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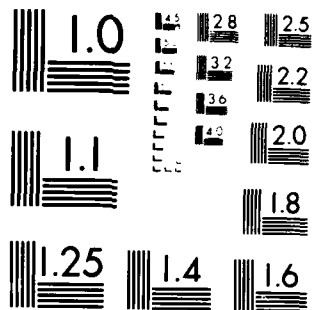
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) One of the objectives of this research was to study and to interpret the behavior of films at solid electrodes. With a sound understanding of the characteristics of submonolayer, monolayer and thicker films and their effect on electrochemical processes, it should be possible to apply this knowledge to understanding important solution heterogeneous processes, such as corrosion and electrocatalysis (by underpotential metal deposition). A second objective was to develop new approaches to studying electrochemical reactions at solid			

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↓ electrodes, particularly the use of controlled hydrodynamics, in order to provide new diagnostic criteria for elucidating complex electrode processes. Another goal was to apply solid electrode structures to analytically important problems.

Underpotential metal deposition studies at polycrystalline gold and platinum have led to a thermodynamic interpretation of the isotherm for the underpotential deposition (UPD) of lead and silver. The relationships between the underpotential, work function, point of zero charge, and coverage have been obtained in the absence of specific adsorption. Preliminary studies of the change of point of zero charge with underpotential coverage of silver on gold confirm the theoretical predictions, and demonstrate that there is a double layer charging current that accompanies the change in point of zero charge with change of UPD coverage. The thermodynamics and kinetics of the underpotential deposition of silver on gold have been successfully interpreted using the isotherm and ring shielding currents obtained at a rotating ring-disk electrode to separate the double layer charging currents from the instantaneous flux of UPD species at the disk electrode.

✓ A study of the electrocatalysis of the oxidation of formic acid by the UPD of lead, bismuth or thallium on polycrystalline platinum has shown that the third body hypothesis is a satisfactory explanation. It is necessary, however, to take into account the selective UPD of these metals and the uncatalyzed oxidation process on the various crystal planes of platinum. The lack of catalysis of the formic acid oxidation process by UPD silver and copper has been shown to be caused by the selective UPD of these metals on the platinum plane which contributes least to the uncatalyzed oxidation process.

↑ The theory of hydrodynamic modulation at a rotating disk electrode was extended to the electron transfer and preceding homogeneous reaction cases. Use was made of the experimental technique in our UPD and thick film studies. In particular, the formation of thick iodine films on platinum was demonstrated to be totally under mass transfer control. The ultimate thickness of the film can be described in terms of reversible electrode potential for the iodine/iodide couple, the triiodide equilibrium and diffusion of iodide ion through the iodine film. Hydrodynamic modulation was also applied to the interpretation of the current-potential response of photoelectrochemical cells having "pinned junctions". The approach outlined can, in principle, be used for illuminated, unpinned semiconductor/electrolyte interfaces.

The analytical application of porous electrode structures to trace analysis of aqueous solutions led to the development of pneumatoamperometric method. In this method a volatile, electroactive solute is purged from solution using a nonelectroactive gas and the gas stream impinged on the gas phase side of a porous electrode held at potential to electrolyze the electroactive species. If the solute is not volatile, a chemical reaction is carried out to produce a volatile species. This technique has nanogram sensitivity, and has been used to determine iodide, iodate, cyanide, arsenic, antimony, tin, osmium, ruthenium and a wide variety of oxidizing agents.

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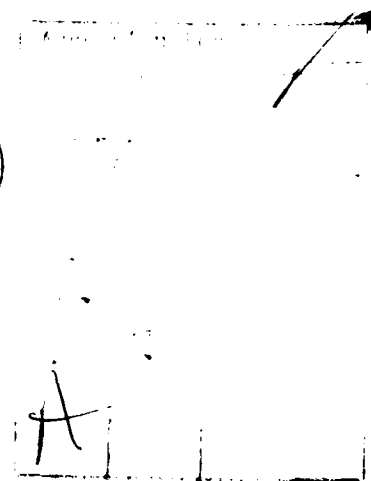
**Fundamental Studies of Underpotential Metal Deposition
And
Trace Analysis Using Solid Electrodes**

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SUMMARY OF WORK SINCE 15 MAY 1978

INTRODUCTION

One of the objectives of this research was to study and to interpret the behavior of films at solid electrodes. With a sound understanding of the characteristics of submonolayer, monolayer and thicker films and their effect on electrochemical processes, it should be possible to apply this knowledge to understanding important solution heterogeneous processes, such as corrosion and electrocatalysis (by underpotential metal deposition).

A second objective was to develop new approaches to studying electrochemical reactions at solid electrodes, particularly the use of controlled hydrodynamics, in order to provide new diagnostic criteria for elucidating complex electrode processes.

Another goal was to apply solid electrode structures to analytically important problems. A major facet of this aspect of our research involved using porous electrode structures to detect electroactive species originally present a gas phase, or introduced into a gas phase by purging from an aqueous solution phase using a non-electroactive gas stream.

Summary of Solid Electrode Film Studies

Underpotential Deposition Studies

Our early studies of underpotential deposition (UPD) involved determining the general characteristics of the UPD process for silver on gold [1,2]. In these studies the rotating ring-disk electrode (RRDE) technique was validated, as was the sinusoidally hydrodynamically modulated rotating disk electrode (SHM RDE) technique. These, and subsequent experimental and theoretical underpotential metal deposition studies at polycrystalline gold and platinum have led to a thermodynamic interpretation of the isotherm for the underpotential deposition (UPD) of lead and silver [19,24]. No partial charge exists on the adsorbed silver or lead species. The relationships between the underpotential, work function, point of zero charge, and coverage have been obtained in the absence of specific adsorption. Preliminary studies of the change of point of zero charge with underpotential coverage of silver on gold confirm the theoretical prediction that the point of zero charge is a linear function of UPD coverage and demonstrate that there is a double layer charging current that accompanies the change in point of zero charge with change of UPD coverage. Furthermore, the anomalous adsorption isotherm parameters found are due to the gradual variation of the work function of the substrate with UPD coverage. Dynamic electrosorption valency measurements show that conditions for a priori separability of double layer and faradaic processes do not exist.

The kinetics of the underpotential deposition of silver on a gold disk electrode of a RRDE have been successfully interpreted using the previously determined isotherm, and the ring shielding currents obtained at the rotating

ring electrode of the RRDE. The ring shielding currents permitted the calculation of the instantaneous flux of UPD species at the gold disk electrode [17,23,24]. The actual currents at the gold disk of the RRDE are contaminated with double layer charging currents associated with the change in point of zero charge in both potentiostatic and potentiodynamic experiments. The rate of UPD is under mixed control by mass transport and adsorption coupled with charge transfer. The charge transfer coefficient for the UPD process is comparable to that found at bulk silver, but the exchange current density was several orders of magnitude smaller. The dependence of exchange current and double layer capacitance upon applied potential suggests the formation of randomly adsorbed structures at low coverages and more ordered structures at higher coverages.

A study of the electrocatalysis of the oxidation of formic acid oxidation by the UPD of lead, bismuth or thallium on polycrystalline platinum has shown that the third body hypothesis is the basis of a satisfactory explanation. It is necessary, however, to take into account the selective UPD of these metals and the uncatalyzed oxidation process on the various crystal planes of platinum [26]. As is well known, the catalytic process is actually the inhibition of the poisoning of the platinum substrate by parallel second order reactions that occur along with the main reaction to produce carbon dioxide. The species formed by these parallel reactions are bonded to more than one platinum site. The presence of another inert species on the electrode surface inhibits the formation of these multiply bonded surface species which can rapidly cover the entire surface and prevent the primary oxidation process. We compared the inhibition of hydrogen adsorption peaks by the various UPD species with the crystallographic plane associated with the peaks characteristic of these planes. This comparison showed that UPD lead, bismuth, thallium, and mercury have little or no selectivity for adsorption on Pt(111), Pt(110) and Pt(100), the principal planes in a polycrystalline platinum surface. Thus they distribute randomly on the various planes and are available to function as a third body on Pt(100) and Pt(110), the planes at which formic acid electrooxidation proceeds most rapidly. However, UPD silver and copper initially adsorb preferentially on Pt(111), which has the least catalytic activity for formic acid electrooxidation, and the multiply bonded adsorbates are free to form on Pt(100) and Pt(110) as if no UPD species were present.

Thick Iodine Films on Platinum

A current-potential curve obtained using a linear voltage scan in solutions containing more than a few millimolar of iodide ions shows a sudden decrease in limiting current for iodide oxidation. The decrease is caused by the precipitation of solid iodine on the electrode surface. We studied this process under potentiostatic conditions [17,21], and the dissolution of the film under open circuit conditions [16] at the RRDE and the SHM RDE. These investigations demonstrated that the film forms and dissolves under solution mass transfer and iodine species film diffusion control. Initially, during the formation of the film, there is little hinderance to the oxidation of iodide ion, but quite suddenly the film changes structure and the rate of oxidation of iodide decreases. We interpret this to represent a compacting of

an initially porous iodine film and that the current limiting process becomes the transport of iodide ion via a Grotthuss-type chain transfer mechanism.

Electrochemical Theory and Techniques

Hydrodynamic Control

In 1972 we first demonstrated the analytical utility of hydrodynamic control of rotation speed at a RDE. Since then we have developed the theory of the method, with a special emphasis on sinusoidal modulation of the rotation speed. During an earlier AFOSR grant period, we developed the theory for a reversible electrode process under conditions of hydrodynamic relaxation and the theory for charge transfer kinetics in the absence of hydrodynamic relaxation.

The theory of hydrodynamic modulation at a rotating disk electrode was extended to the electron transfer and preceding homogeneous reaction cases, taking into account hydrodynamic relaxation [2,3,6]. Use was made of the experimental technique in our UPD and thick film studies. In particular, the formation of thick iodine films on platinum was demonstrated to be totally under mass transfer control. The ultimate thickness of the film can be described in terms of reversible electrode potential for the iodine/iodide couple, the triiodide equilibrium and diffusion of iodide ion through the iodine film.

Hydrodynamic modulation was also applied to the interpretation of the current-potential response of photoelectrochemical cells having "pinned junctions" [18,20]. The approach outlined can, in principle, be used for illuminated, unpinned semiconductor/electrolyte interfaces.

The use of hydrodynamic control in electrochemistry is now generally recognized and was the subject of a symposium held at the Eastern Analytical Symposium in New York City, November 1983.

Primary Resistance of a Ring Electrode

In connection with the interpretation of pseudo-collection effects caused by uncompensated ohmic potential drops at a RRDE, we investigated the primary resistance of a ring electrode. Our initial approach was a numerical one, but we were able to obtain a closed form solution for the problem by using an existing result for the analogous capacitance problem [4].

Uniformly Accessible Electrodes

The problem of identifying what electrode geometries are uniformly accessible, i.e., have constant current density at all points on the electrode surface, is a fundamental one. Uniformly accessible electrodes are highly advantageous because the theoretical treatment of electrode kinetic problems is much simplified. However, experimental restraints can prevent using electrode configurations known to be uniformly accessible, and the literature has examples of modified geometries developed because of such experimental

problems. The question arises for such geometries, and others yet to be proposed, whether uniform accessibility exists. We have outlined a simple approach to deciding this question without solving the convective-diffusion equation for the particular geometry [22], and give the simple geometries that provide uniform accessibility.

Application of Porous Electrode and Membrane Structures

The analytical application of porous electrode structures to trace analysis of aqueous solutions lead to the development of pneumatoamperometric method. In this method a volatile, electroactive solute present in solution is purged from solution using a nonelectroactive gas and the gas stream impinged on the gas phase side of a porous electrode held at potential to electrolyze the electroactive species. If the solute is not volatile, a suitable chemical reaction is carried out to produce a volatile species. This technique has been demonstrated to have nanogram sensitivity, and has been used to determine iodide, iodate, cyanide, arsenic, antimony, tin, osmium, ruthenium and a wide variety of oxidizing agents [9-12,14,15]

Another application of a porous electrode structure was the development of a laboratory demonstration of a miniature sensor capable of detecting gaseous species that are electroinactive because of kinetic reasons, but which can react rapidly with bromine [13]. The configuration used involved a thin layer cell, one face of which was a conventional porous gold electrode supported on porous Teflon and the other face was a fritted glass disk coated with porous platinum. The thin layer was filled with 4.0 molar HBr, and bromine was electrogenerated at constant current at the platinum electrode and then reduced to bromide at the gold electrode whose potential was held on the limiting current for this reduction process. A third, working, electrode behind the fritted disk completed the electrochemical cell. A gas stream, containing a bromine-reactive species such as sulfur dioxide, was impinged on the Teflon membrane. The sulfur dioxide diffuses through the membrane to the gold/solution interface and into solution, reacts with bromine, and thus reduces the current due to bromine reduction at the porous gold electrode. This current decrease is proportional to the sulfur dioxide concentration in the gas phase. The sensitivity of the detector was better than one part per million for sulfur dioxide. Besides providing a miniature sensor (1 cm in diameter and 5 cm long), this work demonstrated the practicality of applying this variation of a constant current coulometric titration to a host of species that are volatile and have been determined by a reagent that can be electrogenerated.

A final example of the use of a porous membrane was the development of a hand-held atmospheric carbon dioxide monitor [21]. This device consists of a thin layer cell, one face of which consists of a porous Teflon membrane. The membrane, on the cell side, has a pair of interdigitated conductance electrodes deposited upon it. The cell is filled with deionized water from a closed loop which passes water on demand through a mixed bed ion exchanger. On exposing the membrane to the atmosphere, carbon dioxide diffuses into the thin layer cell and the conductance increases as a result of the formation of hydronium and bicarbonate ion. Equilibrium is reached in about 16 seconds. A

simple displacement pump is used to replace the water in the thin layer cell when the next determination is required. As configured, the device is temperature compensated in the range 5 to 40 °C, is linear in the range 0 to 100% CO₂, has a sensitivity of 0.01% and a reproducibility of $\pm 0.02\%$, and does not need recalibration for weeks at a time.

Analytical Application of the RRDE

The ring electrode shielding technique was applied to the analysis of solutions containing Ag(I), Bi(III), Cu(II), Ag(I), or Fe(III), and mixtures of Ag(I) and Cu(II) at 0.1 to 1 micromolar concentration levels [5]. Linear scan voltammetry was used at the disk electrode of the RRDE with voltage scan rates in the range 20 to 200 mV/s. At constant ring electrode potential, the ring electrode current response is insensitive to the charging and surface processes currents at the disk electrode, and depends only on the flux of electroactive species reaching it. As the disk electrode potential changes, the flux of a given species reaching the ring electrode changes in a well understood way. Thus plots of ring current vs disk potential have a shape resembling a mirror image of the ideal current-potential at the disk electrode. Very high ring current sensitivities were required in this application, and in order to handle the problem of residual ring current offsetting the current-potential curve, a modification of the conventional dual potentiostat circuitry is given.

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