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FUNDAMENTAL SOLID ELECTRODE STUDIES RELATED TO CORROSION PREVEN--ETC(U)
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FINAL REPORT

Fundamental Solid Electrode Studies Related to Corrosion Prevention, Fuel Cells and Batteries

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ABSTRACT

The study of surface phenomena at solid electrodes related to electrochemical power sources and corrosion processes was the major goal of this research. In particular, three kinds of surface processes were investigated: (1) Underpotential metal deposition, (2) neutral species adsorption and (3) insoluble film formation. New electroanalytical and electrochemical techniques were developed specifically for the purpose of studying such surface processes. These techniques made it possible to prepare solutions with extremely low levels of poisoning substances, to distinguish between surface and mass transport controlled processes, and to perform quantitative studies at the micromolar levels of electroactive species that arose in our studies.

Underpotential deposition, UPD, of thallium, mercury and silver on gold have resulted in the determination of accurate adsorption isotherms and highly precise determination of the electrosorption valency, γ. γ-values for silver show a minimum near a surface coverage of 0.5. No minimum has ever been discovered before. We believe that this minimum is caused by either a superlattice phenonema and/or a change in double layer structure. Mercury UPD studies established the existence of a spontaneous coulostatic process that can produce UPD for open circuited metal electrodes.

Carbon monoxide, selected as a model neutral species adsorbate, was shown to exist in a number of adsorbed states on platinum. When adsorbed at very cathodic potentials, a portion of the adsorbate corresponds to a reduced CO species. CO adsorbed at less cathodic potentials can exist

in two forms, the relative amounts of each form depending on the flux of incoming CO. All forms are quantitatively oxidized to CO_2 at anodic potentials. Periodic, or single pulse, oxidation currents can be observed at constant potential.

Model studies of a classic three component dental amalgam (Ag, Hg, Sn) demonstrate that only tin dissolves and that a protective silver chloride film forms. All the mercury remains bound as either a silver or tin solid amalgam. Studies on copper-nickel alloys (100% Cu to 0% Cu) in neutral chloride media showed that copper is selectively leached from a thin surface layer of the alloy and that the rate of corrosion is then determined by rate of dissolution of nickel from the top of this layer.

PROJECT REPORT

The objectives of this research required the development of special experimental techniques and new electrochemical methodologies. These studies were carried out in parallel with the performance of the primary goals of the research. In this report it is convenient to discuss the experimental and methodolical studies before describing the fundamental solid electrode studies.

The preparation of extremely pure supporting electrolytes is vital to solid electrode studies. We investigated, and have used, an electroadsorptive method which proved quite successful. Supporting electrolyte of ordinary purity was passed through a porous electrode bed potentiostatted at an appropriate potential thereby electrolyzing and adsorbing interferring impurities rapidly from a large volume of solution (3). Supporting electrolytes prepared this way were found to poison highly sensitive reactions, e.g., oxygen reduction at platinum, a much slower rate than was ever observed before by us.

In connection with performing computer controlled electrochemical experimental procedures, two versatile and simple electrochemical function generators were developed. One was based on an analog circuitry with simple logic providing the necessary switching (6) while the other was a totally digital device based on an up-down counter and a 16 bit digital to analog converter (5). Both devices function either under computer control or manually, and were used extensively through the research reported below.

The possibility of the production unstable free radical intermediates arose during one of our organic oxidation studies. In order to test this hypothesis we participated in the development of a highly sensitive electrolysis cell designed for in situ generation of radicals in an e.s.r. spectrometer (7). The cell, which possesses cylindrical geometry, is several orders of magnitude more sensitive in its ability to detect radicals then previously reported cells, has almost an ideal electrode geometry for potentiostatic control and works well with water or high resistance organic solvents.

The rotating ring-disk electrode (RRDE) technique was the prinicpal one used by us in our solid electrode studies. Under conditions used to detect the production or consumption of extremely small amounts of intermediates at the disk electrode, uncompensated ohmic potential drops may produce disk electrode and ring electrode currents that differ from conventional RRDE theory. An equivalent circuit for the RRDE system was established (4) and a closed loop, positive feed back bipotentiostat devised which corrected for these interferring phenomena (11). Theoretical and experimental studies of primary resistance phenomena at ring electrodes were also undertaken in order to further elucidate these uncompensated ohmic potential effects. In our original study (10), the mathematical problem was solved numerically, while in a more recent note, a closed form solution confirming our original work was repeated (24).

In another connection, we reported an explicit quadratic solution for determing the diffusion coefficient from rotating disk electrode (RDE) data (9). It is based on Newman's improved treatment of the convective-diffusion problem at the RDE.

A variety of electroanalytical methods were developed for the analysis of micromolar concentration levels in solution. These electroanalytical methods were by-products of the fundamental studies. They included stripping analysis methods at a continuously mercury-coated electrode (2), fundamental and second harmonic alternating voltammetry at the RDE (15) and RRDE shielding techniques (22).

Theoretical and experimental studies of new electrochemical methodologies were undertaken to make it possible to distinguish between convective-diffusion controlled electron transfer and adsorption processes, and convective-diffusion controlled and non-convective diffusion controlled surface processes. In a joint study with John Albery, we treated the response of the ring electrode of a RRDE when applied to a periodic current at the disk (12). Periodic disk electrode control functions give valuable information about adsorption phenenoma.

Using another approach, the angular velocity of an RDE was modulated sinusoidally about a constant center speed, and the corresponding disk current response measured using phase sensitive detection. This approach makes it possible to isolate out very small convective-diffusion controlled currents from larger surface process currents. Various hydrodynamic and electrochemical situations were studied theoretically and verified experimentally. Among these were the fast electron transfer case (8), and the mixed electron and mass transfer case (20,21).

The use of linear scan voltammetry at an RDE and at a RRDE is especially valuable in studying the surface states of electroactive adsorbates, a problem of considerable importance in underpotential deposition studies. The isopotential point methodolgy is based on producing families of current-potential curves having common intersection points (1) using linear scan voltammetry and the theory is analogous to that for spectrophotometric isosbestic points.

Underpotential deposition (UPD) studies included thallium on gold (14), mercury on gold (19), and silver on gold (23). In the thallium studies we found that extensive thallium ion adsorption occurs before UPD of zerovalent thallium takes place. Monolayer coverage occurs very close to the Nernst potential. In the mercury-gold system, monolayer coverage is again reached close to the Nernst potential. In both the thallium and mercury UPD cases, there is no evidence of alloy (amalgam) formation. This result is consistent with the surface energies leading to UPD formation. Migration of the underpotential deposit into the gold substrate does not occur until thicker deposits of thallium or mercury form on the gold substrate.

Our most recent silver UPD study on gold was performed potentiostatically under computer control (23). Extremely accurate charge and coverage data were obtained. A minimum in the electrosorption valency was observed near 50% surface coverage, presumably as a result of a superlattice phenomena. Problems in reaching true equilibrium UPD coverage of Ag were found, and methods for reaching equilibrium coverage (from higher and lower coverage) were established. More than five atom layers of silver must be deposited on gold before the electrode reaches the Nernst potential.

An unsuspected coulostatic process leading to UPD was discovered and investigated. The theory for coulostatic UPD was developed and verified at a gold RRDE for the depostion of Hg(I) on Au (17). The theory for coulostatic UPD in the presence of a simultantious heterogenous chemical process was also developed and verified on Au using Hg(II) for the reactions

$$\mathrm{Hg(II)} + \mathrm{Au} \rightleftarrows \mathrm{Hg\text{-}Au} + \mathrm{Hg(I)}$$

$$\mathrm{Hg(I)} + \mathrm{Au} + e\ (\text{double layer}) = \mathrm{Hg\text{-}Au}$$

(Hg-Au represents UPD mercury) (18). A particularly interesting feature of the Hg(II) system is the observation that when a gold electrode is open-circuited at any potential in the region between gold oxide formation and the Nernst potential, there is an initial potential shift in an anodic direction and then the potential shifts cathodically until the Nernst potential is reached. Both kinds of coulostatic processes have important technological implications since they represent previously unsuspected ways in which a "clean" metal surface may be covered with trace metals present in a solution surrounding the metal. Such UPD deposits can effect electrocatalytic properties of the metal in energy generation or synthetic applications and can also effect corrosion rates of the metal by creating or inhibiting local cells.

Our corrosion studies involved two model systems. The first one involved on a classic dental amalgam (a three phase mixture of Ag_2Hg_3, Sn_{7-8} Hg and Ag_3Sn). It demonstrated that corrosion occurred via formation of soluble tin species and was inhibited by the formation of an insoluble AgCl surface film. All mercury produced by the corrosion process reacted with excess Ag_3Sn phase. This RRDE study should serve as a model for evaluating new dental amalgam formulations. According to J. M. Carter of the SUNY Dental School the RRDE method has considerable advantages over existing methods that are extremely tedious, and take months to yield the equivalent information.

Our corrosion studies of copper-nickel alloys over their entire range of composition in neutral chloride media clearly demonstrated that corrosion proceeded in two stages. Initially, the fresh alloy surface undergoes selective leaching of copper, which dissolves almost reversibly, until a nickel-rich layer forms. This layer has many defects (is "porous"). Since the nickel layer inhibits further copper corrosion, the alloy corrodes at a rate determined by the kinetics of the oxidation of the nickel surface. The thickness of the nickel-rich layer is determined by the rate of transport of copper from the bulk of alloy to the solution/alloy interface.

Our studies involving carbon monoxide were undertaken for two reasons. CO is a classic poison for hydrogen fuel cell electrode at low temperatures. Second CO adsorbtion on platinum and its electrochemistry while adsorbed is of fundamental electrochemical interest because CO represents the simplest carbon containing molecule showing activity on platinum. There is a considerable literature on this subject, but still many unanswered questions. In our first study in acid media, we used electrochemical mass spectroscopy to demonstrate the stoichiometry of CO absorption and hydrogen inhibition, and to prove the formation of a reduced CO species that required 3 electrons/mole to form CO_2 (13). In most recent study we have observed, in acid media, the presence of oscillatory currents under potentiostatic conditions, the existance of a fairly stable limiting current at the RDE in dilute CO solutions, rather than the rapidly poisoned currents seen at high concentration, and

As a result of our carbon monoxide studies, conditions were found that permitted a stable and light weight carbon monoxide detector to be constructed. A patent has been issued (see Project Patent section) and has been assigned to the United States Government.

CONCLUSIONS

Solid electrode studies using modern electrochemical methodologies are well suited to answering fundamental scientific questions relating to electrical energy production and storage, and metal corrosion. Major problems common to both technologies require a detailed understanding of the metal (conductor)/solution interface. The interfacial electrochemical studies completed in this project have successfully dealt with 1) understanding corrosion phenomena in a homogeneous alloy and a three phase alloy, 2) determining surface coverages and associated changes in surface charges during the underpotential deposition of three different metals on a gold substrate 3) examining the nature of adsorbed CO at platinum, and 4) developing new methodologies and diagnostic criteria of general usefulness in understanding metal/solution interfaces.

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PROJECT PATENTS

Name of Inventor	Title of Invention	Patent Application Serial Number	Patent Issued On
Stanley Bruckenstein and William G. Sherwood	Electrochemical gas monitor	USP 4,057,478	8 November 1977

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