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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 completed studies of the ferrous-ferric electron transfer rate in which the effects of electric field, entropic effects in the free energy and quantum effects are included for the first time in the calculation of the rate of an electrochemical (heterogeneous) reaction rate. These new results confirm assumptions made in our earlier calculations. The ferric ion has been modelled in a dissociable polarizable model showing for the first time that, as we suggested earlier, the six fold coordination of this ion in aqueous solution is stabilized by the three body interactions arising from the polarizability of water. In our studies of oxides, we have completed a Hartree self consistent calculation of the electronic structure of fayalite. The calculation utilizes a new method which takes phenomenological account of local electron correlations which have plagued electronic structure calculations of oxides for a long time. No electronic structure calculation of fayalite has been previously reported to our knowledge. Similar methods have been used to calculate the electronic structure of a vacancy in rutile (TiO_2). The results show for the first time that the screening donor electrons are anisotropically distributed around the vacancy.

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 ferrous-ferric transition. We have utilized a new molecular dynamics model which takes full account of the electric field from the electrode (using a method developed by us earlier[2]) and employing new algorithms to compute the free energy barriers. In this way we include entropic and electric field effects in

a much more realistic way than in our earlier simulations[1] . The results confirm the validity of our earlier approximations, but also provide new results. We show that the free energy barrier is a quadratic in the reaction coordinate as we assumed earlier and as in Marcus theory, but that the curvature is a function of electric field, unlike our earlier assumption or Marcus theory. The model provides a quantitative estimate of the equilibrium potential for the reaction for the first time in this kind of a simulation. The result is within about a factor of 2 of the experimentally observed equilibrium potential.

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 [3] . During the period of this report we have, in collaboration with J. Rustad, incorporated a ferric ion in this model. The results show that the effects of polarizability stabilize the six-fold coordination of the ferric ion in water as we suggested earlier [4-5] and provide a basis for studying the effects of water polarizability on the electron transfer process.

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 cupric ion, described in a recent publication in Physical Review Letters[6] where a molecular dyanmics model and calculated results from it are also reported. A second paper[7] 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. An invited review of work on the Jahn Teller effect in liquids is in preparation [8].

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[9] 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. A later calculation of the conductivity [10-12] showed 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. A detailed description of the innovative code used in this work appeared recently[13]. During the reporting period, we have developed Hartree self consistent calculations within tight binding models for several oxides. We have made a study of the relative efficiency of proposed Hartree self consistent methods using equation of motion techniques and direct exact matrix diagonalization methods. Depending on the method of implementation, the

computational effort associated with the equation of motion method scales with N or with N^2 while the computation associated with exact diagonalization scales as a higher power of N, where N is the number of orbitals in the basis. At large enough N the equation of motion methods will therefore be more efficient. However we find that the coefficients in the scaling relations are such that the crossover occurs at about 10^4 orbitals, which is somewhat larger than current computational resources can feasibly consider. Accordingly, for the present time we are using exact diagonalization methods for the Hartree studies. We have completed a study of a single oxygen vacancy in rutile. In this system and also in a study of iron oxides to be described below, we take account of local correlation effects, known to have large qualitative effects on electronic structure in transition metal oxides, by a new phenomenological method which makes use of experimental ionization potentials for isolated ions. By this means we find that the self consistent potential around the oxygen vacancy in rutile is of very short but finite range (as we had assumed earlier [14-15]) but also that the potential is very anisotropic, as we had not previously suspected. Using similar methods we have developed band structures of fayalite and wustite, both expected to be important in the passivation of iron.

Several papers on our related work on a model for high temperature superconductivity appeared recently [16-18] . The synergy between these two programs has been very useful and significant.

During the grant period, 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 appeared[19]. 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. Three papers in this volume were coauthored by the PI.

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Personnel during the grant period:

Nacir Tit, collaborator, International Center for Theoretical Physics, Trieste, Italy.

James Rustad, Collaborator, Pacific Northwest Laboratories

X. R. Wang, collaborator, 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.

Naichang 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. "Phase Diagram of the Two Dimensional Disordered Hubbard Model in the Hartree-Fock Approximation", (with C. Dasgupta), Rapid Comm. of Physical Review B47, 1126 (1993).

2. "Mean Field Predictions of the Dilute tJ Model for High Temperature Superconductiv-

ity" (with J. W. Halley, S. Davis and X-F Wang), Condensed Matter Theories, Vol. 8, L. Blum and F. B. Malik, eds. p. 71 (1993),

3. "Role of Oxygen Vacancies in Anodic TiO_2 Thin Films" (with N. Tit ,M. Michalewicz and H. Shore) Applied Surface Science 65-6, 246 (1993)

4. "A Polarizable, Dissociating Molecular Dynamics Model for Liquid Water" (with J. R. Rustad and A. Rahman), J. Chem. Phys. 98, 4110 (1993)

5. "Jahn Teller Effect of Cations in Water: The Cupric Ion in Water", (with X. R. Wang and L. Curtiss), in "Models of the Electrode Electrolyte Interface", ,Electrochemistry Society Proceedings volume 93-5, J.W. Halley and L. Blum eds., The Electrochemical Society, Pennington, N.J. p. 42 (1993)

6. "Calculations of Electronic and Atomic Structure of the Electrode-Electrolyte Interface", (with D. Price), in "Models of the Electrode Electrolyte Interface", Electrochemistry Society Proceedings volume 93-5, J.W. Halley and L. Blum eds., The Electrochemical Society, Pennington, N.J. p. 255 (1993)

7. "Model for the Effects of Phase Separation on Corrosion of Zinc-Nickel Coatings of Steel", , in "Models of the Electrode Electrolyte Interface", Electrochemistry Society Proceedings volume 93-5, J.W. Halley and L. Blum eds., The Electrochemical Society, Pennington, N.J. p. 306 (1993)

8. " Possibility of 2 Types of Localized States in A 2-Dimensional Disorde red Lattice"(with N. Tit, N. Kumar and H. Shore) Physical Review B 47, 15988 (1993)

9. "Calculation of Inelastic Light Scattering Spectrum in the Two Body Approximation", (with M. Korth and A. J. Wissink), Phys. Rev. B48, 7399 (1993).

10.""New Approach to the Observation of the Condensate Fraction in Superfluid Helium Four", (with C. E. Campbell, C. F. Giese and K. Goetz), Physical Review Letters, October 11, 1993.

11."Structure of the Condensate in Helium Four and Some Possible Ways to Observe It", Journal of Low Temperature Physics, December, 1993.

12." A Novel Approach to the Observation of the Condensate Fraction In Superfluid Helium Four" , Physica (in press)

13."Theoretical Analysis of an Experiment to Measure the Condensate Fraction in Superfluid Helium Four" (with C. E. Campbell) Physica (in press)

14."Invariance of the Mobility Edge in Anodic Titanium Oxides" (with N. Tit and H. B. Shore) Int'l Journal of Modern Physics B7, 361 (1993)

Invited Talks During the Grant Period:

Jet Propulsion Laboratory, February 1993

San Diego State University, April 1993

UC Berkeley, May 1993

Almaden Research Center, IBM, June 1993

LT20 Satellite Conference, Minneapolis, August 1993

International Low Temperature Conference, Eugene, OR, August 1993

DOE Corrosion Contractors Meeting, Golden Colorado, September 1993.

Kansas State University, Manhattan, October 1993

NASA Contractors meeting, January 1994

Many Body Theory meeting, Texas A & M, January 1994

Microgravity meeting, Wash. D. C., January 1994

AIAA meeting, January 1994.

Other Federal Support

NASA "The Condensate Fraction in Liquid Helium Droplets" 1/1/93-12/31/95, $270,000 for one PI (JWH) and 3 Co-PI's.

DOE "Modelling of Transport in Lithium Polymer Electrolytes for Battery Applications" DE-FG02-93ER14376,9/15/93-9/14/96, $286,800

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