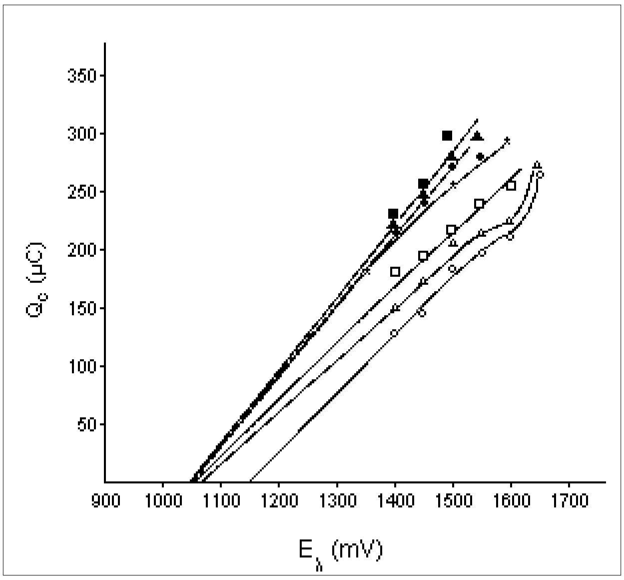


Figure 5b: Anodic charges (Q_a) versus anodic potential limit (E_λ) for different values of periods of waiting in TlAc and $TlNO_3$. Sweep rate v = 100 mV/s. For TlAc: (o) 4 mins, (Δ) 10 mins, (□) 20 mins. For $TlNO_3$: (●) 4 mins, (▲) 10 mins, (■) 20 mins.

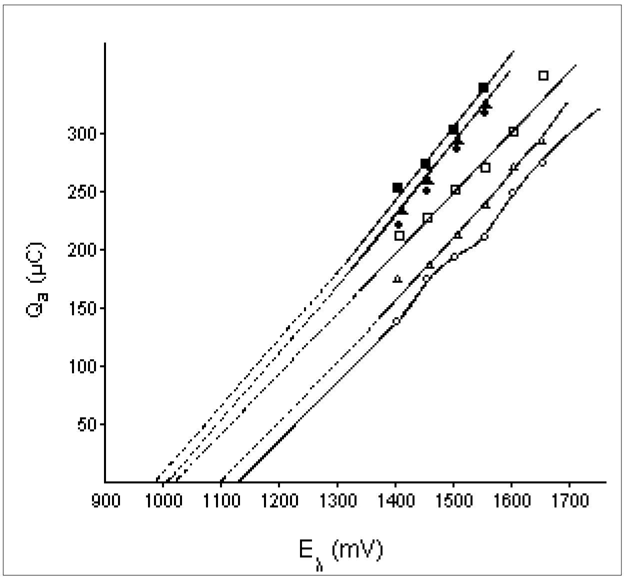
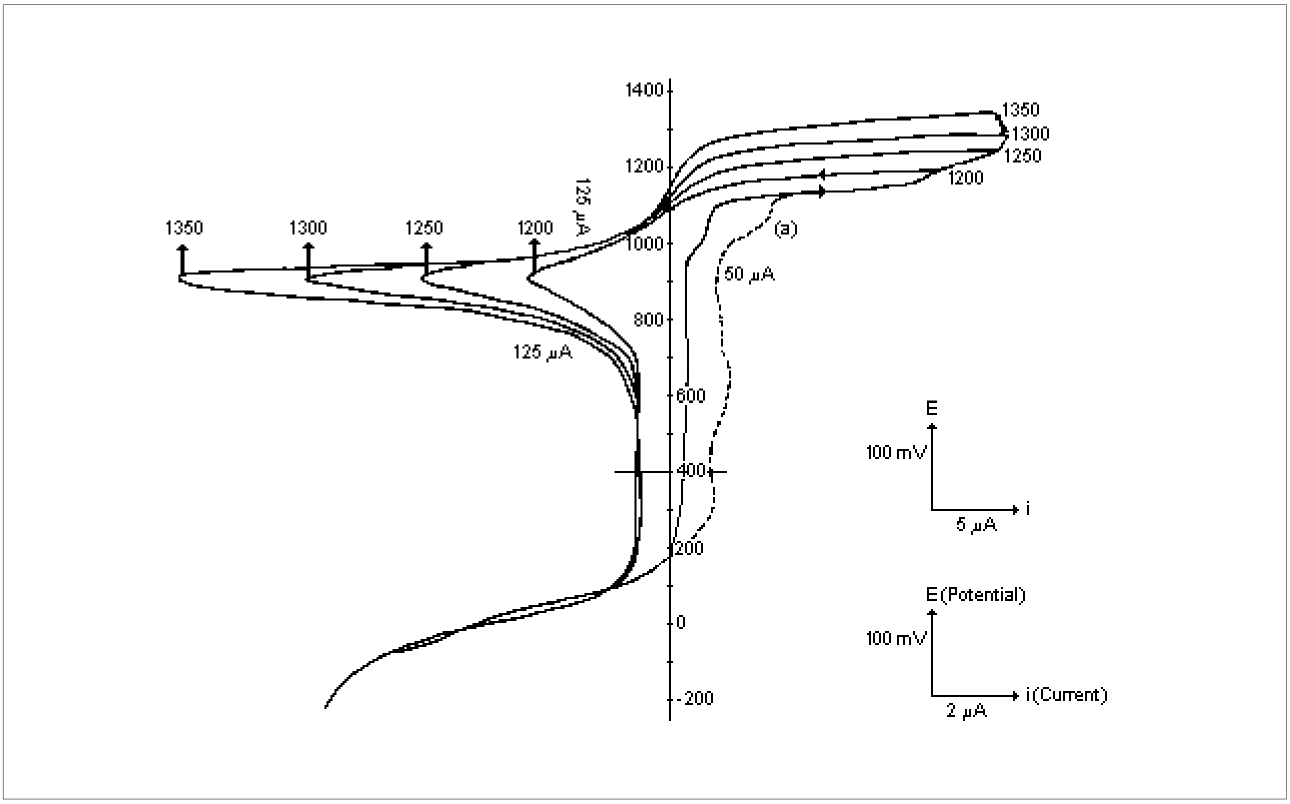


Figure 6: The i-E curves obtained in 1N H_2SO_4 of Au electrode which was kept at -1.0 V for 60 minutes in 1N $H_2SO_4 + 10^{-4}$ M TlAc. Sweep rate v = 50 mV/s.



tent with the current-potential curves obtained in a medium containing TI(I) ions. But the comparison of Figures 2–4, shows that the change in the roughness factor is a much more important factor. In Figure 4 anodic currents are larger. In Figures 5a and 5b, anodic and cathodic charges are plotted as a function of time versus oxidation potential (E_λ).

The increments on the amount of charges in $TINO_3$ depending on the periods of waiting are less than that of the amount of charges in TIAc. We can also say that surface adsorption of acetate in TIAc may inhibit TI deposition. As the period of waiting increases, the amount of charges found get closer to that found on the electrode in $TINO_3$. Finally, as dissolution of TI results in the same roughness factor, charges give closer values. $Q–E_\lambda$ curves give a value of ~ 1050 mV, i.e. more negative than 1150 mV which is the appearance potential of anodic current in 1N H_2SO_4 and this value is the same with that obtained for $Q \rightarrow 0$ for longer periods of waiting. This shows that another reaction takes place on the surface in addition to the formation of oxide film. In Figure 6, curves that show coming back from different E_λ potentials together with H_2 evolution without ceasing the current in 1N $H_2SO_4 + 10^{-4}$ M TIAc during for 60 mins, are give maximum (a) has been obtained less characteristic during the period of 45 mins for waiting. As this maximum has been observed repeatedly almost at the same value, it should be an adsorption maximum. Beginning potential of this maximum, E_λ value for $Qc \rightarrow 0$, and the potential in which the anodic charge begins to increase in 1N $H_2SO_4 + 10^{-3}$ M TIAc are almost the same. Maximum (a) is possibly related to the reaction $TI(I)_{ad} \rightarrow TI(III)_{ad}$.

In Figures 5a and 5b the increase of the anodic and cathodic charges in TI(I) as a function of the period of waiting can be explained by the contribution of the reaction $TI(I)_{ad} \rightarrow TI(III)_{ad}$ as well as the increase of the roughness factor.

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