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**A KINETIC ANALYSIS OF THE UNDERPOTENTIAL DEPOSITION OF
THALLIUM ON COPPER**

by

David Arne Berg, B.Sc.

Carleton University

**A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science**

Department of Chemistry

Carleton University

Ottawa, Ontario, Canada.

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" A Kinetic Analysis of the Underpotential Deposition
of Thallium on Copper."

submitted by David Arne Berg, B.Sc.
in partial fulfilment of the requirements for the degree of
Master of Science

R. G. Banadas

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Chairman, Department of Chemistry

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ABSTRACT

The underpotential deposition (UPD) of thallium on electropolished copper electrodes was examined in aqueous solutions of chloride, perchlorate and sulphate base electrolytes. Two distinct UPD peaks were observed and their respective charges of formation are reported. The dependence of the peak potential (E_p), peak pseudocapacitance (C_p) and the peak half-width ($\Delta E_{1/2}$) for the first monolayer UPD peak were analyzed in detail according to the method proposed by Conway and co-workers. The role of different anionic effects on the adsorption mechanism of formation of the first monolayer is described. The second UPD peak is suggested to be formed by an instantaneous nucleation and growth mechanism from the analyses of cyclic voltammetry data and current-time transients obtained by potentiostatic pulse technique.

Results of the pH effects on the main UPD peak of Tl on Cu are presented and it is shown that, at high pH values, the formation of copper oxide/hydroxide did not hinder the full monolayer underpotential deposition of thallium.

Photoacoustic spectroscopy (PAS) was used as an ancillary *in-situ* technique for the investigation of underpotential deposition (UPD) of thallium on polycrystalline copper. The PAS signal generated by 605 nm radiation was found to increase upon deposition of Tl on Cu. Since underpotential deposition is generally a monolayer event,

the limit of detection obtained for this technique was estimated to be 0.05 of a monolayer. The PAS results support the conclusion that the second UPD peak is due to a second discrete monolayer rather than a filling in of vacant sites in the first monolayer. The use of PAS to study the thallium system at pH 12 confirmed that removal of Cu_2O from the electrode surface occurred at a sufficient rate that it did not interfere with the underpotential deposition of thallium.

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INTRODUCTION

Preface:

Electrode reactions are heterogeneous processes and often involve considerable complexities of a wide nature. In addition, modern electrochemistry has a unique nomenclature and as such it seems appropriate to commence with the definition of certain terms and concepts that will aid in the understanding of this research project.

(i) The Development of Electrochemical Kinetics :

Analysis of an electrode process involves the study of charge transfer across interfaces. A simple redox process of the type

will be employed for the development of the electrochemical equations. The thermodynamically reversible potential of such a reaction is related to the differences in free energy between the reactants and the products.

$$E_{rev} = - \frac{\Delta G}{n F} \quad (2)$$

The net current density flowing at any potential is expressed in terms of the difference between the forward and backward rates of reaction:

$$i = i_f - i_b = nF(k_f c_O - k_b c_R) \quad (3)$$

where c_O and c_R are the surface concentrations of the oxidized and reduced species respectively. Differentiation between the surface concentration of the reactant and that in the bulk solution is necessary only when the rate of the charge transfer reaction is far greater than the rate of diffusion of the reactant to the electrode surface. In this work the rate of charge transfer is considered to be slow enough that all concentration terms will refer to that of the reactant in the bulk solution.

From transition state theory, the relationship between the rates of reaction and the potential is given as

$$k_f = k_1 \exp[-\beta nFE/RT] \quad (4)$$

$$k_b = k_{-1} \exp[(1 - \beta) nFE/RT] \quad (5)$$

β is known as the symmetry factor and βnFE represents the degree to which the energy barrier for the forward reaction has been lowered.

The system described thermodynamically is, by necessity, at equilibrium. By definition then the forward and reverse reactions are proceeding at an equal rate ($k_f = k_b$) and the net current is zero. The amount of additional change in potential (from E_{rev}) required to generate a net current density is known as the overpotential (η). There are

two major causes of the experimentally observed overpotential. The first, and kinetically significant cause, is the activation overpotential. This overpotential is the result of the fact that the charge transfer reaction must be electrically driven, or activated, to proceed at a given rate. The second major type of overpotential is known as the concentration overpotential. It becomes a significant factor when mass transport becomes a limiting factor in the reaction kinetics. If a reaction is under diffusion control, the resulting change in concentration of the reactant at the electrode surface ($c_{\text{surface}} \neq c_{\text{bulk}}$) results in a change in the potential difference across the interface. It is the first of these sources of overpotential that is being considered in this manuscript.

Introduction of the overpotential into equations 4 and 5 leads to;

$$k_f = \frac{i_o}{nFc_O} \exp[-\beta nF\eta/RT] \quad (6)$$

$$k_b = \frac{i_o}{nFc_R} \exp[(1-\beta)nF\eta/RT] \quad (7)$$

where $\eta = E_{\text{app}} - E_{\text{rev}}$ and i_o is known as the exchange current density and reflects the rate of forward and back reactions at equilibrium ($i_o = i_f = i_b$). Substituting equations 6 and 7 into equation 3 yields

$$i = i_o \left\{ \exp\left[\frac{-\beta nF\eta}{RT}\right] - \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \right\} \quad (8)$$

This expression is known as the *Butler-Volmer equation* after the scientists from whose work it evolved [1,2] and it is the fundamental equation in electrochemical kinetics. It was the development of this relationship that gave a theoretical basis for the empirical

Tafel relation $\eta = a - b \log i$ published in 1905 [3]. The ability to generate large changes in the current density (i) through small changes in the difference between applied and equilibrium potentials is the point that distinguishes electrochemical from chemical kinetics.

(ii) The Concept of Underpotential Deposition (UPD):

The phenomenon of underpotential deposition (UPD) has been recognised since the early 1900's [4] and has been known by a number of names from metal adsorption to adatom deposition to the formation of monolayer metal films [5]. A number of comprehensive reviews have been written on the subject: [5,6,7] in recent years, the most thorough being that by Kolb [6]. Initial interest in these metallic monolayers was sparked by the apparent violation of Nernst's law with metals being reduced and oxidized on foreign substrates at potentials positive to their reversible Nernst potential. A clearer picture of the phenomenon can be given through the use of an example.

If a thallium electrode was placed in a solution containing thallos ions, the potential measured with respect to a reference electrode would be the reversible potential of the Tl^+/Tl couple in that solution. If a cyclic voltammogram (CV) was recorded in the cathodic direction, the cathodic current would rise at the reversible potential (depending on the overpotential for deposition), indicating the commencement of the deposition process. However, when the thallium electrode is replaced by a silver electrode and a CV recorded, a cathodic peak associated with the deposition of thallium

is seen over 200 mV positive to the Tl^+/Tl reversible potential, as shown in Fig. 1. The area under this peak (roughly $200 \mu\text{C}/\text{cm}^2$) represents the charge required for the deposition of a single monolayer of thallium on silver. The large cathodic currents associated with the bulk deposition of thallium are not seen until the reversible potential has been exceeded. As is generally the case, in an electrochemical reaction, an overpotential must be applied to drive the reaction. In the case of the cathodic deposition of a metal, the overpotential would be negative to the reversible potential.

The fact that Tl deposition is occurring at potentials positive to the Tl^+/Tl reversible potential does not contradict thermodynamics because this reversible potential refers to the free energy change in the reaction

where $\text{Tl}-\text{Tl}_{\text{crys}}$ implies that the thallium ion is discharged and becomes part of the thallium crystal lattice. The free energy change and corresponding reversible potential refer to the formation of a bond between the deposited thallium atom and atoms of the same metal on the surface. UPD can be represented by the reaction

which is a different reaction altogether and has therefore, a different reversible potential. The fact that this deposition occurs at a more positive potential shows that the $\text{Tl}-\text{Ag}_{\text{crys}}$ bond is more stable than the $\text{Tl}-\text{Tl}_{\text{crys}}$ bond.

Figure 1. Cyclic Voltammogram of thallium deposition on a polycrystalline silver electrode from 0.75 mM Tl_2SO_4 / 0.5 M Na_2SO_4 / 1 mM HClO_4 , 100 mV s^{-1} . CV courtesy of *J. Electroanal. Chem.*, 65 (1975) 915.

(iii) UPD and the Nernst Equation.

The Nernst equation describing the concentration dependence of the equilibrium potential of a reversible reaction is

$$E_{rev} = E^{\circ} + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad (11)$$

When considering a reaction of the type

the activity of the deposited metal is generally assumed to be constant and set to unity. It has been pointed out however that when an electrode surface is covered by only trace amounts of a foreign metal then the activity of the deposit should be less than unity and vary with coverage [6]. The variance of the activity with coverage is linked to the previous section in that the metal atom being deposited on the foreign substrate is a different reaction thermodynamically than deposition on an identical substrate. The availability of Ag sites for the UPD of Tl would become a controlling variable similar to the concentration of Tl^{+} in solution. The Nernst equation then becomes

$$E_{rev}(\theta) = E^{\circ} + \frac{RT}{ZF} \ln \frac{c_{Tl^{+}} f_{Tl^{+}}}{\theta f_{Tl}} \quad (13)$$

where $f_{Tl^{+}}$ and f_{Tl} represent the activity coefficients of the metal ion in solution and the deposit and θ the coverage. The above equation will always yield equilibrium potentials more positive than the Nernstian potential of the bulk phase but it does not take into

account the specific interaction mentioned above between the deposit and the foreign substrate. The specificity of this interaction results in different underpotential ranges being observed for the same metal on different substrates. These differences are generally accounted for by adding a system-specific quantity E_a to E° . It is this system specific quantity that has been correlated to the work function differences of the participating metals [8]. In order to arrive at a quantitative description of the UPD process, Kolb introduced the term "underpotential shift" (ΔU_p). The points of reference chosen as an indication of the energetic differences between UPD and bulk deposition were the peak potentials of the bulk stripping peak (generally within 10 mV of the reversible potential) and the most anodic of the underpotential stripping peaks. It is this potential difference that is known as ΔU_p and it represents the difference in bond energies between the depositing atom and a foreign substrate and that of the same metal.

(iv) The UPD of Thallium on Copper:

The underpotential deposition of thallium on non-noble metals has not been widely studied. The Tl/Cu system has practical use in the catalytic properties displayed in oxygen reduction [9]. Thallium cuprate superconductors have been reported [10] and the possibility of preparing them by electrodeposition is presently an on-going interest in our laboratory.

A relatively small number of publications have appeared on the underpotential deposition of thallium on copper. The work of Schmidt and Gygax [11] was probably the first of these studies to be published. They investigated the UPD of Tl(I) on polycrystalline Cu from chloride solution using linear sweep techniques. In a solution of 6.61×10^{-4} M Tl^+ , 0.5 M KCl, pH=5 at a scan rate of 0.1 V min^{-1} two UPD peaks were found. The underpotential shift (ΔU_p) was 230 mV for stripping. Kolb et al [8] have shown an anodic stripping curve for Tl on polycrystalline Cu in 1M Na_2SO_4 ($[\text{Tl}^+] = 1 \times 10^{-3}\text{M}$, scan rate = 20mVs^{-1}) with a stripping peak at around -0.5 V (SCE) and a small shoulder on the bulk peak. ΔU_p was around 330 mV. In the investigation of oxygen reduction on Pt and Cu surfaces modified by underpotential adsorbates, Kokkinidis and Jannakoudakis [9] have shown a cyclic voltammogram for the UPD of Tl on polycrystalline Cu in 0.5 M HClO_4 ($[\text{Tl}^+] = 2.5 \times 10^{-3}\text{M}$, sweep rate = 20 mVs^{-1}) with two UPD peaks. The main stripping peak had a ΔU_p of 300 mV. The small second peak was near the reversible potential. Another oxygen related work was that by Materlik et al [12] on X-ray standing wave fluorescence analysis of electrodeposited Tl on single crystal Cu(111). Cyclic voltammograms for Tl on Cu in 0.5 M Na_2SO_4 (10^{-3} M TlNO_3 , 100 mVs^{-1}) were presented with two UPD peaks and one stripping peak. ΔU_p was approximately 330 mV. The paper highlighted the influence of O_2 presence in the electrolyte on the Tl/Cu voltammogram. In connection with UPD of Tl on Cu, a theoretical investigation by Kuznetsov et al [13] concluded that, in the adsorption of Tl on Cu, alloy formation was energetically unfavourable. To date, no significant mechanistic or kinetic analysis of the Tl/Cu system have been reported in the literature.

(v) Kinetic Analysis Through Cyclic Voltammetry:

One of the most simple and yet powerful techniques often used for underpotential studies is cyclic voltammetry [6]. The potential of the working electrode, controlled by a potentiostat, is changed at a constant rate by a ramp voltage from a sweep generator. Any reaction occurring at the working electrode is seen as a current superimposed on the base current in the current/potential profile. However, it was generally considered an inadequate technique by itself in determining the kinetics of an electrode reaction. Recent developments in the field of computer simulation of the kinetic behaviour of surface reactions, started mainly by the works of Conway's school [14,15,16], and continued by Bosco and Rangarajan [17] and Noel et al [18], have now made kinetic analysis possible through a linear sweep voltammetric approach. The model proposed by Conway has seen some use in the field of UPD [19,20,21,22] and will be employed for the majority of the kinetic analysis of the Tl/Cu system.

(vi) Fundamental Parameters used in the Conway Model:

Conway et al [14] have proposed a theoretical treatment for the kinetic behaviour of a simple 1 electron transfer surface reaction. As such, it appears to be appropriate for analyzing the kinetics of the Tl/Cu UPD system using the linear sweep voltammetric

results obtained by the author. At this juncture, an outline of the theoretical model, along with definitions of the fundamental parameters, will be given. It should also be pointed out that this model applies only to an adsorption controlled process.

Conway showed that, for a reaction of the type

(where M represents the free metal surface sites $(1 - \theta_B)$ reacting with A from solution to form the chemisorbed species MB on the surface at a coverage of θ_B) the equation for the dependence of i on V at a sweep rate $s = dV/dt$ was

$$i = Q \frac{d\theta_B}{dt} = Q [k_1 c_A (1 - \theta_B) \exp(\frac{\Delta V}{b} - (1 - \beta)g\theta_B) - k_{-1} \theta_B \exp(-\frac{\Delta V}{b} + \beta g\theta_B)] \quad (15)$$

where

$$\Delta V = V_i \pm st - E^\circ \quad (16)$$

and $b = RT/\beta F = 2RT/F$ ($\beta=0.5$); E° is the standard reversible potential for the reaction, V_i the starting potential of the sweep and g the parameter, introduced by Frumkin [23], that accounts for lateral interactions between the adsorbed species B. Positive values of g correspond to repulsion in the adsorbed layer and negative values to attraction.

Solution of equation 15, through numerical analysis, for the absence of lateral interactions ($g=0$) lead to the i - V profiles shown in Fig. 2. For purposes of clarity, the

Figure 2. Series of C vs. V profiles showing the progression from reversible to irreversible behaviour. Diagram courtesy of *J. Electroanal. Chem.*, **75** (1977) 49.

curves were represented in terms of the adsorption pseudocapacitance C as a function of potential ($C = i/s = (Q/s)d\theta_B/dt$ and is defined later in this text). The peaked shape of the current-potential profile is due to the exponential increase of the current with increasing potential being countered by a reduction in the reaction rate as the free surface sites $(1-\theta_B)$ diminish. The profiles shown here demonstrate the changes in peak shape as the sweep rate s is increased and the surface reaction goes from a reversible process to an irreversible one.

The main quantities characterizing the behaviour of the current peaks in Fig. 2 are the peak potential E_p , the half-width $\Delta E_{1/2}$, and the peak pseudocapacitance C_p . Plots of C_p and $\Delta E_{1/2}$ vs. $\log s/k$ (where s/k is a reduced sweep rate, k being the rate constant of the reaction being studied - Fig. 3) clearly show the transition from reversible to irreversible behaviour. The irreversible branch of the E_p vs. $\log s/k$ plot is equivalent to a Tafel relation for the surface reaction with a slope of $b = 2.3(2RT/F)$. In a later paper [16], Conway further developed the kinetic model by extrapolating the irreversible branch of a ΔE_p vs. $\log s$ plot (derivation follows) to the reversible potential and from the intersect, determining a sweep rate s_0 (reversibility parameter), considered by Conway to be analogous to an exchange current density i_0 . It is from the determination of this reversibility parameter that the remainder of the kinetic parameters are determined.

Conway [16] derived the quantitative significance of s_0 by considering the relation for the peak potential, developed by Srinivasan and Gileadi [24], when the reaction considered (14) is irreversible and the interaction parameter g is not considered.

Figure 3. Plots of V_p (E_p), C_p and $\Delta V_{1/2}$ ($\Delta E_{1/2}$) values from Fig. 2 vs. $\log s/k$ showing the transition from reversible to irreversible behaviour. Diagram courtesy of *J. Electroanal. Chem.*, 75 (1977) 49.

$$E_{p,irr} = - \left(\frac{RT}{\beta z F} \ln \frac{\beta z F}{k_1 c_o RT} + \frac{RT}{\beta z F} \ln[-s] \right) \quad (17)$$

Equation 17 gives a logarithmic dependence of the irreversible peak potential $E_{p,irr}$ on the sweep rate s . By introducing the shift of $E_{p,irr}$ from the reversible value of $E_{p,r}$, $\Delta E_p = E_{p,irr} - E_{p,r}$ a Tafel-type relation was derived.

$$\Delta E_p = - \left(\frac{RT}{\beta z F} \ln \frac{\beta z F}{RT k_1 c_o} + \frac{RT}{\beta z F} \ln[-s] \right) - \frac{RT}{z F} \ln k_1 c_o / k_{-1} \quad (18)$$

Rearrangement gave

$$\Delta E_p = b \log s_{o,p,c} - b \log[-s] \quad (19)$$

where

$$s_{o,p,c} = \frac{RT}{\beta z F} k_1^{(1-\beta)} k_{-1}^{\beta} c_o^{(1-\beta)} \quad (20)$$

is the value of s_o at the peak potential which would be derived from measurements conducted at various cathodic sweep rates. It should be noted that if $\beta \neq 0.5$ then the cathodic and anodic reversibility parameters would differ. The expression for the anodic reversibility parameter is

$$s_{o,p,A} = \left(\frac{RT}{(1-\beta) z F} k_1^{(1-\beta)} k_{-1}^{\beta} c_o^{(1-\beta)} \right) \quad (21)$$

In most real systems where an absorbed monolayer is formed on the surface, lateral interactions are significant. As these interactions change the values of $E_{p,r}$ and $E_{p,irr}$ only an apparent reversibility parameter $s'_{o,p}$, can be obtained experimentally.

$$V_{p,irr} - V_{p,r} = -b \log s'_{o,p} + b \log s \quad (22)$$

where $V_{p,r}$ and $V_{p,irr}$ represent the changes to $E_{p,r}$ and $E_{p,irr}$ caused by the lateral interactions. The reversibility factor is then related to the experimentally accessible apparent reversibility parameter through the following expression.

$$\log s_{o,p} = \log s'_{o,p} - \log \left(1 + \frac{g}{2} (1 - \theta_{p,irr}) \right) + \frac{g}{4.6} (\theta_{p,irr} - 0.5) \quad (23)$$

The values of g and $\theta_{p,irr}$ have been tabulated for different values of $\Delta E_{1/2}$ [18].

A term that has not been clearly defined is the adsorption pseudocapacitance. For the intermediate MB formed in the charge transfer process (Eq. 14), the fractional coverage is also associated with a faradaic charge q_F . If a charge of dq_F is required to change the coverage by $d\theta$, then

$$dq_F = i_F dt = q_1 d\theta \quad (24)$$

where q_1 is the amount of charge required to form a complete monolayer. As the adsorption is potential dependent, it follows that

$$d\theta = \frac{\delta \theta}{\delta \Delta \phi} d\Delta \phi \quad (25)$$

where $\Delta \phi$ represents the change in potential. Substitution of Eq.(25) into (24) gives

$$\frac{dq_F}{d\Delta\phi} = \frac{i_F dt}{d\Delta\phi} = q_1 \frac{\delta\theta}{\delta\phi} \quad (26)$$

The expression $dq_F/d\Delta\phi$ satisfies the definition of a differential capacity but it is not a capacity because as such it would hold the charge added to it (whereupon the electrical potential would change in direct proportion to the charge added) and there would be no current flow. Because the charge is, in fact, dependent on the flow of current, the relation seen in Eq. (26) is known as a pseudocapacitance.

The remaining significant factor that determines peak shape, and the kinetics of the reaction, is the interaction parameter g . The existence of lateral interactions between the adsorbed species on the electrode surface has the effect of lowering and broadening the peak when repulsive interactions exist ($g > 0$). When attractive interactions are present ($g < 0$), narrowing and increased heights of the peaks are observed. The relationship between peak shape and g , for both reversible and irreversible conditions, are shown in Fig. 4. It should be noted that at values of $g \leq -4$, adsorption is no longer considered to be the mechanism of deposition. The mechanism of nucleation and growth is represented by these indications of strong attractive interactions. The most important parameter used in characterizing the interactions in the surface layer is the half-peak width $\Delta E_{1/2}$. Tabulated results comparing $\Delta E_{1/2}$ values with g values are given in Noel's work [18].

Figure 4. Plots of the C vs. V profile demonstrating the effect of various positive and negative g values under reversible (a) and irreversible (b) conditions. Diagram courtesy of *J. Electroanal. Chem.*, 75 (1977) 53.

(vi) Two-dimensional Nucleation and Growth:

The terms introduced to this point have dealt with the electrochemical adsorption process. In the case of metal monolayer formation, it has been stated by Lorenz et al [25] that the mechanism of UPD is adsorption unless the interaction parameter g reaches the theoretical critical value of -4 . However, Bewick and Thomas [26,27,28,29] have pointed out that the behaviour seen in the Pb/Ag and Tl/Ag UPD systems points to a mechanism of nucleation and growth rather than one of adsorption even if the calculated g values are less than the limiting $g = -4$. Aside from the large negative interaction parameter, there are other factors that will indicate a nucleation and growth mechanism.

The first of these factors involves recording the current-time transients of the UPD system. This is accomplished by pulsing the voltage of the working electrode to the potential representing the completion of the monolayer and then recording the current signal vs. time. Theoretical treatment of these current-time transients [30] has shown that non-uniformity in the decline of the transient is an indication of a phase transition process.

The other factor that is indicative of a mechanism incorporating a nucleation step is the existence of a nucleation overpotential. Experimentally, this appears as a separation on the potential axis between deposition and stripping peaks. In an adsorption

process the deposition/stripping should be symmetrical with respect to the electrode potential [29].

(vii) Photoacoustic Spectroscopy (PAS):

Continued interest in the area of UPD stems from the ability to generate monolayer and sub-monolayer deposits; a number of UPD systems have displayed interesting catalytic properties [31]. As a monolayer event, UPD is of fundamental interest since the deposits represent an interim state between atoms and bulk metal. Confirmation of the findings on the Ti/Cu UPD system presented in this thesis (and published elsewhere [32]) was sought using an ancillary technique.

Since underpotential deposition is normally a monolayer process on the electrode surface, it is necessary to find techniques with the sensitivity required to probe surface events. Additionally, it is desirable to be able to determine surface events *in-situ*, since any analysis carried on outside the electrochemical cell is prone to contamination from various sources. Optical techniques, such as reflectance [33] and ellipsometry [34], have been used to examine electrode surfaces. Photoacoustic spectroscopy (PAS) is a sensitive optical method that has both the required sensitivity and the ability to provide *in-situ* information about the electrode surface, modified by UPD. It is generally easier to perform and theoretically less complicated to analyze than ellipsometry and does not require the measurement of small changes (typically a 1-2% difference) in large reflected intensities as do reflectance techniques. In PAS, as in all photothermal spectroscopies,

the signal generation stems from the absorption of energy in a sample rather than the transmission of light through it or reflected from it. Analytical signals generally are linear functions of the absorbance change of the surface on which the UPD monolayer grows.

Photoacoustic spectroscopy has been established as a useful analytical technique and has been well described in a number of reviews [35,36]. Intensity-modulated light impinging on a sample is absorbed in the sample. Non-radiative decay of some or all of the absorbed energy into heat will result in periodic localized heating of the sample medium. The consequence of this is that heat will diffuse and dissipate into the surroundings. This periodic heating will result in the generation of elastic (acoustic) waves in the sample medium which are then detected by a piezoelectric transducer. PAS can also be carried out using a microphone attached to the rear surface of the electrode but the use of a piezoelectric device is simpler and less expensive. PAS has been used to examine oxides [37,38], cadmium electrode passivation [39], ions adsorbed at the electrode-electrolyte interface and development of colour in WO_3 [40]. Under conditions of a highly reflective substrate, PAS can be used successfully for monolayer investigation [62]. Yoshihara et al. [41] recently evaluated the feasibility of PAS in their study of the UPD of thallium and lead on silver and found it to be very successful. PAS studies of the UPD of Tl on Cu may generate new information not available by electrochemical techniques alone.

EXPERIMENTAL

(1) Electrodes:

(i) Working Electrodes:

The working electrodes used in the majority of the experiments were constructed from 5 mm diameter copper rod (Aesar, 99.999%). One centimetre lengths of the copper rod were soldered to brass mounts and the entire assembly encased in a scotch cast epoxy resin. The brass mount was threaded and the electrode assembly mounted on a teflon holder by means of a brass screw running through the centre of the teflon. A low noise coaxial connector (1074-1,1075-1, Kings Electronics Co. Inc.) was soldered to the other end of the brass screw and flush-mounted in the teflon. This assembly allowed for a reliable low-noise connection of the working electrode to the potentiostat. O-rings were placed between the epoxy-coated copper and the teflon holder to ensure there was no seepage of the electrolyte during experiments. The teflon holder was tapered to give an air tight seal in a 24/40 glass joint.

The working electrode-transducer design for *in-situ* PAS investigation of Tl UPD on polycrystalline Cu is shown in Figure 5. An 8 mm disc electrode of 99.99% purity

Figure 5. Schematic diagram of the copper working electrode employed in the PAS investigations.

copper (Aesar), 1 mm in thickness, was soldered to a threaded brass tube which facilitated electrical connections. Inside the brass tube was a thin teflon spacer which served to electrically shield the piezoelectric transducer from the Cu disc electrode and to mechanically hold it in place against the electrode. The piezoelectric transducer, a 5 mm diameter cylinder (10 mm in length) of lead zirconate titanate (American Piezo Ceramics Inc.), was fitted inside the teflon sleeve and acoustically coupled to the electrode back using a viscous electrically-insulating paste (Wakefield Engineering, Inc., Thermal Compound 120-2). Thin electrical leads, soldered to fired-on silver electrodes on both ends of the transducer, were brought past the spacer and out through the brass tube. The electrode-transducer assembly was then housed in a cured resin shell which was threaded into a large teflon stopper fitted with a spring-loaded electrical contact to the brass tube. O-rings were used between the teflon and the epoxy resin to ensure against leakage of the electrolyte into the interior while the electrode was immersed. The whole assembly was fitted for an opening in the side of the electrochemical cell. All electrical leads were fed through a pore in the teflon stopper.

ia) Surface Preparation.

When preparing the surface of the copper working electrodes for experiments, two methods of polishing were utilised. Mechanically polished electrodes were first roughly cleaned using 600 grain emery paper. The electrodes were then polished for five minutes using 0.1 micron alumina powder (Baikalox) supported on BAS microcloth pads which

were in turn mounted on an "in-house designed" polishing wheel. Maximization of surface reproducibility was sought by using a fixed speed of rotation for the polishing wheel and by monitoring the time of polishing. At the end of polishing, the electrode was thoroughly rinsed with triply distilled water and transferred to the electrochemical cell with the surface protected by a drop of the triply distilled water.

Electrochemically polished electrodes also underwent the initial cleaning with the 600 grain emery paper. The electrode was then immersed in a commercial electropolishing tank (Vacumetrics, cat.# 50100) containing 67% orthophosphoric acid as outlined by Tegart [42]. The electrode was polished at a low current density ($\sim 15 \text{ mA/cm}^2$) for thirty minutes. At the end of polishing the electrode was thoroughly rinsed with triply distilled water and transferred to the electrochemical cell. Once the working electrode was introduced to the cell it was held at the starting potential for one minute before the cycle was started to allow for equilibration of the system. For reproducibility, it was necessary to clean the electrode after each voltammetric cycle.

ii) Auxiliary Electrodes.

The auxiliary electrode employed in all experiments were constructed platinum foil (surface area $> 10 \text{ cm}^2$) arc-welded to platinum wire embedded in pyrex holders. The same Kings low noise coaxial connectors were used for connection to the potentiostat.

iii) Reference Electrodes.

The reference electrode used throughout the majority of the experiments was a saturated calomel electrode (13-620-51, Fisher Scientific). Due to concerns of chloride contamination, the early experiments in the sulphate medium were performed using a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. The $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrodes were constructed as depicted in Fig. 6.

Once constructed, the operating potential of the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode was measured against a saturated calomel electrode over a period of 24 hours. The measured potential (-0.379 V) compared favourably

Figure 6.

with the calculated value of -0.364 V. This reference electrode was not employed for the majority of the experiments due to noise and mechanical stability problems. Bubbles would develop in the $\text{Hg}/\text{Hg}_2\text{SO}_4$ paste necessitating the reconstruction of the electrode. Any mechanical vibrations also tended to dislodge the mercury pool from behind the paste which also lead to the reconstruction of the electrode. Each reconstruction and stabilization took approximately two days to complete and after experiencing a number of successive undesirable incidents use of this electrode was discontinued. However the

early use of this reference electrode established the value of the underpotential shift (ΔU_p) in the sulfate medium at 290 mV. Any significant chloride contamination would diminish the magnitude of the underpotential shift and this effect was not observed after repeated use of the calomel electrode. All potentials quoted in this text are in reference to the SCE.

(2) Electrochemical Cells:

The two styles of electrochemical cells employed in this study were constructed from pyrex glassware. Each cell was of the basic three compartment configuration with the working electrode being housed in the main compartment of the cell. The chamber for the auxiliary electrode was separated from the main compartment by a length of glass tubing and a glass frit. The compartment for the reference electrode was attached to the main body of the cell using a luggin capillary housed in a ball joint. The ball joint made it possible for the tip of the luggin to be positioned as close as possible to the surface of the working electrode (~ 1 mm.). Control of this distance was necessary for accurate ohmic drop corrections.

Both cells were equipped with a two-channel inlet for the introduction of purified N_2 to the cell. Prior to the introduction of the working electrode, the N_2 was bubbled through the electrolyte by means of a tapered glass tube. When the working electrode was ready for insertion the N_2 was passed over the electrolyte, providing an inert blanket and minimizing the risk of oxygen poisoning during the insertion of the working

electrode. The N_2 was exhausted through a bubbler, keeping the interior of the cell isolated from the atmosphere.

A depression was built into the bottom of each cell so that a magnetic stirrer could be used to improve the efficiency of the degassing process. Electrolytes were bubbled and stirred for one hour before the commencement of experiments. The experiments involved in the kinetic analysis were carried out in a cell in which the working electrode was introduced through a 24/40 ground glass joint housed in the ceiling. In the PAS studies the working electrode was introduced through a similar joint mounted in the side of the electrochemical cell. This arrangement held the surface of the electrode perpendicular to optical windows mounted in the opposite side of the cell.

(3) Chemical Reagents:

All salts required for the preparation of the electrolytes were used as purchased (Fisher reagent grade) with the exception of the thallous perchlorate. This salt was prepared by digesting thallium shot (99.999%, Aesar) in vacuum distilled perchloric acid (99+ %) and recrystallizing twice from triply distilled water.

Problems were encountered during the preparation of stock $TlCl$ solutions. Although solubility data from the HCP (0.29 g/100 cc.) indicated that a 12 mM solution could be prepared. In practice however, it was necessary to heat the solvents to get sufficient $TlCl$ dissolved for a 1 mM solution of Tl^+ . With this low a concentration, it

was necessary to dissolve the TiCl_3 in a heated 0.5 M NaCl solution and then accurately determine the Ti^{3+} concentration using flame emission atomic absorption.

All solutions were prepared using triply distilled water. The distilled water provided by the chemistry department was put through a two stage Corning still by direct feed. The first stage was a simple distillation to lower ion concentrations while the second distillation was from an alkaline permanganate solution for the removal of organic impurities.

The nitrogen used for the purging of oxygen from the electrolytes was zero grade (Central Oxygen Ltd.). The N_2 was further purified by being passed through an oxygen trap (C36065, Chromatographic Specialties Inc.) followed by a bubbling tower containing a solution of vanadous chloride over a bed of zinc amalgam [43]. The N_2 was then passed through two more bubbling towers containing triply distilled H_2O before being introduced to the electrochemical cell.

(4) Instrumentation:

A schematic diagram of the equipment used in the kinetic studies of the Ti/Cu UPD system is given in Fig. 7. Potentials were controlled by a B.C. Stonehart 1200 potentiostat and a PAR 170 programmer. Signals were recorded using a Nicolet 3901 storage oscilloscope and/or a HP7047A X-Y recorder. The cell was housed in a Faraday cage, and all connections made with shielded cable in an attempt to limit noise.

Figure 7. Schematic diagram of the apparatus employed for the kinetic studies of the TI/Cu UPD system.

The experimental setup used in the PAS studies is shown in Figure 8. The electrochemical cell was a standard three electrode system, consisting of the copper working electrode, a Luggin capillary leading to a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode. The voltage applied to the working electrode was cycled by means of a potentiostat and programmer (Stonehart Associates, model BC1200 and EG&G PARC, model 175) and the current output was recorded on an X-Y recorder (Hewlett-Packard, model 4047). The cell itself was fitted with an optical window opposite to the copper electrode surface. The cyclic voltammogram and the PAS signal acquisition were carried out simultaneously.

The excitation beam from an argon ion-pumped dye laser (Spectra-Physics models 164 and 375B), 605 nm and typically 90 mW, was directed onto the copper electrode surface through the clear glass window at normal incidence. This wavelength (605 nm) was chosen since it is not well absorbed by copper [37] and the background PAS signal due to the copper was thus minimized. The excitation beam was mechanically chopped at 500 Hz, which gave the best overall signal-to-noise ratio with our frequency-tuned detection system. The signal from the piezoelectric transducer was fed directly into a lock-in amplifier (Stanford Research model SR510) and associated SR565 data acquisition software. In all cases, 60 Hz and 120 Hz line filters and a 3 s time constant were employed. The PAS signal (lock-in amplifier output) was monitored as a function of time (ie., potential applied to the working electrode) on a personal computer.

Figure 8. Schematic diagram of the apparatus used in the PAS investigation of the TI/Cu system.

RESULTS AND DISCUSSION

(1) Cyclic Voltammograms (CV).

The initial studies performed on the Tl/Cu system were carried out on a mechanically polished copper working electrode. Typical CV's for the deposition-stripping process of Tl(I) on Cu_{mech} in chloride and sulphate solutions are presented in Figures 9 and 10. In both solutions there was one major UPD peak with indications of a second peak being seen before the onset of bulk deposition (-800 mV vs SCE). Reference to Bewick's work [26] indicated that the surface preparation of the electrode was crucial in the study of monolayer formation and it was this information that prompted the investigation of electropolishing as a viable means of surface preparation.

The initial investigations employing electropolishing revealed two distinct UPD peaks in both the sulfate and chloride solutions (Figures 11 and 12). The only conditions to be changed in recording the CV's seen in Fig. 9 and 10 and those presented in 11 and 12 was the means of surface preparation. Aside from the discovery of two distinct UPD peaks (Fig. 11 and 12), as opposed to one (Fig. 9 and 10), the appearance of the main UPD peaks was radically altered. Peak splitting and/or shoulders on the major UPD peak were not apparent on the mechanically polished copper electrode but were clearly visible on the electropolished surface. There was also a 30% reduction in the charge

Figure 9. Cyclic voltammogram of Tl deposition on a mechanically polished polycrystalline Cu electrode from 0.5 M KCl, $[Tl^+] = 10^{-3}$ M, 25 mV s^{-1} .

Figure 10. Cyclic voltammogram of Tl deposition on a mechanically polished polycrystalline Cu electrode from 0.5 M Na_2SO_4 , $[Tl^+] = 1.4 \times 10^{-3}$ M, 25 mV s^{-1} .

Figure 11. Cyclic voltammogram of Tl deposition on an electrochemically polished polycrystalline Cu electrode from 0.5 M Na_2SO_4 , $[\text{Tl}^+] = 1.4 \times 10^{-3} \text{ M}$, 25 mV s^{-1} .

Figure 12. Cyclic voltammogram of Tl deposition on an electrochemically polished polycrystalline Cu electrode 0.5 M KCl, $[Tl^+] = 10^{-3}$ M, 25 mV s^{-1} .

density associated with the major UPD peak (charge density = area under peak in a current/voltage profile) when switching from the mechanically polished to the electrochemically polished electrode. All of these changes are directly related to the change in the nature of the working electrode's surface.

The decrease in the charge density associated with the formation of the first monolayer was due to a change in the actual surface area of the working electrode. Micrographs at a magnification of 10,000 times (Fig. 13) show the distinct difference in the roughness of the electrode surface brought about by the two methods of polishing. Although the mechanically polished electrode appeared, to the naked eye, to have a smooth and highly reflective surface, large pits and striations left by the abrasive became visible under magnification. Therefore, although the apparent surface area of the electrode was still 0.2 cm^2 , the actual surface area would be close to double that figure.

The appearance of the second UPD peak was also directly related to the method of surface preparation. It is a well established fact that the preparation of a metal surface by means of mechanical polishing leads to a severely deformed zone near the surface of the metal and that this zone has different properties than those of the bulk metal [44]. Electropolishing however, leaves an undistorted metal lattice behind. When electropolishing copper, it has been found that [100] planes in the fcc structure have the lowest dissolution rate while the [111] planes have the highest dissolution rate [45]. The differences in dissolution rates would lead to the faceting (crystallographic etch pattern) of a polycrystalline electrode, exposing areas of distinct crystal planes [46]. The differences in surface structure would be reflected in the structure of the first UPD

(a)

(b)

Figure 13. Scanning Electron Micrographs of (a) a mechanically polished polycrystalline Cu electrode and (b) an electrochemically polished polycrystalline Cu electrode. Magnification = 10000 x.

monolayer and if that morphology was different enough from that of bulk thallium, then there could be enough of an electronic difference between the thallium monolayer and crystalline thallium to allow for the second UPD monolayer. In the case of the mechanically polished electrode, it could be that the distortions of the copper lattice are severe enough to minimize the structural differences between the initial thallium monolayer and bulk thallium. The fine detail displayed in Fig. 11 and 12 could also be explained by the appearance of the distinct crystallographic zones produced by the electropolishing. Due to the increased detail available on the electropolished surface, the remainder of the studies performed employed this method for the copper electrode preparation.

The effect of the presence of the chloride ion on the UPD process has been well documented [6]. It is felt that it is the degree of specific adsorption of the anion that determines the effect the anion presence will have on the UPD process. Three different anions of varying specific adsorptivity (the specific adsorption of the anions considered decreases in the series $\text{Cl}^- > \text{SO}_4^{2-} > \text{ClO}_4^-$ [6]) were used in the kinetic studies of the Tl/Cu system. Representative CV's are given in Fig.'s 14-16. In all three solutions two major UPD peaks were seen. The underpotential shift (ΔU_p), calculated as the distance between the first (most positive) stripping peak and the bulk stripping peak, was 220 mV in the chloride, 290 mV in the sulphate, and 320 mV in the perchlorate solutions. Similar results were reported earlier [8,9,11] and it was felt that changes in the

Figure 14. Cyclic voltammogram of a copper electrode in 0.5 M KCl. $[\text{Ti}^+] = 10^{-3}\text{M}$, 100 mV s^{-1} .

Figure 15. Cyclic voltammogram of a copper electrode in 0.5 M Na_2SO_4
 $[\text{Tl}^+] = 1.4 \times 10^{-3} \text{ M}$, 100 mV s^{-1} .

Figure 16. Cyclic voltammogram of a copper electrode in 0.5 M NaClO₄.

[Tl⁺] = 10⁻³ M, 100 mV s⁻¹.

underpotential shift were due to changes in the work function and/or the electronegativity of the working electrode brought on by the presence of the specifically adsorbed anions [6]. Kolb's model for UPD predicted an underpotential shift of 330 mV for the Tl/Cu system which would indicate that there was little or no interaction between the perchlorate anion and the copper substrate. The second UPD peak, located near the reversible potential, was found to be more distinct than those shown in previous works. The visibility of the finer features was attributed to the electrochemical polishing of the copper electrode. It was also noted that the presence of peak-splitting and shoulders were most pronounced in the chloride solution and least evident in the perchlorate solution. This trend could be interpreted as an indication that the peak-splitting, as well as ΔE_p , are linked to the degree of specific adsorption of the anion present.

(2) Deposition Mechanisms.

Figures 17,18,19 show the dependence of peak potential (E_p), peak pseudocapacitance ($C_p = I_p/s$), and peak half-width ($\Delta E_{1/2}$) on sweep rate (s) for the first stripping peak of Tl on Cu in chloride, sulphate, and perchlorate solutions respectively. The shapes of the curves correspond to those predicted by Conway and co-workers for an electrode reaction with a single adsorbed species [14].

The values of $\Delta E_{1/2}$ differ from those predicted for Langmuirian-type adsorption (in the absence of lateral interactions, the interaction parameter $g = 0$). For reversible conditions ($s \rightarrow 0$) and $g=0$, the predicted $\Delta E_{1/2} = 91$ mV. The experimental values of

Figure 17. Plot of $\Delta E_{1/2}$, C_p ($= i_p / s$), and E_p vs $\log s$ in 0.5 M KCl.
 $[\text{Ti}^{+}] = 10^{-3} \text{ M}$.

Figure 18. Plot of $\Delta E_{1/2}$, C_p ($= i_p / s$), and E_p vs $\log s$ in 0.5 M Na_2SO_4 .
 $[\text{Tl}^+] = 1.4 \times 10^{-3} \text{ M}$.

Figure 19. Plot of $\Delta E_{1/2}$, C_p ($= i_p / s$), and E_p vs $\log s$ in 0.5 M NaClO_4 .
 $[\text{Tl}^+] = 10^{-3} \text{ M}$.

$\Delta E_{1/2}$ are roughly 65, 32, and 30 mV in the chloride, sulphate, and perchlorate media respectively. A shift of $\Delta E_{1/2}$ to lower values is indicative of attractive interactions in a chemisorbed monolayer and is characteristic of UPD monolayers for metals [16]. From the calculations of Noel et al [18], the interaction parameter was found to be -0.9 for the chloride, -2.2 for the sulphate, and -2.3 for the perchlorate solutions. The difference in the g values can be explained by the different degrees of anion adsorption if one assumes that the adsorption of the anions on the thallium adatoms leads to a reduction of the attractive interactions between the thallium adatoms. As stated earlier, the specific adsorption of the anions considered decreases in the series $\text{Cl}^- > \text{SO}_4^{2-} > \text{ClO}_4^-$ [6]. This then would explain the smaller negative g value in the chloride solution but the near equality of g values in the sulphate and perchlorate solutions requires some additional explanation. The investigations of Schmidt and Gyax [11] on the UPD of Tl on Cu showed that the Cl^- adsorption on the Cu substrate and on the Tl monolayer were the same. Similar data for the Tl/Cu system in the SO_4^{2-} medium was not available but the study of Tang and Furtak using a quartz crystal microbalance [51] indicated that under Tl UPD on Ag in Na_2SO_4 solution, a rather large desorption of SO_4^{2-} ions takes place in the course of Tl deposition. Thus if one accepts the validity of this observation for the Tl/Cu system it could explain the similar g values found experimentally for the SO_4^{2-} and ClO_4^- solutions. Indications that the desorption of sulfate was taking place with the introduction of thallium can be seen in Fig. 20. The CV recorded in 0.5 M Na_2SO_4 (—) shows a large reduction peak, centred at -1.25 V vs. SCE, before the onset of hydrogen evolution at -1.7 V. When the magnitude of the reduction reaction and the

Figure 20. Cyclic voltammograms of a Cu electrode in 0.5 M Na_2SO_4 (—) and 0.5 M Na_2SO_4 containing $[\text{Tl}^+] = 1.4 \times 10^{-3} \text{ M}$ (---), 100 mV s^{-1} .

constituents of the electrolyte were considered, the reaction occurring at -1.25 V must have involved either H₂O and/or the sulfate anion. As hydrogen evolution was already identified as the reaction commencing at -1.7 V it was concluded that the large peak represented a reduction of the sulphate anion. Reference to the Handbook of Chemistry and Physics (HCP) gave the following reaction

with an E_{rev} of -1.18 V vs. SCE. When Tl₂SO₄ was added to the electrolyte (---) the peak associated with the sulphate reduction shifted 650 mV in the cathodic direction. The appearance of this large overpotential indicated that the sulphate reaction was not favourable on a thallium substrate which in turn would imply that the deposition of the Tl monolayer would remove the specifically adsorbed sulphate anions.

Fig. 21 shows the dependence of peak current (I_p) on sweep rate (s). For all three solutions investigated the dependence in log-log coordinates was a straight line with a slope of approx. 1.0. In the region of transition from reversible to irreversible behaviour, a decrease in the slope was observed. The log-log relationship was seen to return to linearity with the same slope as before the deviation. This result corresponded with the theoretical predictions for an adsorption controlled UPD process [47], according to which the dependence of I_p on s is expressed, for reversible and irreversible processes, as

$$I_p = \frac{\kappa F}{4RT} s \quad (28)$$

and

Figure 21. Dependence of peak current on sweep rate for the stripping peak at - 0.56 V in 0.5 M KCl. [Ti⁺] = 10⁻³ M.

$$I_p = \frac{\kappa F}{5.42 RT} s \quad (29)$$

where κ is a monolayer charge.

An adsorption mechanism does not appear to play a role in the formation of the second monolayer. Fig. 22 shows the dependence of $\Delta E_{1/2}$ on s for the second UPD peak. The $\Delta E_{1/2}$ values were between 0 and 40 mV which suggested that the mechanism for deposition was one of nucleation and growth rather than adsorption [17,18]. According to Noel [18], $\Delta E_{1/2}$ tends to $31.4/\beta n$ as $s \rightarrow \infty$ for both instantaneous and progressive nucleation mechanisms. From this limiting value and the experimental $\Delta E_{1/2,\infty} = 40$ mV, the transfer coefficient was calculated to be ~ 0.8 which was close to the value ($\beta=0.7$) found for the first UPD peak following the adsorption mechanism in the sulphate solution. The expected behaviour in the reversible region ($s \rightarrow 0$) would be an increase in $\Delta E_{1/2}$ with increasing ν for instantaneous nucleation and $\Delta E_{1/2} \sim 0$ for progressive nucleation [18]. The trend seen in Fig. 22 would seem to indicate that the mechanism followed in the second UPD peak was instantaneous, rather than progressive, nucleation and growth.

Another indication that the second UPD peak followed a nucleation and growth mechanism was seen in the current-time transients (Fig. 23). As the pulsing potential moved from the region of the first peak ($E_p = -0.46$ V) to that of the second ($E_p = -0.76$ V), the transient changed from one of monotonic decay (-0.55 V) to a transient with a distinct shoulder (-0.625 V) which then developed a small peak (-0.724 V), or rising

Figure 22. Plot of $\Delta E_{1/2}$ vs $\log s$ for the peak occurring at -0.71 V in $0.5 \text{ M Na}_2\text{SO}_4$. $[\text{Ti}^+] = 1.4 \times 10^{-3} \text{ M}$.

Figure 3. Dependence of current-time transients on potential in 0.5 M Na_2SO_4 .
 $[Ti^{+}] = 1.4 \times 10^{-3} M$.

portion. Transients with rising portions were found for the UPD of Tl on Ag [26], Pb on Ag [28] and Pb on Cu [48] and were attributed to a two-dimensional nucleation and growth mechanism. UPD systems with two peaks, one following an adsorption mechanism, the other an electrocrystallization model, have been reported for Tl [20] and Co [21] on glassy carbon.

(3) Peak Charge (Q)

Fig. 24 shows the dependence of charge (Q) under the stripping peaks on sweep rate (log s) in the sulphate solution. The dependencies were similar in the perchlorate and chloride solutions. In the reversible region ($s \rightarrow 0$) the Q value appeared to be constant at around $200 \mu\text{C cm}^{-2}$ ($190\text{--}210 \mu\text{C cm}^{-2}$) which would indicate the presence of a complete monolayer. In the irreversible region Q decreased with increasing s to a value of $150 \mu\text{C cm}^{-2}$. The value of $200 \mu\text{C cm}^{-2}$ corresponds with values of monolayer charge (Q_m) for a monovalent metal [6]. Experimental values of Q for Tl(I) UPD on polycrystalline Cu [8,9,11], determined from the plots in the reference articles, lie in the region of $220 \mu\text{C cm}^{-2}$.

A decrease of Q with increasing s was observed by Lorenz et al [49] for Tl(I) on Au. The authors suggested that the phenomenon was connected with diffusion limitations in the solution. Experiments using a rotating disc electrode have shown that the behaviour displayed cannot be accounted for solely through diffusion effects. It was interesting to note that the Q value at high s, $\cong 150 \mu\text{C cm}^{-2}$, lies between the value for monolayer

Figure 24. Dependence of the stripping peak charge on sweep rate in 0.5 M Na_2SO_4 ,
[Tl^+] = 1.4×10^{-3} M.

charge given by Schmidt and Gygax [11] assuming a close-packed hexagonal Tl overlayer on polycrystalline Cu ($160 \mu\text{C cm}^{-2}$) and the value calculated using the assumption of square packing ($140 \mu\text{C cm}^{-2}$) [50].

The charge of $100 \mu\text{C cm}^{-2}$ found for the second UPD peak was half that found for the first monolayer. There are a number of factors this lower charge could be attributed to. The first of these would be a less accurate determination of Q due to the overlapping of the bulk peak. Other factors would include the changing of the layer structure, the possibility of a change in the number of surface active sites and a reduction in the contributions to charge from the desorption of SO_4^{2-} . Deposition of two successive monolayers of Tl on Ag were reported by Bewick and Thomas [26] and Tang and Furtak [51]. In the former paper, the charge for the two peaks were reported as $200 \mu\text{C cm}^{-2}$ for the first monolayer and $120 \mu\text{C cm}^{-2}$ for the second.

(4) Kinetic Analysis of the Adsorption-UPD Process.

Using the methods proposed by Angerstein-Kozłowska and Conway [16], on the basis of the experimental data shown in Fig. 17-19 it is possible to evaluate rate constants and reversibility parameters for the UPD process. The analysis is based on the experimentally accessible apparent reversibility parameter $s'_{o,p}$, the value of which is determined from the intercept of the reversible and irreversible branches of the E_p vs. $\log s$ plot. Taking into account the lateral interaction one determines the reversibility parameter $s_{o,p}$.

$$\log s_{o,p} = \log s'_{o,p} - \log [1 + \beta g (1 - \theta_{p,irr})] + \frac{\beta g}{2.3} (\theta_{p,irr} - \theta_{p,r}) \quad (30)$$

where g - interaction parameter

β - transfer coefficient found from the slope of the irreversible branch of the E_p vs. $\log v$ plot.

$\theta_{p,r}$ - reversible peak coverage = 0.5

$\theta_{p,irr}$ - irreversible peak coverage, found from Noel et al [18]

From this value the standard reversibility parameter s_o° and the standard rate constant K° are calculated.

$$\log s_o^\circ = \log s_{o,p} - (1 - \beta) \log C_{Tl} \quad (31)$$

and

$$K^\circ = \frac{s_o^\circ (1 - \beta)}{2RT/zF} \quad (32)$$

where C_{Tl} is the thallium ion concentration in solution (mol dm⁻³).

From the value of s_o° the value of the exchange current density can be determined as

$$i_{o,p} = C_{r,p} \times s_o^\circ \quad (33)$$

where $C_{r,p}$ is the peak pseudocapacitance in the reversible region.

The experimental data and calculated kinetic parameters are given in Table 1. As can be seen the s_o° and i_o values increase in the order $\text{ClO}_4^- < \text{SO}_4^{2-} < \text{Cl}^-$; i.e. with the

SOLUTION	EXPERIMENTAL DATA						CALCULATED DATA		
	$\Delta E_{1/2}$ (mV)	g	$\theta_{p,irr}$	β	$C_{r,p} \times 10^{-3}$ $\mu F cm^{-2}$	$S_{o,p}$ $V s^{-1}$	S_o^o $V s^{-1}$	$\kappa^o \times 10^{-3}$ $cm^3(l-\theta)$ s^{-1} $mol^{-(1-\theta)}$	i_o $mA cm^{-2}$
KCl $C_{n^+} = 10^{-3}M$	65	-0.9	0.61	0.54	3.2	2.3	72.4	0.70	232
Na ₂ SO ₄ $C_{n^+} = 1.4 \times 10^{-3}M$	32	-2.2	0.59	0.68	5.4	1.3	24.0	0.15	132
NaClO ₄ $C_{n^+} = 10^{-3}M$	30	-2.3	0.58	0.62	5.5	0.62	19.1	0.15	105

Table 1. Experimental Data and Calculated Kinetic Parameters for the Main UPD Peak in the Ti/Cu System.

increase in the specific adsorption of the anion. This corresponded with experimental data of Angerstein-Kozłowska and Conway on the influence of anions (SO_4^{2-} and ClO_4^-) on the kinetics of hydrogen adsorption on a Pt electrode [16]. The i_0 values for all three solutions lie in the limits between 53 and 367 mA cm^{-2} reported by Hermann et al [52] for the UPD of Tl on Au from the solution of 0.1 M TlNO_3 , 1 M Na_2SO_4 .

(5) pH Effects.

There are two factors to be considered when examining the effect of pH on the UPD of Tl(I) on Cu. There are the changes in the state and active concentration of Tl and there is also the formation of Cu-oxide layers on the electrode surface. Fig. 25 shows the dependence of the peak potential (E_p) for the first stripping peak, in a solution of $10^{-3}\text{M Tl}_2\text{SO}_4$, 0.5 M Na_2SO_4 , on the pH. At lower pH E_p was constant at -450 mV while at higher pH values E_p shifted linearly towards more negative values with a slope of 60 mV per decade of pH. The dependence is similar to that obtained by Amadelli et al [53] in a study of pH influence on the UPD of Tl on Au. At low pH E_p is determined by the equilibrium

and is independent of pH. Amadelli attributed the pH dependence at higher pH to the processes

Figure 25. Dependence of peak potential on pH in $0.5\text{ M Na}_2\text{SO}_4$.

$[Tl^+] = 1.4 \times 10^{-3}\text{ M}$.

The Nernst equation for the latter reaction would display a potential dependence of -60 mV per decade of pH. The unanswered question is the actual nature of the $TlOH_{ads}$ species and the mechanism of their formation.

The solubility of Tl_2O in hydrated form is determined by [54]

$$\log(a_{Tl^+}) = 13.90 - pH \quad (37)$$

At the Tl^+ concentration of 2×10^{-3} M the formation of the oxide as a bulk phase would be expected at a $pH > 14$. From Fig. 25 it can be seen that the negative shift of E_p commenced around a pH of 10. Possible explanations for the apparent discrepancy include the existence of a soluble $TlOH$ complex, a large increase of the Tl^+ or OH^- concentration at the surface of the electrode due to adsorption, and the interaction of the thallium ions with surface copper oxides. Adžić et al [55] have shown an interaction of Pb ions with $AuOH$ under UPD of Pb on Au. The fact that the peak potentials for both the bulk deposition and the second UPD peak were independent of the changes in pH led to the conclusion that the dependence of E_p (1st peak) on the changing pH was related to the copper substrate in the UPD region and that reaction (c) did not occur on a thallium covered copper substrate.

The cyclic voltammogram in Fig. 26 consists of two continuous scans in the sulphate solution with a pH of 11. A freshly cleaned electrode was held at -0.35 V for one minute before the first cycle was initiated. Comparison of the two cycles indicated that

Figure 26. Cyclic voltammograms of a copper electrode in 0.5 M Na₂SO₄. (---) first scan, (—) second scan. [Tl⁺] = 1.4 × 10⁻³ M, pH = 11, 25 mV s⁻¹.

the large peak at -0.65 V.(2a) was related to the first UPD peak but that it was overlapped by the peak found at -0.55 V (1a). Peak 1b may be related to the reduction of a form of copper oxide. At the starting potential of -0.35 V, in a solution of pH 11, the most probable form of oxide present would be Cu₂O, due to the reaction

with $E^0 = -0.365$ V. (SHE) [56]. Ambrose et al [57] found a voltammetric peak for this reaction in 1.0 M. KOH at ~ -0.55 V (SCE). The presence of a pre-peak at -0.69 V was also reported and was tentatively assigned to the formation of a soluble hydroxide according to

Droog et al [58] reported that the first stage in the anodizing of a copper electrode was the electrosorption of oxygen species at potentials negative to the peak of bulk formation of Cu₂O. This may be complicated further by the anion present. According to Drogowska et al [59] the presence of the SO₄²⁻ ion at pH 12 resulted in the formation of Cu²⁺ ions which precipitated as the hydroxide and the oxide.

In the second cycle, the peak associated with oxide reduction (1a) shifted to a less negative potential (1b) with full separation from the Tl UPD peak (2b). The shift and decrease in the amplitude of the oxide reduction peak reflected the decrease in the amount of the copper oxide formed at the starting potential and, possibly, a change in the nature of the oxide species. The important feature of this voltammogram was the similarity of the anodic peaks associated with the stripping of the thallium monolayer.

This indicated that the presence of the oxide during the first cycle did not hinder the formation of the full Tl monolayer. Tindall and Bruckenstein [60] showed that silver could not deposit on a fully oxidized platinum surface. If this observation was valid for the Tl/Cu system one would conclude that the copper oxide reduction proceeded at a sufficient rate to leave the Tl UPD unaffected. Otherwise some interaction between the copper oxide and the Tl ions (see above) would have been observed.

(6) Photoacoustic Spectroscopy

Figure 27a shows a typical cyclic voltammogram for the thallium-copper system. The UPD can clearly be seen by the large cathodic peak centred near -540 mV. It is possible to distinguish a second UPD peak at -770 mV, just prior to the onset of bulk deposition. The observation of a second feature in the underpotential region of the Tl/Cu system is not uncommon and has been reported previously [11,32]. On the anodic side, the bulk stripping is seen first and this is followed closely by the stripping of the second UPD layer. The first UPD layer is then stripped from the electrode surface.

In PAS measurements, all of the excitation light which is not reflected will be absorbed by the electrode to cause periodic heating in a region one thermal diffusion length below the surface. Using optical constants (refractive index, absorptivity) for copper at 605 nm from Johnson and Christy [61] and a refractive index of 1.34 for the non-absorbing electrolyte [38], the reflectivity of the clean Cu electrode surface prior to Tl deposition was found to be 0.81 using Fresnel's equation for normal incidence. When Tl is deposited on the electrode surface, the reflectivity of the copper electrode is decreased and more laser energy is absorbed at the electrode surface. The absorbed light energy is subsequently converted into heat with an efficiency estimated from the work by Sander and Dohrmann to be essentially 100 % [37].

The thermal diffusion length, which is characteristic of the thermal properties of the electrode material involved, is of the order of $300 \mu\text{m}$ ($=[2\kappa/\rho C\omega]^{1/2}$, where κ is the

Figure 27.(a) Cyclic voltammogram of the TI-Cu system at pH 3 in 0.5 M Na_2SO_4 .

$[\text{TI}^+] = 2 \times 10^{-3} \text{ M}$, sweep rate = 25 mV s^{-1} .

(b) PAS signal versus applied potential. Excitation wavelength 605 nm at 90 mW. (●) Cathodic half-cycle, (○) anodic half-cycle.

thermal conductivity ($\text{cal/cm}\cdot\text{s}\cdot^\circ\text{C}$), ρ is the density (g/cm^3), C is the specific heat ($\text{cal/g}\cdot^\circ\text{C}$) and ω is the modulation frequency (Hz)) for copper at a chopping frequency of 500 Hz [62]. This is significantly thinner than the electrode itself (1 mm thickness) and the system may be considered to be thermally thick. As a result, only the properties of the electrode material itself contribute to the PAS signal and the piezoelectric ceramic material in contact with the electrode did not affect the signal generation. The thallium deposit is many orders of magnitude thinner than the thermal diffusion length and as such cannot be expected to affect the thermal properties of the system.

Results of the PAS detection of TI UPD on Cu are shown in Figure 27b. As the applied potential was swept cathodically into the region of the first UPD peak, the PAS signal fell slightly (marked as (I) in the figure) before rising to a relatively flat region (labelled (II) in the figure) corresponding to the voltage region between the two UPD peaks. The PAS signal then rose through the potential region of the second UPD peak, and a very small level region (labelled (III) in the figure) can be seen before the increase in the PAS signal accompanying bulk deposition just prior to the reversal of the sweep. The PAS signals for the anodic scan essentially mirrored those seen during the cathodic scan.

In Figure 27a, the initial decline in the PAS signal (from -460 to -490 mV, region I) may be attributed to the removal of copper oxide by the initial stages of TI UPD [32]. Support for this hypothesis can be seen in the PAS signal obtained in a pH 12 medium discussed below (Figure 28a). The PAS signal (II) corresponding to the voltage region between the two UPD peaks was not as flat as might be expected for a region undergoing

no changes in surface conditions. The gentle rise of the PAS signal in this potential region may be attributed to a change in the nature of the adsorbed Tl layer. Potentiostatic pulses in this region published elsewhere [32] showed the development of a shoulder in the current-time profiles at potentials more cathodic than -0.625V. The development of the shoulder in the current transients, coupled with a gentle rise in the PAS signal, would seem to indicate the occurrence of a possible phase transformation. Yoshihara et al. [41] pointed out that underpotential deposits of Tl and Pb on the (111) faces of silver undergo slow structural changes which are the result of a partial exchange of atoms from the adsorbates and the topmost layers of the substrate. Following region II, the PAS signal rose again with a comparable slope to that observed for the first UPD peak. The charge determined for the first UPD peak was $200 \mu\text{C cm}^{-2}$ which corresponded to the formation of a complete monolayer [32]. The change in the PAS signal amplitude for the second UPD peak was comparable to that for the first UPD peak although the charge for the second peak was only $100 \mu\text{C cm}^{-2}$. Schmidt and Gygax [11] also reported two UPD peaks in the Tl-Cu system but attributed the second UPD peak to a filling in of a single monolayer with the total charge of $380 \mu\text{C cm}^{-2}$ being explained by a roughness factor of 2.25-2.50. If the two peaks found in the UPD region represented the filling in of one monolayer, the PAS rise for the second UPD peak should only be a fraction of that seen for the first UPD peak. The comparable change in the PAS signal amplitude would then support the claim that two monolayers were deposited rather than a filling in of an incomplete first monolayer. Possible explanations for the smaller charge associated with the second monolayer were given in Section 3.

With the onset of bulk deposition, the PAS signal rose once again. Holding the electrode at increasingly negative potentials in the bulk region gave rise to a constant rate of increase in the PAS signal as expected.

The PAS signal for the anodic portion of the scan mirrored that of the cathodic scan, although it is interesting that the second UPD plateau (labelled IV in the figure) which appears immediately after the bulk stripping peak is less well resolved than the corresponding plateau on the cathodic side. A point made obvious by the PAS signal at more positive potentials was the apparent reversibility of the first UPD process as indicated by the degree of overlap between the cathodic and anodic voltages. The diminishing separation between the anodic and cathodic scans may be related to the different mechanisms shown for the two UPD peaks [32] with adsorption (first UPD) being the more reversible process than the one associated with nucleation and growth (second UPD).

In a previous study a linear relationship was found between E_p and pH for the first UPD monolayer [32]. Above pH 10, the cathodic UPD peak was totally obscured by the large peak associated with the reduction of Cu_2O but the similarity of the anodic peaks indicated that the UPD process was not hindered by the presence of the oxide. PAS scans were obtained at pH 12 in our experiments to clarify the UPD process in this high pH region. In cyclic voltammetry the presentation of multiple sweeps is not uncommon and the features of the individual cycles are easily discernible but even in this case of only two cycles, the corresponding PAS responses were highly obscure. As a result, the individual sweeps are presented singly along with the corresponding PAS

response. In Figure 28a the first cycle at pH 12 is presented. The dramatic pH effect is seen by the large cathodic peak occurring at about -730 mV with no apparent electrochemical reversibility in the anodic scan. However, the presence of 4 peaks in the anodic portion of the voltammogram would seem to indicate that Tl UPD has occurred albeit with some shift in E_p .

In Figure 28b the corresponding PAS signal is distinctly different from Figure 27(b). The PAS response throughout the cathodic region is nearly flat, exhibiting almost no change in signal as the oxide is removed, suggesting the copper oxide layer was quite substantial. The rise of the PAS response near -800 mV may be attributed to the bulk deposition of Tl. In the portion of the PAS response corresponding to the anodic region of the cyclic voltammogram, three declining voltage regions are discernable. The separation of these regions by small level areas might suggest the removal of the Tl bulk deposit and the two monolayers. The brevity of the decline in the PAS signal associated with the first monolayer (*) before the ensuing gradual rise associated with the formation of the Cu_2O suggests that the oxide is regenerated while the Tl monolayer is being removed.

In Figure 29a, the second sweep of the cyclic voltammogram at pH 12 is given. The large differences in the appearance of the cathodic scan have been attributed to a reduction in the amount of Cu_2O present [32]. The large cathodic peak centred near -600 mV represents the oxide reduction but the shoulder at -640 mV could represent the latter stages of formation of the first Tl monolayer. The deposition of the second monolayer is represented by the small cathodic peak at -770 mV. The anodic scan is identical to

Figure 28.(a) First sweep of the cyclic voltammogram for the Tl-Cu system at pH 12 in 0.5 M Na_2SO_4 , $[\text{Tl}^+] = 2 \times 10^{-3}$ M, $s = 20 \text{ mV s}^{-1}$.

(b) PAS signal versus applied potential. (●) Cathodic half-cycle, (○) anodic half-cycle.

Figure 29.(a) Second sweep of the cyclic voltammogram for the Tl-Cu system at pH 12.

(b) PAS signal versus applied potential. (●) Cathodic half-cycle, (○) anodic half-cycle.

that seen in Fig. 28a which would indicate that the TI UPD process was unaffected by the amount of oxide present.

In Figure 29b, the reduced oxide presence is indicated by a lower PAS signal (8.7 μV) at the beginning of the cycle. The decline in the PAS response associated with the reduction of Cu_2O can be seen to commence at -600 mV before the rise associated with the formation of the first UPD monolayer (**). Although spanning a smaller voltage range (-685 to -750 mV), the subsequent plateau corresponds well to that seen (II) in Fig. 27b. This flat portion in the PAS signal was attributed to the completion of the first TI monolayer. The diminished increase in the PAS response (**) associated with the formation of the first monolayer (7 to 7.6 μV as compared to 5.8 to 7.4 μV seen in Fig. 27b) suggests that a significant portion of the first monolayer was deposited during the reduction of the copper oxide. The cathodic PAS signal from -685 to -825 mV in Fig. 29b is a condensed version of the cathodic response seen in Fig. 27b with the plateaus attributed to monolayer completion (I and II in Fig. 5b and II and III in Fig 3b) having similar PAS response levels.

CONCLUSIONS

The underpotential deposition of thallium on polycrystalline copper in aqueous media has been thoroughly investigated. During the examination of this system, it was found that the surface preparation of the copper electrode was crucial to the observance of the UPD phenomenon. When using an electrochemically polished electrode, two distinct UPD peaks were observed. Kinetic analysis of the first monolayer UPD peak was performed using the model proposed by Conway and co-workers. The kinetic parameters for this monolayer were defined in terms of the peak potential, the peak half-width and the peak pseudocapacitance. It was suggested that the second UPD peak was formed by an instantaneous nucleation and growth mechanism.

The anionic dependence of the UPD process was also investigated and it was found that only the behaviour of the first monolayer was effected. The degree to which the anion was specifically adsorbed to the copper surface was the determining factor in the anionic influence.

The consequences of modifying the pH of the system was also investigated. Similar to the findings in the anion effect study, only the first monolayer was effected. Although the deposition process was obscured at pH values greater than 10, the appearance of the anodic scan lead to the conclusion that the formation of the first monolayer was not hindered by the presence of the copper oxide.

The use of PAS has clarified two main points regarding the Tl-Cu system: (i) two distinct monolayers existed in the UPD region, and (ii) the removal of Cu_2O from the electrode surface in basic media occurred at a sufficient rate that it did not interfere with the formation of the Tl monolayer.

PAS is sufficiently sensitive to monitor sub-monolayer deposits and as such has the potential to characterize the stages in multi-component deposition systems [63] provided the optical properties of the component species are suitably different from one another. With appropriate modification to the experimental system to allow variable angle of incidence, it would also be possible to investigate the optical constants of UPD metals using PAS [37].

Future studies of this system would be greatly enhanced by the use of single crystal copper electrodes. The interpreted effects of the electrochemical polishing could be clarified through the investigation of the UPD process on the different crystal faces. A more thorough analysis of the second UPD peak, along with the effects of substrate orientation, would also prove interesting. It would also be interesting to compare the kinetic results obtained through the use of Conway's model to results obtained using rotating disc and ring/disc electrodes.

The number of studies involving underpotential deposition are once again increasing with the advent of two new *in-situ* surface analysis techniques [64,65]. The recent development of *in-situ* Scanning tunnelling microscopy (STM), and atomic force microscopy (AFM), has made it possible to see individual atoms on the surface of the immersed polarized electrode. Although these techniques have already been used to

confirm indirect conclusions based on electrochemical techniques [65], the nature of these current techniques does not allow for the direct determination of the dynamics of the surface processes being studied.

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