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

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ABSTRACT

In this project, reaction rates were predicted by numerical methods, in a collaboration with Argonne National Laboratory . Emphasis is on electron transfer and transport involving ions known to be important in enhancing stress corrosion cracking in light water reactors and on electron transfer at oxide surfaces. In the latter part of the grant period we placed increased emphasis on development and use of self consistent tight binding methods for this kind of study. We showed that by careful fitting of results from first principles plane wave calculations,we could model surfaces and interfaces oxides and metals using these methods. We obtained results for the titanium/titanium oxide interface in this way and completed a model of the ruthenium dioxide surface using our innovative self consistent tight binding molecular dynamics methods. We completed development of a description of liquid water within the self consistent tight binding context and studied the rutile water 110 interface to determine if it is hydroxylated. A self consistent tight binding study of titanium metal surfaces demonstrated the usefulness of this method for metals. In collaboration with the Argonne group, we extended the tight binding calculations on rutile titania to the anatase form and made the first calculations of the relative stability of anatase and rutile as a function of crystallite size. We completed studies of small anatase particles in water using the method and found significant distortions of nanoparticle crystallite shapes as a consequence of interactions with the water.

The objective of this work was to calculate reaction 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 collaborated with quantum chemist Larry Curtiss and the experimental x ray diffraction group headed by Hoydoo You 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. We studied the ferrous-ferric electron transfer rate [1]. More recently we studied the cuprous-cupric electron transfer reaction [2]We found that the reaction was adiabatic, unlike our prediction for the ferrous-ferric one. We also undertook a study of the capacitance of the copper water interface, using new direct dynamics molecular dynamics methods in which the electronic structure of the electrode is treated by first principles plane wave methods[3]. A major conclusion is that the electric fields at the interface are much more strongly screened by the electrons of the metal than was allowed in earlier theoretical models.

In the study of oxides, our newly developed self consistent tight binding methods[4–5] include crystal field effects and are explicitly fit to first principles calculations of bulk

rutile by the Chelikowsky group here at Minnesota[6] . The results give excellent values for the work functions of low index rutile surfaces and very reasonable numbers for the surface energies and surface relaxation of low index surfaces[7]. The molecular dynamics version of this code was used to study the structure of polarons in rutile as a function of temperature for the first time [8]. We demonstrated that it is also possible to make realistic representations of the electronic and atomic structure of metallic surfaces using these self consistent tight binding molecular dynamics methods and studied titanium surfaces [9] and titanium-titanium dioxide interfaces [10, 11] . The method was also extended to magnetic systems and we showed[12]that it could be used to predict complex magnetic spin structures.

To study water oxide interfaces, we completed development of a self consistent tight binding molecular dynamics code for water. We made studies of water on ruthenium dioxide for which there are significant corrosion applications[13]. Results for water water on the 110 surface of rutile titania including investigations of the dependence of wetting on the stoichiometry of the surface are reported in references14-16.

Studies of nanoparticles of titania were carried out using SCTB methods and were consistent with the experimentally observed anatase to rutile transition as a function of crystallite size[17]. Calculations of anatase nanoparticles in water[18] showed quite dramatic effects of the water on the nanoparticle morphology.

Work in collaboration with J. Bording of Brookhaven to model cuprate high temperature superconductors using SCTB methods continues.

In related work, we collaborated with workers at Pacific Northwest Laboratories on simulations of iron-oxide water interfaces [19–20]

References

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11.P. Schelling and J. W. Halley in "Solid Liquid Interface; Theory" J. W. Halley, ed. ACS publications (2001) p.142

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15.J. W. Halley, Y. Duan, K. Lidke, A. Wynveen and M. Zhuang, in Condensed Matter Theories Volume 17, M. P. Das and F. Green, editors, Nova Science Publishers, NY (2003) p. 257

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17.A. S. Barnard, S. Erdin, Y. Lin, P. Zapol and J. W. Halley, Phys. Rev. B 73, 205405 (2006)

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19.J. R. Rustad, B. P. Hay and J. W. Halley, Journ. Chem. Phys. 102, 427 (1995)

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. B. P. Hay and J. W. Halley, Surface Science 385, 217 (1997).

Personnel during the grant period:

Barton Smith, postdoctoral associate 1992-94

Naichang Yu, postdoctoral associate 1992-94

Yu Zhou, 1995-97

Alain Mazzolo, 1996-98

Sean Walgran, Ph. D. 1999

James Rustad, collaborator, Pacific Northwest Laboratories

Larry Curtiss, collaborator, Argonne National Laboratory.

Jan Bording, collaborator, Brookhaven National Laboratory.

Min Zhuang, postdoctoral associate, 2000-2002, self consistent tight binding studies of magnetic oxides and the oxide-metal interface.

Serkan Erdin, postdoctoral associate 2002-2005, metal-vacuum and metal oxide interface.

Patrick Schelling, graduate student, 1995-1999, Ph. D. 1999, tight binding models of oxides,currently associate professor of physics and University of Central Florida

You Lin, graduate student, electronic structure of oxides, 2001-2005, Ph. D. 2005. SCTB simulations of water on oxides, currently post-doctoral associate at University of Southern Florida.

Weilin Zhang, graduate student, multiscale modeling of stress corrosion cracking, 2002-2008

Relevant Publication during this grant period:

"Dynamical Properties of the Anderson Localization Model in the Short-Time Critical Regime" (with H. Shore) Physical Review Letters 66, 205 (1991)

"Temperature Dependence of the Heterogeneous Ferrous/Ferric Electron Transfer Reaction: Comparison of Experiment and Theory", (with L. A. Curtiss, J. Hautman, N. C. Hung, Z. Nagy, Y. -J. Rhee and R. M . Yonco), Journ. of the Electrochemical Society, 138, 2032 (1991)

"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)

"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)

"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)

"Equation of Motion Method for the Electronic Structure of Disordered Oxides" (with M. Michalewicz, H. Shore and N. Tit), Computer Physics Communications 71, 722(1992)

" 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)

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

"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)

"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)

"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)

" 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)

"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)

"Simulation Study of the ferrous-ferric electron transfer at a metal- aqueous electrolyte interface" with B. Smith, J. Chem. Phys. 101, 10915 (1994)

"Molecular dynamics simulation of iron(III) and its hydrolysis products in aqueous solution" (with J. R. Rustad and B. P. Hay), Journ. Chem. Phys. 102, 427 (1995)

"Electronic Structure of the Passivation Layer: New Computational Methods and Results" (with N. Yu) Materials Science Forum 185-188, 389 (1995)

"Jahn Teller Effect of Molecular Complexes in Liquid Solutions" (with X. R. Wang) Modern Physics Letters B8, 1319 (1994)

" Electronic Structure of Point Defects in Rutile" (with N. Yu) Phys. Rev. B51, 4768 (1995)

"Studies of the Interdependence of Electronic and Atomic Dynamics and Structure at the Electrode-Electrolyte Interface", Electrochimica Acta 41, 2229 (1996)

"Molecular Dynamics Calculation of the Cuprous-Cupric Electron Transfer Reaction at a Copper-Water Interface" (with S. Walbran and B. Smith) Proceedings of the Conference Electron and Ion Transfer in Condensed Media, Theoretical Physics for Reaction Kinetics, A. A. Kornyshev, M. Tosi and J. Ulstrup, eds, World Scientific, Signapore (1997) p. 212

"Ewald Methods for polarisable Surfaces with Application to Hydroxylation and Hydrogen Bonding on the 012 and 001 Surfaces of α-Fe_2O_3", E. Wasserman J. R. Rustad A. R. Felmy . B. P. Hay and J. W. Halley, Surface Science 385, 217 (1997).

"What New Models Reveal About the Meaning of Grahame's Capacitance Data" (with A. Mazzolo, S. Walbran and D. L. Price) in " The Electrochemical Double Layer " C. Korzeniewski and B.E. Conway, The Electrochemical Society, Pennington, NJ, Proceedings Volume 97-17 (1997) p. 33

"Molecular Dynamics/Electronic Structure Calculations of the Metal-Electrolyte Interface" (with D. L. Price) in " The Electrochemical Double Layer " C. Korzeniewski and B.E. Conway, The Electrochemical Society, Pennington, NJ, Proceedings Volume 97-17 (1997) p. 47

"Molecular Dynamics Study of the Cu-Water Interface in the Presence of Chlorine" (with Y. Zhou, A. Mazzolo, D.L. Price) International Journal of Thermophysics 19, 663 (1998)

"First Principles Simulations of the Electrode- Electrolyte Interface" (with A. Mazzolo, Y. Zhou and D. L. Price), Journal of Interfacial and Electroanalytical Chemistry 450, 273 (1998)

"Self-Consistent tight binding atomic-relaxation model of titanium dioxide" (with P. K. Schelling and N. Yu) Physical Review B58, 1279 (1998)

"Theoretical Modeling of the Solid/Liquid Interface: Chemically Specific Simulation Methods" (with S. Walbran and D.L. Price), "Interfacial Chemistry", A. Wieckowski, editor , Dekker Inc., New York (1999) p.1-18

"Model for the electrostatic response of the copper-water interface" (with S. Walbran A. Mazzolo and D. L. Price), Journal of Chemical Physics 109, 8076 (1998)

"Theory and Experiment on the Cuprous-Cupric Electron Transfer Rate at a Copper Electrode", (with B.B. Smith, S. Walbran, L. A. Curtiss, R. O. Rigney, A. Sujianto, N. C. Hung, R.M. Yonco and Z. Nagy, Journ. of Chem. Phys. 110,6538 (1999)

" Simulation Methods for Chemically Specific Modeling of Electrochemical Interfaces", J. W. Halley, P. Schelling and Y. Duan, Electrochimica Acta 46, 239 (2000)

"Localization of Polarons: Realistic Calculation in Adiabatic Approximation"(with P. Schelling) Phys. Rev. B62, 3241 (2000)

" Chemical Physics of the Electrode-Electrolyte Interface" ", J. W. Halley, S.Walbran and D.L.Price, Advances in Chemical Physics 116,337 (2001)

" Self Consistent Tight Binding Molecular Dynamics for Realistic Simulation of Oxide Behavior", J. W. Halley, P. K. Schelling and M. Zhuang, in "Proceedings of the Third Recontres du Vietnam: Superconductivity, Magneto-Resistive Materials and Strongly Correlated Systems", Nguyen Van Hieu, Tran Thanh Van and Gang Xiao, eds. Vietnam National University Press (2000) p. 137

"Modeling of Semiconductor-Electrolyte Interfaces with Tight Binding Molecular Dynamics" (with P. Schelling) "Solid Liquid Interface; Theory" J. W. Halley, ed. ACS publications (2001) p.142

"Direct Dynamics Simulations of the Copper Water Interface: Successes and Problems" (with S. Walbran) "Solid Liquid Interface; Theory" J. W. Halley, ed. ACS publications (2001) p.10

"Self Consistent Tight Binding Method for the Prediction of Magnetic Spin Structures in Solids: Application to MnF_2 and MnO_2" (with Min Zhuang), Physical Review B 64, 024413 (2001).

"Multiscale Modeling of Many Body Systems",J. W. Halley, Y. Duan, K. Lidke, A.

Wynveen and M. Zhuang, in Condensed Matter Theories Volume 17, M. P. Das and F. Green, editors, Nova Science Publishers, NY (2003) p. 257

'Self Consistent Direct Dyanmics Studies of Interfaces" J. W. Halley, Y. Lin and M. Zhuang, Farad. Discuss, 2002, 212, 85-95

"Application of Self Consistent Tight Binding Method to the Study of Anatase Nanocrystals", J. W. Halley, S. Erdin, Y.Lin and Peter Zapol, Proceedings of CMT27 , Nova 27th International Workshop on Condensed Matter Theories (CMT-27), SEP 15-20, 2004, Condensed Matter Theories 19 , 61-68 (2005)

"Self-consistent tight-binding study of low-index titanium surfaces", Serkan Erdin, You Lin and J. Woods Halley, Phys. Rev B 72, 035405 (2005)

"Modeling of TiO_2 Nanoparticles" A. S. Barnard, S. Erdin, Y. Lin, P. Zapol and J. W. Halley, Phys. Rev. B 73, 205405 (2006)

"Self Consistent Tight Binding Molecular Dynamics Study of TiO_2 Nanoclusters in Water",J. Woods Halley, Serkan Erdin, You Lin, Peter Zapol, Journal of Electroanalytical Chemistry 607, 147 (2007)

Relevant Invited Talks During the Grant Period:

DOE contractors', Brookhaven National Laboratory, September 1991

University of Northern Iowa, seminar, April 1991

National Association of Corrosion Engineers, April 1992

Gordon Conference on Water, July 1992

DOE contractors, Illinois, Champaign Urbana, September 1992

Symp. on the Electrode-Electrolyte Interface, ECS, Toronto,Oc* *tober, 1992

Chemistry Dept, UC Berkeley, June 1993

IBM San Jose, June 1993

DOE Corrosion Contractors' meeting , Golden Co, September 1993

Kansas State University, October 1993

Pacific Northwest Laboratories, Richmond, Washington January 31, 1995

Electrochemistry Society Meeting, Reno, NV , May 24, 1995

DOE Corrosion Contractors' meeting, Penn State, State College, September 14-15,1995

Adriatico Research Conference on Electron and Ion Transfer in Condensed Media, International centre for Theoretical Physics, Trieste, Italy July 15-19, 1996

Grahame Symposium of the Electrochemistry Society, Montreal, May 5-9, 1997

Institute for Theoretical Physics, Santa Barbara, May 1997

Argonne National Laboratory, August 27, 1997

DOE Corrosion Contractors Meeting, Minneapolis, September 19, 1997

July 1998, Aspen Center for Physics, Physics of Oxides program

DOE Corrosion Workshop, Sept 18,19, 1998 Sandia

Pacific Northwest National Laboratory Workshop on Charge Transfer, Sept 21-22, 1998 (invited)

Recontres du Vietnam Conference on Oxides, Hanoi, January 4-8, 1999 (invited)

DOE Workshop on Corrosion of Aluminum, OHare March 23-25, 1999

Pacific Northwest Laboratories Workshop July 21,22, 1999

International Society of Electrochemistry, Sept 5-10, 1999, Pavia Italy)

Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan, October 17-22, 1999 Honolulu

hird International Workshop on Materials Science, November 1-5, 1999, Hanoi, Vietnam

Carr-Parrinello Workshop, March 17-19, 1999, Minneapolis, Minnesota

Computer Simulation in Electrochemistry Symposium at the American Chemical Society meeting, August 20-24,2000 , Washington DC

April 2002, Faraday Discussion 121, The Dynamic Electrode Surface, Berlin, Germany

Brookhaven National Laboratory, Corrosion Contractors meeting, September 2002

ITIMS anniversary meeting in Hanoi, Vietnam, December 2002; seminars at the Institute of Physics and the University of Hanoi.

Michael Weaver symposium, ACS meeting, New Orleans, March 2003

ECS meeting, Paris, April 2003.

Grand Challenges in Modeling the Assembly and Properties of Nanomaterials, Argonne National Laboratory, August 2003

Condensed Matter Theory Meeting, Toulouse France, September 2003

Electrochemistry Society Meeting, Orlando Florida, October 2003

Dynamics of Disordered Materials Conference, Hanoi, Vietnam , February 2004

Electrochemistry Society Meeting , Honolulu, October 2004

Seminar at University of the United Arab Emirates, December 2004

Seminar , CINVESTAV-Merida, Yucatan, Mexico, June 2005

Seminar, Institute of Physics, Vietnam Academy of Science and Technology, Hanoi, March 2006