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Final Report
Grant AFOSR-151-63

A Study of the Kinetics and Mechanism
of Electrolytic Film Formation Reactions

November 1, 1962 through October 31, 1964

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Principal Investigator: C. G. Enke

C. G. Enke

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Completed Project Summary
AIR FORCE GRANT AFOSR-151-63

1. Title: A Study of the Kinetics and Mechanism of Electrolytic Film Formation Reactions.
2. Principal Investigator: Professor C. G. Enke
3. Inclusive Dates: November 1, 1962 through October 31, 1964.
4. Grant Number: AFOSR-151-63
6. Senior Research Personnel: none beside the principal investigator.
7. Junior Research Personnel:

Assistants in Research:

Mr. Louis Ramaley

Mr. Ronald Brubaker

Mr. G. D. Robbins

In addition the research of Mr. Michael Vasile and Mr. William Weir was supported by the Grant though they received no salary from the Grant.

8. Publications:

1. Mercury-coated Platinum Electrodes, Ramaley, Brubaker, and Enke, Anal. Chem. 35, 1088 (1963).
2. A Versatile Triangular Sweep Generator, Weir and Enke, Rev. Sci. Inst., 35, 833 (1964).
3. The Preparation and Thermodynamic Properties of a Palladium-Hydrogen Electrode, Vasile and Enke, J. Electrochem. Soc., August, 1965.
4. Instrumentation for the Measurement of the Electrical Double-Layer Capacitance at Solid Electrodes, Ramaley and Enke, accepted for publication in J. Electrochem. Soc.
5. The Double-Layer Capacitance of Silver in Perchlorate Solution, Ramaley and Enke, accepted for publication in J. Electrochem. Soc.

9. Abstract of Objectives and Accomplishments:

The study of surfaces is becoming increasingly important. Many times more is known about the bulk properties of chemical materials than is known of their surfaces. The surface of a material must be quite different from the interior chemically because surface atoms or molecules cannot be bonded to similar material on all sides. A large fraction of chemical reactions of industrial importance take place on surfaces, e.g. catalytic reactions, plating reactions, etc., and the state of the surface is known to have a profound effect on the course and rate of the reaction.

Most of the tools and techniques that have been recently developed for surface study are measurements made in a vacuum and are not suited to the study of surfaces under practical reaction conditions. The long range objective of this research was to develop electrochemical tools for studying the electrode-electrolyte interface and to apply them to systems of interest. Electrochemical techniques are particularly promising for the study of conducting surfaces because a change of a small fraction of a small surface can result in an easily detectable change in capacitance or surface charge.

A triangular sweep generator was designed and constructed for use with potential sweeping experiments. This instrument has the advantages of controlling the sweep rate and the positive and negative sweep limits independently. The palladium-hydrogen electrode was studied to investigate its use as a superior reference electrode, in this research, to the platinum-hydrogen electrode. The procedure for making suitable palladium-hydrogen reference electrodes was established and, in addition, the thermodynamic properties and the potential-composition curve for the palladium-hydrogen system were obtained. The Pd-H reference electrode has been very useful.

Two new techniques for the measurement of double-layer capacitance at solid

electrodes were developed. One is particularly useful in obtaining capacitance values over a wide potential range rapidly and/or as a function of time. Impurity absorption effects are obvious and minimized. The other technique gives quick qualitative information on the effect of the measuring frequency on the measured value of the double-layer capacitance. As a result of this work, a new model for the frequency effect has been proposed.

Capacitance measurements as a function of frequency, potential, time, and pH were made on silver electrodes in perchlorate solutions. Silver is shown to behave quite similarly to mercury in its capacitive behavior.

During the course of the research on platinum surface oxides (Air Force Contract AF 49(638)-467) a method of wetting a platinum surface with liquid mercury was discovered. This discovery has led to many interesting applications of solid-supported mercury surfaces in this laboratory and others. An investigation of the wetting process was carried out under this grant. The basis of the wetting action is shown to be an intermetallic compound formed of platinum and mercury at the interface between the two metals.

Final Report on Grant AFOSR-151-63

Period Covered: November 1, 1962 through October 31, 1964

This grant was a renewal of the contract AF 49(638)-973 which ran for the two years previous to the period of this report. Included in this report are results and publications of several projects begun during the previous contract period and concluded during the period of this report.

Mr. William Weir held an NSF Fellowship and thus received no salary from the grant. Much of his equipment and supplies were, however, provided by this grant. During this period he completed the design of a triangular sweep generator which was needed for potential sweep studies of film formation reactions. The resulting instrument produces a symmetric or asymmetric triangular waveform of high quality with sweep rates continuously variable from 5 mV/sec to 2000 V/sec, independent of amplitude; positive and negative sweep limits are independently variable from 0-3 V relative to a reference level which is itself variable with respect to signal ground. Provision is made for controlling the output voltage at a preset level prior to initiation of the sweep, and the sense of the initial sweep may be selected. The cyclic sweep may be halted at either limit, either mechanically or electronically. An auxiliary output provides a square wave with peak-to-peak amplitude equal to the peak-to-peak amplitude of the triangular waveform, based at signal ground, and with period regulated by the sweep rate controls.

A copy of the reprint describing this instrument is attached to this report.

The electrochemical potential of the palladium - hydrogen system was studied by Mr. Michael Vasile, who held various fellowships and received no salary from the grant. He measured the potential of a palladium - hydrogen electrode as a function of the composition of the electrode, temperature, and pH. The objective of these studies was to prepare a palladium - hydrogen reference electrode which could be used in hydrogen free solutions. The potential was found to be a function of the

electrode composition in the α phase, and β phase, and independent of composition in the $\alpha + \beta$ phase region. Equations were derived from fundamental thermodynamics which fit the potential vs. composition data in the α phase and in the $\alpha + \beta$ phase region, as well as the temperature dependence observed. A good procedure for preparing a palladium - hydrogen reference electrode was developed.

A copy of the manuscript describing this work which was submitted to the Journal of the Electrochemical Society and which will be published there in the August, 1965 issue, is attached to this report. Reprints will be sent when they are available.

Mr. Louis Ramaley developed two new methods for the measurement of double-layer capacitance at solid electrodes and applied these techniques to measurements of silver electrodes. One method, involving the application of a rectangular current waveform, is convenient for obtaining qualitative information on the frequency dispersion of the double-layer capacitance. The other, involving the application of a small sinusoidally varying potential of constant amplitude, is capable of an accurate and very rapid determination of capacitance over a wide potential range. A copy of the manuscript describing these techniques which has been accepted for publication in the Journal of the Electrochemical Society is attached to this report. Reprints will be sent when they are available.

The electrical double-layer capacitance of silver was studied in 1 N sodium perchlorate solutions as a function of pH, method of surface preparation, and electrode potential. The results suggest that the double-layer structure on silver and mercury may be very similar. A model explaining the frequency dispersion of double-layer capacitance on solid electrodes is proposed, and qualitative substantiating evidence is given. Attached to this report is a copy of a manuscript describing these measurements. It has been accepted for publication in the Journal of the Electrochemical Society and reprints will be sent when they are available.

During the course of the research on platinum surface oxides (Air Force Contract AF 49(638)-467) a method of wetting a platinum surface with liquid mercury was discovered. A communication describing this discovery was published in the July 1963 issue of Analytical Chemistry. A reprint of the communication is attached to this report. This discovery has led to many interesting applications of solid-supported mercury surfaces in this laboratory and others.

Mr. Ronald Brubaker, who worked on the data for the communication mentioned above, went on to study the mechanism of the wetting process. His thesis work shows that an intermetallic compound is formed between the mercury and the platinum. When the mercury covered platinum electrode is made sufficiently anodic, the mercury dissolves into the solution. When all the mercury metal has dissolved, the mercury in the Hg-Pt compound will begin to dissolve, but a more anodic potential is required. By measuring the coulombs required to dissolve the Hg coating and the Hg from the compound for various preparations and pretreatments, an estimate of the rate of compound formation was obtained.

In addition, Mr. Brubaker investigated the use of the mercury coated platinum electrodes for polarography and anodic stripping voltammetry. A rotating electrode configuration was found which gave reproducible results, had linear response, and was extremely sensitive. Mr. Brubaker's thesis is currently in the final draft stage and a copy of it will be submitted as soon as it is available. The manuscript and reprints from the anticipated publication of this work will also be submitted when available.

In summary, during the period of this grant, a new instrument was developed and two new techniques for double-layer measurements were developed and applied to silver electrodes with valuable results. The Pd-H electrode was analyzed both practically and theoretically, and a method for mercury-coating platinum was discovered, explained, and found to be of great practical value. The entire research effort of four graduate students was supported over the period of the grant.

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13 ABSTRACT A summary is presented of an investigation on the development of electrochemical tools for studying the electrode-electrolyte interface and on their application to systems of interest. A triangular sweep generator was designed and constructed for use with potential sweeping experiments, and the palladium-hydrogen electrode was studied. Two new techniques for the measurement of double-layer capacitance at solid electrodes were also developed. Capacitance measurements were made on silver electrodes in perchlorate solutions, and a method of wetting a platinum surface with liquid mercury was discovered. (U)		

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