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ELECTROCHEMISTRY OF FUEL CELL ELECTRODES

by
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Semi-Annual Technical Summary Report
covering period through March 30, 1965

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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, were 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 overall 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. A detailed analysis of the factors affecting hydrogen overvoltage requires measurements of double-layer capacity, activity coefficients, temperature dependence of hydrogen overvoltage, work function, and interfacial tension.

During this report period, the studies of hydrogen overvoltage and double layer capacity on indium and thallium amalgams have been completed. Studies of the interface structure indium amalgams and electrolytes, and the relation of electronic properties of the electrode to the parameters of the hydrogen evolution reaction, have been continued with studies of interfacial tension and work function. The results of some of this work have been presented in Technical Memoranda Nos. 16, 17, and 18, and are summarized below. We have also summarized the work in progress, which will be reported in future technical memoranda.

Double Layer Capacity of Thallium Amalgams

Measurements of double-layer capacity and zero charge potential have been made on 10, 30, and 40% thallium amalgams. These results have been compared with existing literature data. The integrated capacity curves agree with literature values for experimental electrocapillary curves. The surface concentration of thallium, at potentials where overvoltage measurements have been made, is one half to three-fourths of the bulk concentration. In contrast to results reported in the literature, the double-layer capacity of 40% thallium amalgam shows no dependence on frequency, within experimental error in the range from 0.5 kc to 10 kc. This work was reported in detail in Technical Memorandum No. 16.

Hydrogen Overvoltage on Thallium Amalgams

Measurements have been made of hydrogen overvoltage, in 0.1 M $HC10_4$, at temperatures from 14° to 69°C, at dropping amalgam electrodes containing 10.0 and 40.6 mole percent thallium. The overvoltage is 20 to 30 millivolts higher on 40% thallium amalgam than on mercury. When corrections are made for the effect of the diffuse double layer, the exchange current for hydrogen discharge at 25°C is found to decrease by a factor of 2 on going from mercury to 40% thallium amalgam. The temperature dependence of overvoltage gives an enthalpy of activation (extrapolated to the reversible hydrogen potential) of 22.3 ± 0.4, 21.2 ± 1.1, and 23.1 ± 0.3 kcal/mole for mercury, 10% thallium amalgam, and 40% thallium amalgam respectively. Thus, both the overvoltage and the enthalpy of activation are higher on thallium amalgams than on mercury. This work was reported in detail in Technical Memorandum No. 17.

Hydrogen Overvoltage on Indium Amalgams

Hydrogen overvoltage has been measured at temperatures from 14°C to 66°C, using dropping amalgam electrodes containing 10.0, 20.0, 40.0, and 63.0 mole % indium. The enthalpy of activation was extrapolated to the reversible potential, and corrected for the effect of the diffuse double layer. For the most concentrated amalgams, it is approximately 1 kcal/mole lower than for mercury. This change is consistent with the decrease in overvoltage with increasing indium content at constant temperature. This work was reported in detail in Technical Memorandum No. 18.

Interfacial Tension of Indium Amalgams

A method has been developed for determining interfacial tension by fitting a theoretical curve to the experimentally measured shape of a sessile drop. A computer program is used to generate solutions to the non-linear differential equation describing the drop shape. Absolute measurements of interfacial tension for amalgams containing up to 64 mole % indium were made in 0.1 M $HC10_4$ at 25°C. These were combined with previously measured values of zero charge potentials and differential capacity, to generate a family of electrocapillary curves from which the surface excess was calculated using the Gibbs equation. The surface excess is negative, and passes through a maximum negative value at approximately 20 mole % indium. The parameters of the hydrogen evolution reaction on indium amalgams correlate with the bulk electronic properties of the amalgams, but not with the surface composition. This work is summarized in Technical Memorandum No. 19, which will be issued in [illegible], 1965.

Adsorption of Ions on Indium Amalgams

Measurements have been made of the zero charge potential and double layer capacity on indium amalgams in fluoride solutions. These results have been compared with our previous measurements in perchloric acid (Technical Memorandum No. 15). The specific adsorption of these ions depends strongly on the concentration of indium in the amalgam. In contrast to mercury, the fluoride ion is more strongly adsorbed than is the perchlorate ion; this difference is greatest at the highest indium concentrations. These data are presently being analyzed in detail. When measurements of interfacial tension in fluoride solutions have been completed, this work will be summarized in a technical memorandum.

Electronic Work Function of Indium Amalgams

One of the most important electronic properties of an electrode in its influence on electrocatalysis is the electronic work function. For thirty years, electrochemists have used a correlation between zero charge potential and work function which is based on data which may be in error by more than 0.1 volt. The indium-mercury system offers the possibility of examining this relation with an accuracy of ± 0.005 volts over a potential range of nearly 0.5 volts, which is half the accessible range of work functions. From this relation, information can be obtained about the orientation of water molecules at the electrode-electrolyte interface, a factor which is very important in determining the rate of electrocatalytic reactions.

Preliminary experiments using the ionization method for determining the contact potential difference between mercury and the amalgams indicated that superficial oxide films must be completely eliminated in order to obtain accurate measurements. Because of additional uncertainties due to short term changes in the work function of the reference electrode used in the contact potential measurement, and the necessity in any case for constructing a high-vacuum system to prevent oxide formation, we have decided to measure the work function photoelectrically. The main advantage of this technique is that it is an absolute measurement.

The vacuum system for preparing the amalgams and for measuring the photocurrent has been built and tested. Both systems can be evacuated to 10^{-8} torr in about three hours with no bakeout. A 1000 w mercury-Zenon lamp, together with a quartz monochromator, will provide the illumination. The light intensity will be monitored by a photo-multiplier, calibrated with a thermopile, and the photocurrent will be measured using an electrometer with a sensitivity of 10^{-13} amp. By preparing the amalgams under a high vacuum, and by gettering the residual oxygen in the system before measurements, it should be possible to maintain an oxygen-free surface for sufficient time to measure the photo-current over a range of wavelengths. From this data, an absolute value of the work function can be calculated for each of a series of indium amalgams.

III. TECHNICAL MEMORANDA AND PUBLICATIONS

Of the memoranda listed in the previous semi-annual report, the following have appeared in print:

1. "Surface Oxidation of Gold", by S. B. Brummer and A. C. Makrides, J. Electrochem. Soc. 111, 1122-1128 (1964) (Tech. Mem. No. 6)

2. "Hydrogen Evolution at a Dropping Indium Amalgam Electrode", by J. N. Butler and A. C. Makrides, Trans. Faraday Soc., 60, 1664-1676 (1964) (Tech. Mem. No. 10)

3. "Hydrogen Evolution at a Solid Indium Electrode", by J. N. Butler and M. Dienst, J. Electrochem. Soc., 112, 226-232 (1965) (Tech. Mem. No. 11)

4. "The Use of Large Anodic Galvanostatic Transients to Evaluate the Maximum Adsorption on Pt from HCOOH Solutions", by S. B. Brummer, J. Phys. Chem. 69, 562-571 (1965) (Tech. Mem. No. 13)

Thus, all Technical Memoranda through No. 13 have appeared in print with the exception of No. 12, which described a computer program for double layer calculations.

The following have been accepted for publication, and are in press:

Technical Memorandum No. 14: (a) "Galvanostatic Studies of Carbon Monoxide Adsorption on Platinum Electrodes", by S. B. Brummer and J. I. Ford, J. Phys. Chem.; (b) "Comparison of Adsorbed Formic Acid and Carbon Monoxide on Platinum Electrodes", by S. B. Brummer, J. Phys. Chem.

Technical Memorandum No. 15: "The Electrical Double-Layer on Indium Amalgam Electrodes", by J. N. Butler, M. L. Meehan, and A. C. Makrides, J. Electroanal. Chem.

The following Technical Memoranda were issued during this report period.

Technical Memorandum No. 16: "The Electrical Double Layer on Thallium Amalgam Electrodes", by J. N. Butler, accepted by J. Electroanal. Chem.

Technical Memorandum No. 17: "Hydrogen Overvoltage at a Dropping Thallium Amalgam Electrode", by J. N. Butler, E. A. Barron-Apps, and M. L. Meehan, submitted to Trans. Faraday Soc.

Technical Memorandum No. 18: "Temperature Dependence of Hydrogen Overvoltage on Indium Amalgams," by J. N. Butler and M. L. Meehan, submitted to Trans. Faraday Soc.

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