STUDY OF SYNCHROTRON RADIATION FROM WET ELECTRODE SURFACES(U) IBM RESEARCH LAB SAN JOSE CA L BLUM ET AL 30 SEP 85 N00014-81-C-0776
MICROCOPY RESOLUTION TEST CHART
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OFFICE OF NAVAL RESEARCH

PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS REPORT

for

1 October 1984 through 30 September 1985

for

OFFICE OF NAVAL RESEARCH
CONTRACT N0014-C-0776
TASK NO. NR 051-775

STUDY OF SYNCHROTRON RADIATION FROM WET ELECTRODE SURFACES

PRINCIPAL INVESTIGATORS:

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Part I

A. Papers Submitted

1. Fluorescence Detected Surface EXAFS (FDSEXAFS) of Iodine on Platinum: *In Situ* Structural Characterization of an Electrochemical Interface.

   J. Am. Chem. Soc.


   M. L. Rosinberg, L. Blum and J. L. Lebowitz  


   P. T. Cummings and L. Blum  


   L. Blum, C. Caccamo and G. Pizzimenti  
   J. Phys. Chem.

B. Papers Published in Refereed Journals


C. Books in Print


D. Books Published

No books published.

E-F. Patents

No patents filed or granted.

G. Invited conferences

L. Blum, The Electric Double Layer
University of Southampton, Sept. 30, 1984

L. Blum, Analytic Studies of the Electric Double Layer
NBS Gaithersburg, June 10, 1985

J. Gordon, "Weighing the Electrode Surface - The Oscillating Quartz Microbalance,"

Part II

A. Funding History

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<td>October 1, 1981 - September 30, 1982</td>
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B. Current Telephone Numbers

Lesser Blum (809) 763-3390
Joseph Gordon (408) 256-1266

C. Description

The purpose of the project is to probe the structure of the charged liquid:solid interface using synchrotron radiation. The initial experiment is to measure the EXAFS spectrum of a halide on a flat metallic electrode surface. By obtaining the EXAFS spectrum as a function of potential, we should be able to determine the extent of adsorption and how the surface structure changes with coverage. In addition, the theory of progressively more realistic models of the charged interface is being studied:

2. A model for the structure of water with sticky-directional forces is proposed. This model has the correct structure of liquid water and should be more realistic than hard spheres with point dipoles.

3. A model of the charged interface with discrete adsorption sites: In particular, we can solve exactly the one component plasma in two dimensions.

D. Results

Experiment

During 1984-85, we had one run a the Cornell High Energy Synchrotron Source (CHESS) and, taking advantage of the high energy radiation available at CHESS, studied the adsorption of Iodine on Platinum. Using a grazing incidence geometry and fluorescence detection, surface EXAFS of a monolayer of iodine adsorbed on Platinum (111) single crystals was detected. Although the near edge structure was rather noisy, it produced a clearly resolved peak in the Fourier transformed corresponding to an I-Pt distance of \( \sim 2.5 \) Å. (This is a preliminary distance subject revision upon further refinements.) These results demonstrate the feasibility of in situ structural study of electrochemical interfaces using EXAFS.

Theory

In collaboration with the group at Messina, we performed extensive calculations to test the Born-Green-Yvon theory for the primitive (continuum dielectric solvent). We used the most accurate bulk pair correlation functions available, and got very good agreement with computer simulations at high concentrations (up to 2M). For concentrations up to 4M we observe charge layering effects near the electrode walls.

A model with a hard core, a point dipole and a sticky interaction of water was studied. This model reproduces the nearest neighbor, structure of liquid water, and was solved analytically in the Perius - Yevick approximation.

Finally we have also studied a model with sticky lattice sites, which mimics a realistic surface. Exact contact relations can be derived for the average adsorbed density. A two dimensional model has also been solved exactly.

E. Summary of Plans

Experiment

We expect run again at CHESS in November '85 and summer '86 when we will acquire better EXAFS data on the I-Pt system and also examine I on Ag. Beam time will be requested from SSRL (Stanford) for a run in spring '86 to re-examine Br and Pb on Ag. (Competition for beam time at SSRL is intense because of the reduced running schedule which has resulted from their budgetary restrictions.) We also hope to schedule a grazing incidence x-ray diffraction experiment at SSRL or Brookhaven in 1986, in collaboration with groups from LBL or Oak Ridge, respectively.
Theory

We will pursue our effort to get a simple, yet accurate equation for the primitive model which could be used for the ion-dipole mixture and also for the more advanced sticky models.

We intend also to address the problem of the polarizable membrane in which one of the sides is a quantum mechanical system (jellium).

F. Graduate Students

For the next year, two graduate students will participate in the project.

1. Mr. Samuel Torres
2. Mr. Manuel Quijada

Post-doctorals

We expect one post-doc, as yet unknown, to participate.