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TYCO LABORATORIES, INC.

BEAR HILL, WALTHAM 54, MASSACHUSETTS
AREA CODE 617
TELEPHONE 899-1650

438821

ELECTROCHEMISTRY OF FUEL CELL ELECTRODES

by

A. C. Makrides
Principal Investigator

Semi-Annual Technical Summary Report
covering period through March 30, 1964

Contract No. Nonr-3765(00)
dated April 16, 1962
as amended
expiring April 15, 1965

ARPA ORDER No. 302-62
Project Code 9800
Task No. NR 359-443

prepared for:
OFFICE OF NAVAL RESEARCH
Materials Sciences Division
Washington 25, D. C.

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I. INTRODUCTION

The objective of this program is to clarify the molecular basis of electrocatalysis and thereby to provide the necessary scientific framework for the optimization of fuel cell electrodes. Using electrodes of varied chemical composition, we have attempted to show whether their catalytic properties depend primarily upon the intrinsic chemical activity of the individual surface atoms, or upon the energy states of the crystal as a whole. If this distinction can be made, and if quantitative correlations with the atomic or continuum properties can be established, then the design of fuel cell electrodes becomes enormously simplified.

Hydrogen oxidation and reduction, the reduction of oxygen, and the oxidation of formic acid, a soluble organic substance, have been selected for these studies because of their relevance to fuel cell systems and because of their relative simplicity. The electrodes used range from amalgams to III-V semiconducting compounds. The approach is to resolve the over-all reaction on any given electrode into the elementary steps of adsorption, electron transfer, chemical combination of free radicals, etc. , and to determine how the parameters governing the rates of these various steps are related to the electrode composition and structure. The experimental studies currently under way are described below.

II. ELECTROCATALYSIS BY AMALGAM ELECTRODES

The question of whether the continuum properties or the atomic nature of an electrode determines its electrocatalytic properties can be approached directly by using amalgam electrodes. The high overpotential for the hydrogen evolution reaction on mercury makes it easy to detect the effect of catalytic additives. A clean, reproducible surface can be achieved with liquid amalgams by using a dropping electrode; thus, this technique was adopted in our studies.

The first systems investigated were Pt-Hg and Pd-Hg. The results of these studies are given briefly in the last quarterly report and are reported in Technical Memorandum No. 7. It was found that Pt and Pd in solution in Hg have substantially different catalytic properties than bulk Pt and Pd; it was concluded that electrocatalysis in this particular system is primarily a cooperative property and that the behavior of a metal atom is drastically influenced by its environment.

The In-Hg system was investigated in some detail during the past six months (Technical Memoranda No. 9 and 10). This particular system had the advantage of a wide solubility range (up to 70 at % In at room temperature). Three types of studies were carried out: a) thermodynamic data (activities) for In-Hg were obtained by emf measurements, b) the kinetics of the hydrogen reaction on In-Hg amalgams and on pure In were studied, and c) the double layer structure on In-Hg amalgams was studied by capacity measurements.

Activity coefficients for indium and mercury in their liquid amalgams at 25°C were calculated from measurements of emf in a cell without liquid junctions. Within experimental error, the results were described by the empirical equation $\log_{10} \gamma_{\text{In}} = 1.54 (1 - X_{\text{Hg}})^2$, where γ_{In} is the activity coefficient of In referred to infinite dilution, and X_{Hg} is the mole fraction of mercury. The activity of pure solid indium is 21.6 on the same scale. The excess entropy of the mixtures was found to be nearly zero. The standard potential of the $\text{In}^{+3} - \text{In}$ couple was -335.0 mv at 25°C.

The rate of the hydrogen evolution reaction was studied on dropping indium amalgam electrodes containing 0 to 65% In in 0.1 M HClO₄ at 25°C. The potential of zero charge for the same series of amalgams was also determined. The Frumkin correction for the potential drop across the diffuse double layer was used to obtain the exchange current and transfer coefficient for each of the amalgams. The exchange current increased by approximately a factor of ten as the composition varied from 0 to 65% In. Within experimental error the transfer coefficient was 0.50, independent of composition. The current at the zero-charge potential, which gives a measure of the free energy of activation for the discharge reaction, increases by a factor of 10⁴ as the composition varies from 0 to 65% In. The corresponding decrease in the free energy of activation is approximately 5 kcal/mol, and is attributed primarily to a change of work function.

Capacity measurements were also obtained for these amalgams over the same concentration range in 0.1 M HClO₄. These measurements are being extended to LiF and HCl solutions. The results will be analyzed when they are complete.

Measurements of the hydrogen overpotential on pure In, including temperature coefficients, were also carried out and will be reported as soon as they are analyzed in detail.

III. ELECTROCHEMISTRY OF III-V SEMICONDUCTING COMPOUNDS

Binary compounds crystallizing in the zincblende or wurtzite structures show two (111) surfaces of different composition. In the case of GaAs, opposite (111) surfaces are composed only of Ga atoms or As atoms. This property of III-V compounds permits the study of the electrocatalytic activity of two chemically different surfaces of the same crystal.

It was found that p-type and n-type gallium arsenide behave anodically in the same way as p- and n-type germanium; the anodic current on n-type material reaches a limiting current which is controlled by the diffusion of holes from the bulk of the semiconductor; the anodic current on p-type material increases with potential until a surface oxide is formed.

The dissolution behavior of p-type gallium arsenide and p-type gallium antimonide indicates the formation, at positive potential, of arsenic and antimony surface oxides.

Current-potential measurements on the gallium surfaces of n- and p-type gallium arsenide and p-type gallium antimonide are very close, and, at high overpotentials, very similar to measurements on pure gallium.

Current-potential curves on the antimony surfaces of gallium and indium antimonide are very nearly the same, and differ only by about 60 mv from those on the gallium surface. The overpotentials on the antimony surfaces are, however, higher than on pure antimony by some 150 mv.

IV. OXYGEN REDUCTION AND OXIDE FORMATION

Most metals form stable surface oxides in the potential range where oxygen can be reduced. Therefore, a study of the electrochemical properties of surface oxides is a necessary step in any detailed study of the mechanism of oxygen reduction.

A study of the galvanostatic reduction in N HClO₄ of gold surface oxides formed potentiostatically at various potentials was completed (Technical Memorandum No. 6) during the report period. Oxides formed at 1.2 to 1.8 v vs. H⁺/H₂ were reduced at current densities varying between 10 and 1000 a/cm² in molar perchlorate solutions of pH 0.04 to 2.1. It was found that the extent of oxide formation is determined by the potential of anodization, the charge increasing linearly with the potential of formation in the range of 1.4 to 1.8 v. Cathodic chronopotentiograms showed that the reduction of the oxide occurs at a definite potential which depends on the cathodic current density. Current-potential curves, constructed from the cathodic chronopotentiograms, followed a Tafel relation with a slope of 41 mv. The exchange current for oxide reduction decreased with pH and with increasing potential of formation of the oxide. The electrochemical order of the reaction was 1.4 with respect to pH. These results were interpreted in terms of a reaction scheme in which the reduction of an intermediate (Au⁺²) is the slow step in the over-all process.

Some studies of "aging" of potentiostatically-formed oxides have also been carried out during this period. Both galvanostatic and voltammetric reduction techniques were employed. It was found that although the oxide grows very rapidly (viz. 95% of its final, steady-state thickness in 1 sec), its reduction characteristics continued to change appreciably over long periods. Some changes are still observable 5 min. after formation. The origin of these changes is not clear at present.

Further experiments with this system showed that certain cations in solution, viz. Mg⁺², considerably alter the kinetics of reduction of the oxide; however, the amount of oxide at any given potential is essentially unaltered. These effects are probably associated with cation adsorption which modifies the double layer structure.

V. ELECTROCATALYTIC OXIDATION OF FORMIC ACID

The adsorption and oxidation of formic acid on smooth Pt electrodes was studied in HClO_4 solutions by anodic and cathodic chronopotentiometry and by potentiostatic, steady-state techniques (Technical Memorandum No 8). The oxidation rate at each potential was determined as a function of electrode preparation, pH, and formic acid concentration. Anodic pre-treatment activates an electrode for the subsequent oxidation of HCOOH . However, the oxidation rate at any given potential declines with time because of the slow adsorption of a substance which interferes with the subsequent oxidation of HCOOH . The kinetics of adsorption and the extent of adsorption of the blocking substance were determined at a series of potentials. The equilibrium adsorption decreases with potential above 0.35 v and is essentially zero at 0.70 v.

The rate of oxidation of HCOOH is first order with respect to the free surface, the HCOOH concentration, and the pH. The oxidation rate increases with potential according to a Tafel type relation (slope ~ 60 mv) up to potentials of about 0.4 v, but is independent of potential thereafter. The current plateau is not controlled by diffusion. A mechanism for oxidation is suggested in which the slow step is a non-electrochemical, dissociative reaction of HCOOH .

Currently, an experimental study of large anodic galvanostatic transients is in progress in order to identify the poisoning adsorbate on the electrode. This study involves the reversal of the current during oxidation of the adsorbate, which makes it possible to determine how much of the current passed is effective in oxidizing adsorbed material and how much goes in side processes. The side processes are oxidation of the electrode itself and oxidation of unadsorbed formic acid diffusing to the electrode surface.

Present results show a clean separation of these processes. Thus, at low current densities ($\sim 8 \text{ ma/cm}^2$ in 1 M HCOOH), oxidation of adsorbed material predominates at first and, later, oxidation of formic acid diffusing to the interface makes a contribution. The oxidation of the

electrode is, however, considerably retarded. At higher current densities, oxidation of adsorbed material again predominates at first but later oxidation of the electrode itself makes a significant contribution to the current. Oxidation of formic acid diffusing to the electrode is relatively minor.

Using this technique, one finds that for every site (the number of sites was determined from hydrogen adsorption) two electrons are required to oxidize anodically the adsorbed material. The maximum sorption of the blocking substance corresponds to between 300 and 350 $\mu\text{c}/\text{cm}^2$ of anodic charge (depending on what assumption one makes for the relation between real and apparent area). Studies of the over-all adsorption process are being continued and comparison with the behavior of other compounds is planned.

VI. TECHNICAL MEMORANDA AND PUBLICATIONS

The following technical memoranda were issued during this report period:

Technical Memorandum No. 6: "Surface Oxidation of Gold", accepted by the Journal of the Electrochemical Society.

Technical Memorandum No. 7: "Hydrogen Evolution at Dilute Platinum and Palladium Amalgam Electrodes", accepted by Transactions of the Faraday Society.

Technical Memorandum No. 8: "Adsorption and Oxidation of HCOOH on Smooth Pt Electrodes in HClO₄ Solutions", accepted by Journal of Physical Chemistry.

Technical Memorandum No. 9: "Activity Coefficients of Liquid Indium-Mercury Amalgams at 25°C", accepted by Journal of Physical Chemistry.

Technical Memorandum No. 10: "Hydrogen Evolution at a Dropping Indium Amalgam Electrode", submitted to Transactions of the Faraday Society.

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