Progress Report on Department of Energy grant DE-FG02-91ER45455,
"Theoretical Study of Reactions at the Electrode-Electrolyte Interface"

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ABSTRACT

In this project, electron transfer rates are predicted by numerical methods, in a collaboration with Argonne National Laboratory . Emphasis is on electron transfer involving ions known to be important in enhancing stress corrosion cracking in light water reactors and on electron transfer at oxide surfaces. In the report period, we have produced a new theory for description of the Jahn Teller effect in the solvation shell of the cuprous ion in aqueous solution, have implemented it in a molecular dynamics simulation and compared the results with experimental neutron scattering measurements on solutions containing the cuprous ion. A large amount of numerical data has been collected on the transition state of the ferrous ferric electron transfer reaction at an electrode. Work was completed on a polarizable and dissociable model of water for use in the electron transfer studies. New calculations of the conductivity in models of oxides have shown the existence of impurity conduction bands in such models for the first time. The principal investigator organized and edited the proceedings for the first Symposium on Microscopic Models of the Electrode-Electrolyte Interface, held at the Toronto meeting of the Electrochemistry Society in October, 1992 and including lead speaker Rudy Marcus (Nobel prize, 1992 for work in theory of electron transfer).

The objective of this work is to calculate electron transfer rates at electrode electrolyte interfaces with emphasis on electron transfer involving ions known to be important in enhancing stress corrosion cracking in light water reactors. We collaborate with quantum chemist Larry Curtiss and experimental electrochemist Zoltan Nagy of Argonne National Laboratory in this work. The role of the Minnesota group is to provide large scale molecular dynamics and electronic structure calculations and overall guidance in physical theory to the effort. Previous to the grant period on which we report here, the results of a study of the ferrous-ferric electron transfer reaction were completed and reported in 1. In the report period, we continued studies on the characterization of the transition state in the ferrous-ferric transition. The transition state studies of the ferrous-ferric problem were outlined in the proposal for this grant. We obtained a special computation grant from Cray Research for continuation of this work and have accumulated data on more than 200 configurations of water molecules in the presence of a ferric ion for a detailed study of the microscopic nature of the transition state. The study is currently continued by Dr. Barton Smith(see

personnel listing below.)

The experimental program at Argonne has undertaken a study of electron transfer from the cuprous ion to an electrode. This ion is specifically implicated in the stress corrosion cracking studies which motivate the entire program. We have made major progress on the study of the cuprous ion, in preparation to interpret experiments on the electron transfer reaction to a cuprous ion in solution, which are now under way at Argonne. The main problem which differentiates the cuprous ion problem from the ferric-ferrous one is the reported existence of a Jahn Teller effect in the solvation shell of the cuprous ion in aqueous solution. To understand this we discovered that a rexamination of the conceptual basis for defining a Jahn Teller effect in the solvation shell of an ion in solution was required. The resulting picture is described in a recent publication in Physical Review Letters[2] where a molecular dyanmics model and calculated results from it are also reported. A second paper[3] describes a comparison of calculations from the molecular dynamics model with neutron scattering experiments. The conclusion is that, unfortunately, the experimental evidence for observation of a Jahn Teller effect in this ion is not conclusive and we are currently exploring other possible explanations for the observations, including the possibility of ion pairing. Xiang Rong Wang worked on this problem while he was a post- doctoral associate with the group from 1990-92.

Our studies of the effects of the dynamics of the solvation shell of dissolved ions on the electron transfer process depend heavily on the reliability of our molecular dynamics model of water. Recently we completed work on a new molecular dynamics model for water, in which the water molecules are both polarizable and dissociable[4] and have begun work to study the behavior of the solvation shell of the cuprous ion in this model. Other exciting possibilities emerge as a result of the existence of this model, including microscopic studies of reactions involving "protons" (hydronium) and hydroxyl groups in water.

A better understanding of the electronic structure of the disordered oxides characteristic of electrode surfaces is required in order to characterize electron transfer at such surfaces. Aspects of our earlier work on oxides, specifically titanium dioxide, are summarized in a paper[5] in which results of our calculations are used to interpret photoelectrochemical studies of TiO_2 films on titanium electrodes by workers at the Corrosion Center at the University of Minnesota. In this work, we proposed a reinterpretation of photocurrent measurements which had previously been interpreted to suggest that the energy gap in the titanium dioxide had been widened by the existence of disorder in the film. Instead, the calculations show that the gap observed is the gap of bulk titanium dioxide. We expect that states inside the gap should be present due to donors arising from oxygen vacancies but these are not seen in the photoconductivity measurement. We understood this by a later calculation of the conductivity[6] which shows that the mobility gap which is observed in the photoconductivity experiments is not expected to shift at the low vacancy concentrations present, because the donor states associated with the vacancies are localized until they begin to percolate at significantly higher concentrations. (Earlier work on the frequency dependence of the conductivity in disordered conductors was published in Physical Review

Letters. [7]) Our numerical methods for these calculations are innovative, and a detailed description of our code for titanium dioxide has been accepted for publication in Computer Physics Communications[8] . In related work supported by other sources, we have used also used these equation of motion methods to study an innovative model for the origin of high temperature superconductivity, in which oxygen vacancies in the cuprate planes play a key role [9-13] . The synergy between these two programs has been very useful and significant.

During the grant period, the principal investigator co-organized and co-edited (with L. Blum) the proceedings for the first Symposium on Microscopic Models of the Electrode-Electrolyte Interface, held at the Toronto meeting of the Electrochemistry Society in October, 1992. There have been very few meetings devoted exclusively to modeling of this interface, and this one was very successful, lasting three full days and attracting more than 20 invited speakers including 10 from Europe on a very modest budget that did not permit full travel costs to be paid. Sessions were held on electron transfer, solvent structure, ion solvation, electronic structure of the electrode and on fractal aspects associated with rough surfaces. The lead speaker for the symposium was Professor Rudy Marcus and during that same session on electron transfer, Professor Marcus learned through a telephone call from Sweden that he had won the 1992 Nobel prize for his work on electron transfer.

References

1. L. A. Curtiss, J. W. Halley, J. Hautman, N. C. Hung, Z. Nagy, Y. -J. Rhee and R. M . Yonco, Journ. of the Electrochemical Society, 138, 2032 (1991)
2. L. Curtiss, J. W. Halley and X. R. Wang) Physical Review Letters 69, 2435 (1992)
3. J. W. Halley, X. R. Wang and L. Curtiss, proceedings of the Symposium on Microscopic Models of the Electrode-Electrolyte Interface, Toronto ECS meeting , 1992
4. J. W. Halley, J. Rustad and A. Rahman, submitted to J. Chem. Phys.
5. J. W. Halley, M. Kozlowski, M. Michalewicz, W. Smyrl and N. Tit) Surface Science 256, 397 (1991)
6. N. Tit, J. W. Halley, M. Michalewicz and H. Shore in Proceedings of the 6th International Conference on Solid Films and Surfaces (in press)
7. H. Shore and J. W. Halley, Physical Review Letters 66, 205 (1991)
8. M. Michalewicz, H. Shore, N. Tit and J. W. Halley, Computer Physics Communications (in press)
9. J. W. Halley, C. Das Gupta, S. Davis and X-F. Wang, Proceedings of the VIIth International Conference on Many Body Physics, Plenum Press (in press)
10. J. W. Halley, X-F Wang and S. Davis, Physical Review B46, 6560 (1992)
11. J. W. Halley, S.Davis, R. Joynt and P. Samsel, Bulletin of Materials Science (India) 14, 1069 (1991)
12. J. W. Halley, S. Davis and X-F Wang), proceedings of Conference on Condensed Matter Theories, Puerto Rico, June, 1992 (in press)

13. C. Dasgupta and J. W. Halley , Rapid Comm. of Physical Review B (in press)

Personnel during the grant period:

Nacir Tit, graduate student. Ph. D. December, 1991. Electronic Structure of Oxides. Present position: Postdoctoral Associate at International Center for Theoretical Physics, Trieste, Italy.

James Rustad, Postdoctoral Associate 1990-91, Ph. D. 1991 from University of Minnesota. Dissociable model of water. Present position: Pacific Northwest Laboratories.

Xiao Fang Wang, Postdoctoral Associate, 1990-92. Ph. D. 1990 from Columbia University, models of high temperature superconductivity. Presently at Rutgers University.

Xiang Rong Wang, Postdoctoral Associate 1990-92. Ph. D. 1990 from University of Rochester. Jahn-Teller effect in the solvation shell of dissolved ions. Minnesota Supercomputer Institute Fellow. Present position: Assistant professor, Hong Kong University of Science and Technology.

Barton Smith, Postdoctoral Associate 1992-... . Ph. D. 1989 from the University of Colorado. Microscopic studies of the transition state.

Naiching Yu, Postdoctoral Associate 1992-..., Ph. D. 1992 from the University of Virginia. Electronic structure of oxides.

Larry Curtiss, collaborator, Argonne National Laboratory.

Herbert Shore, collaborator, San Diego State University,

Chandan Dasgupta, collaborator, Institute of Science, Bangalore ,India.

Publications during this grant period:

1. "Photoelectrochemical Spectroscopy Studies of Anodic Oxides on Titanium: Theory and Experiment", (with M. Kozlowski, M. Michalewicz, W. Smyrl and N. Tit) Surface Science 256, 397 (1991).

2. "Electronic Properties of Disordered TiO_2 Surfaces: Application of the Equation of Motion Method" (with N. Tit and M. Michalewicz) , Surface and Interface Analysis 18, 87 (1992).

3. "Scaling of the Insulator to Superconductor Transition in Ultrathin Amorphous Bi Films" (with Y. Liu, A. McGreer, B. Nease, D. B. Haviland, G. Martinez, and A. M. Goldman), Phys. Rev. Letters 67, 2068 (1991)

4. "Point defect Disorder in Models of High Temperature Superconductivity" (with C. Das Gupta, S. Davis and X-F. Wang) Proceedings of the VIIth International Conference on Many Body Physics, Plenum Press (in press)

5. " Rare-Earth-Iron-Boron Materials in Industrial Applications", in Semiconductors and Rare Earth Based Materials, World Scientific Pub. , Singapore (1991), p.347

6. "Comparison of the Koster-Slater and the Equation of Motion Method for Calculation of the Electronic Structure of Defects in Compound Semiconductors" (with N. Tit), Phys. Rev. B 45, 5887 (1992)

7. "Water Penetration in Glassy Polymers: Experiment and Theory". (with M. Best, B. Johnson and J. L. Valles), Journ. of Applied Polymer Science (in press)

8. "Equation of Motion Method for the Electronic Structure of Disordered Oxides" (with M. Michalewicz, H. Shore and N. Tit), Computer Physics Communications (in press)

9. "Mean Field Calculations of the Properties of the Dilute tJ Model for High T_c Superconductivity" (with X-F Wang and S. Davis), Physical Review B46, 6560 (1992)

10. " Jahn-Teller Effect in Liquids: General Principles and a Molecular Dynamics Simulation of the Cupric Ion in Water" (with L. Curtiss and X. R. Wang) Physical Review Letters 69, 2435 (1992)

11. "Phase Diagram of the Two Dimensional Disordered Hubbard Model in the Hartree-Fock Approximation", (with C. Dasgupta), Rapid Comm. of Physical Review B (in press)

12. "Mean Field Predictions of the Dilute tJ Model for High Temperature Superconductivity" (with S. Davis and X-F Wang), proceedings of conference on Condensed Matter Theories, Puerto Rico, June, 1992 (in press).

13. "Role of Oxygen Vacancies in Anodic TiO_2 Thin Films" (with N. Tit and H. Shore) in Proceedings of the 6th International Conference on Solid Films and Surfaces (in press).

14. " A Polarizable, Dissociating Molecular Dynamics Model for Liquid Water" (with J. R. Rustad and A Rahman) submitted to J. Chem. Phys.

Invited Talks During the Grant Period:

VIIth International Conference on Many Body Physics,Minneapolis, August 1991.

DOE Corrosion Contractors Meeting, Brookhaven, September 1991.

St. John's University, March 1992.

Michigan Technical University, April 1992.

National Association of Corrosion Engineers, Nashville, April, 1992.

Conference on Condensed Matter Theories, Puerto Rico, June, 1992 .

DOE Corrosion Contractors Meeting, September 1992.

Symposium on the Electrode-Electrolyte Interface, Electrochemical Society, Toronto, October 1992.

Other Federal Support

DOE grant DE-FG02-88ER45338, "Modeling and Experimental Studies of Oxide Covered Metal Surfaces, TiO_2 on Ti: A Model System. 11/1/87-10/31/92. Support for the JWH in the last year was limited to one month of summer salary.

NSF/EAR-9117278 "Collaborative Research: Computational Studies of Thermodynamic and Electrostatic Properties of Water" 2/15/92- 1/31/94(with D. Yuen). Salary for J. Rustad and 2 weeks summer salary.

NASA "The Condensate Fraction in Liquid Helium Droplets" 1/1/93-12/31/95, $270,000 for one PI and 3 Co-PI's. This grant was just awarded.

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