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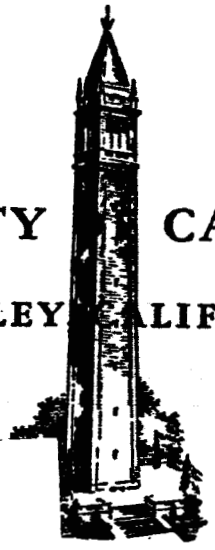

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Semiannual Status Report on

DYNAMIC BEHAVIOR OF POROUS ELECTRODE SYSTEMS

by

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STATUS REPORT FOR PERIOD 1 MARCH 1964 TO 31 AUGUST 1964
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This report covers status of the investigation, Dynamic Behavior of Porous Electrode Systems, during the six-month period of NASA Research Grant NsG-150-61. The work is being conducted in the Department of Chemical Engineering, University of California, Berkeley, under the direction of Professor Charles W. Tobias. The progress of the investigation during this period, direction of future research efforts, expenditures incurred, and personnel involved are reported herein.

I. Progress of Investigation

During the period covered by this report measurements of current distribution in micro-fissure electrodes and preliminary experiments for determinations of effect of structure changes on current distribution in sintered porous metal electrodes have been undertaken. The influence of electrode reaction kinetics on the effective overpotential of flooded porous electrodes has been investigated by an extensive computational program.

A. Micro-fissure Single Pore Electrode Measurements

A series of steady state and transient measurements of current distribution have been conducted in the micro-fissure single pore cell described previously[1], but with electrode depth reduced to 0.28 cm as described in the last semiannual report. These experiments utilized the ferri-ferrocyanide redox reaction (0.1N $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$) in approximately 2N NaOH at 25°C.

Fissure widths over the range of 50-200 microns were employed, and current densities ranging from 2 to 100 ma/cm^2 pore cross section were investigated at steady state. The steady state distributions observed agreed quite well with results predicted by earlier theoretical studies carried out under this project[2]. An improved circuit for balancing potentials among the electrode segments has reduced the severity of the anomalous currents in certain electrode sections which was mentioned in the last report.

Transient current distributions have been investigated for the micro-fissure cell for a fissure width of 200 microns using the same electrolyte as for the steady state experiments.

Current densities of 2 and 4 ma/cm^2 pore cross section were used. The nonuniformity of observed current distributions initially increased quite rapidly (following starting of a specified constant current) and then more slowly over transient periods of 10-30 min. This behavior follows quite closely that predicted by previously mentioned theoretical methods except for some irregular fluctuations in segment currents during the first few seconds of each run.

B. Effect of Changes in Electrode Mixture upon Reaction Distribution

The equipment for measurement of local rates of anodic dissolution of porous sintered metal electrodes has been constructed and preliminary experiments conducted with porous copper electrodes. Well defined mass transfer conditions exterior to the test electrode are maintained by mounting the electrode in the wall of a closed channel through which the electrolyte flows under conditions assuring well developed turbulence. A buffer electrode is provided upstream of the test piece to form a mass transport boundary layer which changes but little over the test section. Examination of electrodes reacted in this system shows that satisfactorily uniform conditions are maintained over their surface.

C. Influence of Electrode Reaction Kinetics on Polarization of Flooded Porous Electrodes

The influence of the electrode reaction kinetic representation used in calculation of the effective overpotential of a flooded porous electrode has been critically examined. Using the computational methods developed earlier in this project[2] the effects of variations of the parameters in a Volmer type kinetic expressions, and those of using limiting linear and Tafel approximations to this expression, were investigated. Polarization curves predicted by earlier and cruder mathematical models for porous electrodes were compared to the present results, illustrating the discrepancies in calculated polarizations that can be attributed to the far reaching simplifying assumptions of this previous work (e.g., assumption of uniform electrolyte composition). This study is described in some detail in the accompanying preprint of a manuscript submitted for publication[3].

II. Direction of Research Effort for September 1964 - March 1965

At the present time, series of experiments determining distribution of reaction during anodic dissolution of porous copper electrodes in H_2SO_4 and silver electrodes in nitrate solutions are in progress. Superficial current densities up to 500 ma/cm^2 will be investigated and duration of current passage varied to trace the entire course of the reaction up to the point of complete dissolution of the material at the face of the electrode.

In the near future two new sequences of measurements will be undertaken with the micro-fissure single pore cell: one involving transients at smaller fissure widths than heretofore studied; the other investigating steady state current distributions in the presence of a flow of electrolyte through the fissure toward the bulk solution at rates sufficient to insure uniformity of electrolyte composition in the fissure.

III. Expenditures

Unexpended funds from this grant as of October 27, 1964, amount to [redacted]. It is anticipated that this amount will be spent, and the grant period terminated, sometime in December 1964.

IV. Personnel

The personnel involved in this investigation at present consists of the principal investigator; a faculty investigator, Professor Edward A. Grens II; a M.S. student, Mr. Richard Alkire; and a laboratory assistant, Mr. Yuya Ogiwara. Dr. Rolf Müller continues in a consulting capacity (receives no compensation).

V. Attendance of Scientific Meetings

Professor Charles W. Tobias attended the meetings of the Electrochemical Society in Toronto, May, and in Washington, October, 1964.

VI. References

1. Müller, R. H., Interim Technical Report II, NASA NsG-150-61, February 1963.

2. Grens, E. A., and Tobias, C. W., Berichte der Bunsengesellschaft fur Physikalishe Chemie 68, 236 (1964).
3. Grens, E. A., and Tobias, C. W., "The Influence of Electrode Reaction Kinetics on the Polarization of Flooded Porous Electrodes", (preprint of paper submitted for publication) 1964.