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Physical electrochemical and electroanalytical studies were undertaken at silver, gold, and platinum electrodes. Underpotential deposition (UPD) studies were undertaken at polycrystalline silver electrodes. Using the electrochemical quartz crystal microbalance, it was shown that Pb(II) species are adsorbed at silver when the Pb(II) exists as an anion in solution. The anionic Pb(II) adsorbate is ultimately reduced to a underpotential Pb(0) with concomitant anion (ligand) expulsion from the electrode surface. Adsorption of sulfide ion (UPD without faradaic charge transfer) also occurs at silver from alkaline sulfide solutions. Three distinct UPD states were identified. The coulostatic formation of UPD Hg(0) at a gold electrode was studied in sulfuric acid using the EQCM. It was found that a monolayer of Hg(0) is formed along with an overlayer of mercury (I) bisulfate. The formation of silver sulfide during the electrooxidation of thioacetamide was established. A theoretical analysis of cathodic stripping peaks based on a hemispherical model with progressive nucleation was performed. The results were used in interpreting inductions times associated with the formation of cathodic stripping peaks at silver electrodes. The uncompensated ohmic potential drop at microelectrodes under steady state diffusion conditions was shown to be susceptible to a theoretical analysis. All microelectrodes under such conditions have the same ohmic potential drop, which was calculated. A very thin rotating electrode was investigated and its behavior characterized and interpreted in terms of existing theory. Studies of modified electrodes were undertaken. A method for determining the current efficiency for the electropolymerization process was developed and confirmed using azulene. The details of ion and neutral species transport on redox switching of polythionine was studied using the EQCM and the mobile species determined in strong acid solutions. Kinetic effects in this system were also studied and it was shown that mass and charge transport are decoupled when the electrode potential changes rapidly.

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FUNDAMENTAL STUDIES OF SURFACE PROCESSES
AND
TRACE ANALYSIS USING SOLID ELECTRODES

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ABSTRACT

Physical electrochemical and electroanalytical studies were undertaken at silver, gold, and platinum electrodes. Underpotential deposition (UPD) studies were undertaken at polycrystalline silver electrodes. Using the electrochemical quartz crystal microbalance, it was shown that Pb(II) species are adsorbed at silver when the Pb(II) exists as an anion in solution. The anionic Pb(II) adsorbate is ultimately reduced to a underpotential Pb(0) with concomitant anion (ligand) expulsion from the electrode surface. Adsorption of sulfide ion (UPD without faradaic charge transfer) also occurs at silver from alkaline sulfide solutions. Three distinct UPD states were identified. The coulostatic formation of UPD Hg(0) at a gold electrode was studied in sulfuric acid using the EQCM. It was found that a monolayer of Hg(0) is formed along with an overlayer of mercury (I) bisulfate. The formation of silver sulfide during the electrooxidation of thioacetamide was established. A theoretical analysis of cathodic stripping peaks based on a hemispherical model with progressive nucleation was performed. The results were used in interpreting inductions times associated with the formation of cathodic stripping peaks at silver electrodes. The uncompensated ohmic potential drop at microelectrodes under steady state diffusion conditions was shown to be susceptible to a theoretical analysis. All microelectrodes under such conditions have the same ohmic potential drop, which was calculated. A very thin rotating electrode was investigated and its behavior characterized and interpreted in terms of existing theory. Studies of modified electrodes were undertaken. A method for determining the current efficiency for the electropolymerization process was developed and confirmed using azulene. The details of ion and neutral species transport on redox switching of polythionine was studies using the EQCM and the mobile species determined in strong acid solutions. Kinetic effects in this system were also studied and it was shown that mass and charge transport are decoupled when the electrode potential changes rapidly.

Keywords: Redox Switching, Polythionine, Kinetics, Electrode Potential. (AW)

RESEARCH COMPLETED UNDER AFOSR SPONSORSHIP

The research undertaken and completed under this grant fell into the areas of physical electrochemistry and electroanalytical chemistry. The completed studies have been categorized below under these headings.

PHYSICAL ELECTROCHEMICAL STUDIES.

Tracking Anion Expulsion During Underpotential Deposition of Lead at Silver Using the Quartz Microbalance. (6). Variations in the electrode mass, charge and pseudocapacitance current have been studied as a function of potential during the underpotential deposition (UPD) of lead at a silver electrode in alkaline solutions. The rotating disk electrode and in situ quartz crystal microbalance (EQCM) techniques were used. New, interesting phenomena have been discovered. Customarily, UPD is ascribed to discharge of dissolved metal ions, and a mass increase would accompany such a UPD process. Surprisingly, a decrease in the weight of the electrode occurred during the entire cathodic process for Pb UPD, rather than an increase in weight that would be expected for a UPD process involving a dissolved Pb(II) species. We found that during the Pb UPD formation process, the entire cathodic charge is transferred to a $Pb(II)_{ads}$ species which is already present on the surface as an adsorbed monolayer. We attribute the observed decrease in mass to OH^- expulsion from the electrode surface. At potentials more negative than the region for Pb UPD formation, an increase in mass not associated with any cathodic current was observed. This mass increase is caused by the adsorption of a Pb(II) species on a Pb-UPD monolayer. Thus, the charge transfer process for formation of an underpotential lead deposit and the increase in electrode mass do not coincide at a silver substrate. A different mechanism is observed for Pb UPD at gold. The combination of EQCM and voltammetric measurements is a powerful means of elucidating UPD mechanisms and tracking expulsion of ligands from the electrode surface.

In Situ Underpotential Deposition Study of Lead on Silver Using the Electrochemical Quartz Crystal Microbalance. Direct Evidence for Pb(II) Adsorption Before Spontaneous Charge Transfer. (10). In situ studies using the electrochemical quartz crystal microbalance (EQCM) have provided unique means for demonstrating the existence of adsorbed anionic lead species at silver and also for tracking anion expulsion during the underpotential deposition (UPD) discharge process. UPD studies of lead(II) at silver were carried out over the pH range 1 to 13. In perchloric acid solutions and acetate buffers, where cations and uncharged Pb(II) species predominate, the UPD process is accompanied by a decrease in electrode mass. This mass decrease is caused by the reduction of adsorbed, negatively charged lead(II) species to UPD Pb(II) and concomitant expulsion of the negatively charged ligand, borate or hydroxide. The potential of zero charge of silver is very negative so that the electrostatic adsorption of anionic lead(II) species is strongly favored, while cationic and uncharged lead(II) species, such as lead acetate, do not adsorb.

Interactions Between Sulfide Ion and Silver Metal. (9). The anodic formation of Ag_2S films at a polycrystalline silver electrode was studied in alkaline solution containing hydrosulfide ion using a rotating ring-disk (RRDE) electrode. We report for the first time on the occurrence of multistate sulfide adsorption (UPD) of sulfide. The total surface coverage in the UPD region is cf. 0.5, which corresponds to an adsorbate have the stoichiometry of Ag_2S_{ads}. Three distinct pairs of oxidation/reduction current peaks were found and are attributed to differences in sulfide adsorption energies at three sites on the silver electrode. Inconsistencies among published reaction mechanisms for silver sulfide formation are discussed.

Induction Time in Stripping Voltammetry at Solid Electrodes. (8). The processes and phenomena causing the appearance of induction times in stripping voltammetry are analyzed. Induction times are observed experimentally at solid electrodes. Two such examples are presented for cathodic stripping voltammetry of phenylthiourea and methylthiourea at silver rotating disk electrodes in alkaline solutions. Induction times are inherent to the formation of deposits via nucleation and growth mechanisms, which are common in stripping voltammetry at solid electrodes. Numerical calculations of the deposition charge (which is directly related to the stripping peak current) as a function of the deposition time have been performed for the hemispherical model with progressive nucleation.

Determination of Hg(I) Adsorption Accompanying the Coulostatic Underpotential Deposition of Mercury on Gold Using the Quartz Crystal Microbalance. (4). Emersion experiments were carried out from 2×10^{-5} M Hg(I) solutions of 0.2 M H_2SO_4 at the gold electrode of a quartz crystal microbalance. Prior to emersion, the gold electrode was open-circuited in this solution and one monolayer, 1.7×10^{-9} g-atom cm^{-2} of underpotential Hg(0) deposited spontaneously by a coulostatic process. Also, 0.29×10^{-9} g-mole cm^{-2} of Hg(I) bisulfate was adsorbed.

Ohmic Potential Drop at Electrodes Exhibiting Steady-state Diffusion Currents. (1). Theory shows that all (micro) electrodes exhibit the same ohmic potential drop provided they are in a steady-state diffusional regime and the cell geometry would yield the electrode's primary resistance. Laplace's equation describes both the steady-state diffusion and the resistance in such electrochemical cells. This experimental situation can be realized using microelectrodes whose dimensions are small enough to obtain diffusional steady-state before natural convection occurs. Expressions are derived for the ohmic potential drop occurring during voltammetry. Two limiting cases are discussed, the electrolysis of a pure binary electrolyte and a binary electrolyte in the presence of a large excess of supporting electrolyte. The results are independent of solvent and the geometry of the microelectrode provided the diffuse double layer is small compared to the diffusion layer thickness.

Interpretation of Polyazulene Electrochemistry Considering the Faradaic Current Efficiency and Capacitive Current Effects During the Growth and Redox Switching Steps. (2). A theoretical analysis of the electropolymerization of polyazulene at a rotating ring-disk electrode is presented. This analysis provides a method for determining the current efficiency of electropolymerization. The oxidation of azulene in polyazulene in acetonitrile as solvent is a convective-diffusion controlled process that proceeds with 100% current efficiency. A positively charged site is associated with at least two non-terminal monomer units in the oxidized form of the polymer. Hydrogen ion has been identified and quantitated as a product of the electropolymerization process. No hydrogen ions are produced by the redox process involving only the polymer film. A theoretical analysis of rotating disk electrode and rotating ring-disk electrode experiments established the advantages and limitations of these purely electrochemical approaches to the study of the growth phase of electropolymerization processes. The results are consistent with the simultaneous production of hydrogen ion and a reduced polymer, and charging the polymer by electrooxidation without producing hydrogen ions. The shift of the halfwave potential during the oxidation of azulene at a polymer coated electrode in the early stages of film growth demonstrates that the mechanism of electropolymerization continues to change until relatively thick polymer films have formed.

Observation of Kinetic Effects During Interfacial Transfer at Redox Polymer Films Using the Quartz Crystal Microbalance. (5). The polythionine system in strong and weak acid solutions exhibits kinetic barriers affecting the transfer of mobile species into and out of the redox polymer film. These effects were studied using the EQCM and are manifested in cyclic voltammetric experiments in two ways. Firstly, the mass-potential curves are sweep rate dependent and secondly the mass-potential curves depend on sweep direction. At sufficiently slow voltage scan rates, limiting shapes of mass-potential curves are obtained. Qualitatively, the behavior may be viewed as resulting from one (or more) kinetic step(s) following electron transfer. Mass and electron transfer are decoupled.

Experimental Observations on Transport Phenomena Accompanying Redox Switching in Polythionine Films Immersed in Strong Acid Solutions (11). Redox switching of polythionine films in strong acid solutions results in film mass changes which are not in agreement with those predicted by a simple permselective mechanism. Notably, the results depend not only upon the specific counter ion and its concentration in the bathing electrolyte, but also on solvent transfer. Whilst solvent transfer is clearly indicated by the data, inclusion of this transfer is insufficient to account for the experimental mass changes. A previous thermodynamic treatment is applied to allow specifically for ion aggregation in the film. Film mass changes, measured using the quartz crystal microbalance, are successfully described in terms of solvent (water) transfer across the polymer/solution interface, and the movement of counter ion (A^-) and hydronium ion (H_3O^+) to form ion pairs ($H_3O^+A^-$) and electrostatically bound net neutral polymer/counter ion aggregates in the polymer phase. Free ions in the polymer film do not contribute significantly to the overall mass change. Permselective behaviour, a sub-set of our treatment, does not apply to the polythionine system in strong acid solutions.

Electroanalytical Studies.

Mechanistic Studies of the Deposition and Cathodic Stripping of Thioacetamide at Solid (Silver) Electrodes. (7). Cathodic stripping experiments of thioacetamide in alkaline solutions, pH = 13, were performed using a rotating silver disk electrode and a silver microelectrode. Applicability of these two electrode system for the determination of thioacetamide over a wide range of concentrations has been found using the stripping peak of bulk silver sulfide. A further improvement of the detection limit is suggested when only an underpotential deposition layer of silver sulfide is formed during deposition. Then cathodic stripping analysis of thioacetamide below 10^{-8} M is feasible. The mechanism for the reactions during the deposition and cathodic stripping of thioacetamide in alkaline media at a silver electrode has been elucidated.

Voltammetry at a Rotating and a Stationary Very Thin Ring Electrode. (3). A very thin ring electrode (VTRE) inlaid in an insulating glass plane was been fabricated and studied. The purpose of this geometry was to increase the current density and attain a higher analytical sensitivity and make possible the determination of faster heterogenous and homogeneous rate constants. Our electrode's inner radius was 4 mm and its width was 0.7 micron. The current-potential and current-time behavior for the reduction of ferricyanide in potassium chloride and iodine in excess iodide were studied at the rotating and the stationary very thin ring electrode. Comparison of the electrochemical data with theory indicated that the ring electrode was approximately 0.3 micrometer below the surface of the insulating plane. This conclusion was verified by means of scanning electron microscopy. A fifteen fold increase in current density as compared to the RDE was attained, and a modelling of the recessed electrode geometry permitted the direct measurement of the rate constant for ferricyanide reduction to ferrocyanide ion.

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All reference a given in the next section entitled **PUBLICATIONS RESULTING FROM AFOSR SPONSORSHIP.**

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PERSONNEL

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Postdoctorals. Dr. C. P. WIlde and Dr. Antonin Trojanek

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