

The Reversible Hydrogen Electrode: Potential-Dependent Activation Energies over Platinum from Quantum Theory

Yu Cai and Alfred B. Anderson*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

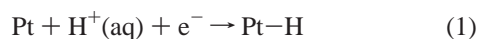
Received: October 15, 2003; In Final Form: April 17, 2004

Potential-dependent activation energies are calculated quantum mechanically, using a local reaction center model, for the hydrogen reduction–oxidation reaction over platinum by the Volmer–Heyrovsky mechanism, $\text{Pt-H} + \text{H}^+ + \text{e}^-(U) \leftrightarrow \text{Pt} + \text{H}_2$ (i), modeled by $\text{Pt-H}\cdots\text{H}^+(\text{OH}_2)(\text{OH}_2)_2 + \text{e}^-(U) \leftrightarrow \text{Pt}\cdots\text{H-H}\cdots\text{OH}_2-(\text{OH}_2)_2$ (ii). A contribution from the electrolyte to the potential of the reaction centers in ii is included in the ab initio Hamiltonian. The reversible potential predicted for i based on model ii is 0.04 V, close to the standard hydrogen electrode value of 0 V, and the predicted activation energy at the predicted reversible potential is 0.076 eV, close to the literature value of 0.12 eV for the apparent activation energy. The theoretical results validate the possibility of the Volmer–Heyrovsky mechanism being followed on platinum.

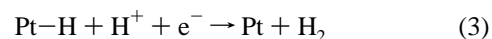
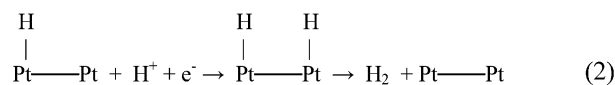
Introduction

Experimental Background. Understanding the mechanisms of hydrogen evolution reactions (HER) and hydrogen oxidation reactions (HOR) on electrode surfaces in various acid and base electrolytes has proven a difficult and ongoing challenge. From the many systems that have been studied and treated with kinetic models it is evident that (i) there is probably no unique mechanism for either the reduction reaction or the oxidation reaction on a given electrode material, (ii) the mechanisms may be different for different surface structures of the same material, (iii) for a given system the HER and HOR reaction mechanisms need not be the same, and (iv) even for well-studied systems, such as platinum electrodes in acids, for which many carefully collected data are available, the determining of mechanisms is a cutting edge research problem. In this paper one of the mechanisms for the hydrogen evolution and oxidation reactions over platinum electrodes in acid electrolyte will be treated quantum chemically.

A brief review of the development of mechanistic understanding is as follows. Beginning with a clean Pt electrode in the double-layer region above ~ 0.4 V, that is, in the HOR overpotential region, as the potential is made increasingly negative, underpotential-deposited (upd) hydrogen, $\text{H}(\text{ads})$, begins to form at ~ 0.4 V by the Volmer reaction:



This hydrogen is referred to as strongly adsorbed. As the electrode potential approaches the hydrogen electrode reversible potential, the coverage of adsorbed H formed by this reaction increases to ~ 1.0 monolayer. As the HER overpotential deposition (opd) region is entered, there are two proposed mechanism choices for H_2 formation: the Tafel reaction, which is the second step in the following sequence, and the Heyrovsky reaction (eq 3),



Whether the Volmer–Tafel mechanism, reactions 1 and 2, or the Volmer–Heyrovsky mechanism, reactions 1 and 3, are followed will depend on Pt–H bond strengths and the activation energies for reactions 2 and 3. For the oxidation reactions the same names are applied with the above reactions reversed. The same mechanisms can be envisioned for HER and HOR on other electrodes.

As discussed in Bockris and Khan, Tafel contributed to the early measurements of the hydrogen evolution reaction.^{1,2} Many studies have been made using many different electrode materials since then, and the focus here will be on some of the more recent ones that attempt to unravel the mechanism, particularly over platinum. Often these studies deal with kinetic equations containing parameters that are not known ab initio but can be adjusted to fit the results of voltammetry measurements. An example is Armand and Clavilier's analysis of H adsorption states on Pt (100) in sulfuric acid.³ This work provided evidence for three states of adsorbed H in the upd region. Weakly held H near the reversible potential and in the HER opd region has been believed to have an ability to participate in the hydrogen reactions, whereas strongly held H is presumed inert. Nichols and Bewick, on the basis of in-situ infrared (IR) spectroscopy, identified a Pt–H vibration on polycrystalline Pt in 1 M H_2SO_4 at potentials less than 110 mV and proposed this weakly held H was consumed during hydrogen evolution.⁴ The more strongly bonded upd H at higher potentials did not yield a vibrational signal, and it was proposed this H was in or below the surface atom layer. Similar observations were made by Ren and co-workers using Raman spectroscopy.⁵ An infrared-visible sum frequency generation (SFG) analysis of Pt (111), (100), and (110) electrodes in dilute sulfuric acid by Peremans and Tadjeddine also showed the presence of Pt–H bonds in the upd potential range.⁶ This study also included the 0 to -1 V opd range and found the SFG spectral feature corresponding to the presence of pairs of H atoms bonded to surface Pt atoms, and

* Corresponding author. Phone: 216-368-5044. Fax: 216-368-3006. E-mail: aba@po.cwru.edu.

these were recommended for consideration as HER intermediates. Conway and Jerkiewicz have discussed the significance of a weakened Pt–H bond for hydrogen evolution.⁷

Conway and co-workers have made a significant contribution to understanding upd and opd H on different crystal faces of platinum in acid and base. They have calculated Tafel plots (electrode potential vs log of the current density) for H₂ evolution from the surfaces in base, where the Volmer–Tafel mechanism is thought to apply, by fitting kinetic equations.^{7,8} Tavares et al., from fitting kinetic equations for H₂ evolution over polycrystalline Pt electrodes in acid to Tafel plots, were able to propose that the Volmer–Heyrovsky mechanism applies to these electrodes in acid.⁹ There are numerous other recent papers concerning HER and HOR over Pt electrodes.^{10–14} Of these the one by Markovic et al.¹⁰ is particularly relevant to this paper. In the Markovic paper results are given for 0.05 M H₂SO₄ solutions over Pt (111), (100), and (110) electrode surfaces. Focusing on the Tafel plots for these surfaces, it was deduced that for HER and HOR potentials the Volmer–Heyrovsky mechanism was being followed over Pt(100), the Volmer–Tafel mechanism was being followed over the (110) surface, and it was unclear which mechanism was being followed over Pt(111). Arrhenius plots of the exchange current densities yielded apparent activation energies at the HER–HOR reversible potential of 0.092 eV for Pt(110), 0.12 eV for Pt(100), and 0.17 eV over Pt(111). Markovic et al. kept the reference electrode at constant temperature while the working electrode was scanned and corrected for the temperature effect. In the experiments a salt bridge was used between the reference electrode at ca. 298 K and the working electrode, which had its temperature varied between 274 and 333 K. According to measurements of Conway and Wilkinson, the resulting thermal liquid junction potential could become several millivolts at the extremes of this temperature range.¹⁵ The effect of a liquid junction potential correction on the above activation energies which were determined from exchange current densities will be small and was not considered. These apparent activation energies will be used for comparison with theoretically calculated activation energies for the Volmer–Heyrovsky mechanism. For discussion of differences between apparent activation energies and “true” activation energies, the reader is referred to ref 1, p 243.

Theoretical Background. Past theoretical work on hydrogen oxidation and reduction over platinum and other materials has consisted of kinetic modeling and parametric fitting of Tafel curves. Underlying this work is the idea that the electron is assumed to transfer from the surrounding electrode to the reaction center when the electrode potential and reaction center electron accepting or donating ability match, as in the model proposed in 1932 by Gurney.¹⁶ There have been several studies pertaining to hydrogen deposition and evolution since then. Butler discussed the hydrogen overvoltage by using the hydronium ion as a model for H⁺(aq) and assuming forms for interaction potentials between hydronium and a nickel surface, and noted that the condition for reversibility is that “the energy of activation is the same from either side”.¹⁷ Krishtalik used a harmonic potential model and, taking into account adsorbate interactions in the Temkin model, noted that at sufficiently negative potential the activation energy for hydronium discharge becomes zero and that at sufficiently positive potential the activation energy for oxidation of adsorbed H atoms becomes zero.¹⁸ Dogonadze et al. developed a formalism for hydronium discharge on metals based on a harmonic potential model and incorporating the dielectric continuum model to treat the energy

of solvation of hydronium.¹⁹ Models have been under development in this laboratory in recent years for making quantum mechanical predictions of activation energies and reversible potentials for electrocatalytic reactions.^{20–23} Our approach to activation energies treats the bonds being broken and formed during an electron-transfer reaction and their immediate environment quantum mechanically. The harmonic molecular potential approximation is not made, but rather actual calculated molecular energies are used and the hydronium ion includes a solvation shell that is allowed to relax, in place of a dielectric continuum approximation. The advanced model used in this paper, which incorporates a contribution to the Hamiltonian in the form of a Madelung sum over ions in a regular array in the bulk electrolyte, has been applied with good accuracy to elementary reactions of H₂O oxidation on Pt,²⁴ O₂ reduction on Pt,²⁵ and hydronium ion reduction on Pt to form Pt–H,²⁶ which is the Volmer reaction given by eq 1.

Theoretical Method

A feature of the theory is the calculation of activation energies for electron-transfer reactions at different potentials of the electrode. To do this, a molecular model (reaction center) for the reactant is chosen. For a reduction reaction this is called the reduction precursor, and for an oxidation reaction it is called the oxidation precursor. The electron transfer is assumed to occur into or out of the reaction center suddenly and nonadiabatically. Electron attachment to the reduction precursor is exothermic by the electron affinity (EA). Upon electron attachment, bond order changes cause the reduction product to form without activation. At equilibrium between the reaction center and the electrode, the relationship between the reaction center’s electron affinity or ionization potential and the electrode potential is

$$\text{EA or IP} = (4.6 + (U/V)) \text{ eV} \quad (4)$$

where 4.6 eV is the thermodynamic work function of the standard reversible hydrogen electrode (ref 1, p 493), U is the electrode potential, and IP refers to the ionization potential, which is the appropriate reaction center property in the case of an oxidation reaction. In the case of the reduction reaction, as the electrode potential is made positive from the reduction precursor potential and given a new value U' , there is an activation energy barrier for the reaction because the reaction center structure must be distorted until its electron affinity is increased to a value satisfying eq 4.

In the model’s current form, for reactions in acid H⁺(aq) are treated as the species H₃O⁺(OH₂)₂ where one proton of the hydronium ion, H₃O⁺, is available for coordination to the molecule to be reduced and the other two are each coordinated by hydrogen bonding to a water molecule. The electron affinity of the reaction center increases when H₃O⁺(OH₂)₂ moves closer to the species to be reduced and when bonds in the species to be reduced stretch. The stretching stabilizes empty σ^* and π^* orbitals that participate in forming the acceptor orbital for the electron causing the reduction. The energy increases attendant to these structure changes from the equilibrium precursor structure are responsible for the presence of an activation energy. There are, however, unlimited structures having the same EA, and the lowest energy one must be found for it is the transition-state structure. In the above-mentioned papers^{20–26} and other papers referenced in them transition states were found by partially constrained pattern search technique. Recently a constrained variation program using the method of Lagrange undetermined multipliers for finding transition states and

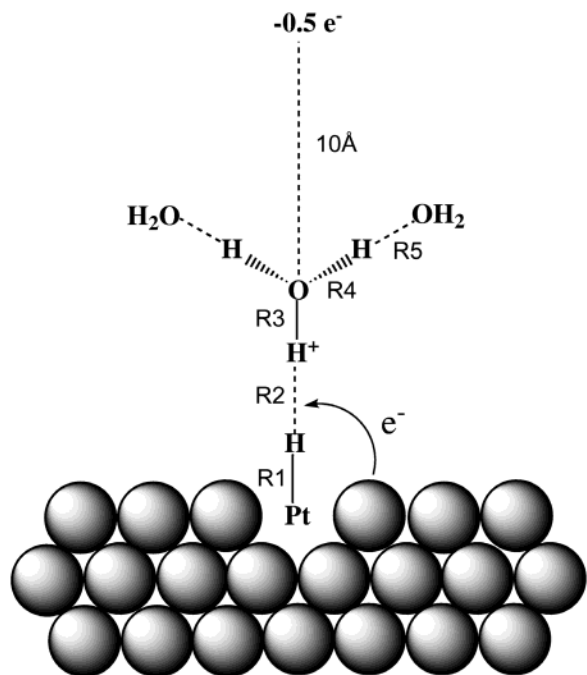


Figure 1. Reaction center model, $\text{Pt}-\text{H}\cdots\text{H}^+(\text{OH}_2)(\text{OH}_2)_2$, for H_2 formation by the Volmer–Heyrovsky mechanism. The charge representing the Madelung sum of ion potentials in the electrolyte is indicated along with the concept that the electron, which has the electrode potential U , comes from the surrounding electrode region, a region represented by shaded Pt atoms that are not included in the calculations.

activation energies for electron-transfer reactions was developed and tested in this laboratory.²⁷ This approach greatly extends the range of applications of the theory because it requires much less computational time. A modified version of this program is used for the present study.²⁸ Another recent addition to the approach is the inclusion of an approximation to the potentials in the reaction center Hamiltonian that are caused by the counteranion to $\text{H}^+(\text{aq})$ and the other ions in the electrolyte.^{24–26} The sum of these potentials is modeled by a point charge of $-0.5 e$ placed 10 \AA from the hydronium ion. This corresponds to a Madelung sum over an evenly spaced lattice of $-e$ charged anions and $+e$ charged cations at about 0.1 M concentration.

For the calculations reported here, the MP2 approach in the ab initio quantum chemical package Gaussian 94 was used.²⁹ The Los Alamos double- ζ basis set LANL2DZ was used for Pt, and the extended 6-31G** basis set was used for H and O. At the present level of modeling, we use equilibrium bond strengths, D_e , without zero-point-energy deduction in place of D_0 . For diatomic Pt–H in its ground state the zero-point energy is 0.14 eV .³⁰ The chemistry studied in this paper involves breaking a Pt–H bond and an O–H⁺ in hydronium, which has a zero-point energy of about 0.19 eV based on the diatomic value from ref 30. The product, H_2 , has a zero-point energy of 0.27 eV ,³⁰ so the zero-point energy contributions to the bond strengths nearly cancel.

Results and Discussion

The model reaction for the Heyrovsky reaction is

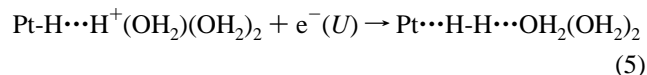


Figure 1 shows the reaction center model and the five bond lengths varied in determining both the reduction and oxidation precursor structures and the transition-state structures. Other

TABLE 1: Values of the Five Bond Lengths (\AA), Defined in Figure 1, That Were Optimized To Produce Reduction Precursor and Oxidation Precursor Structures

precursor structure	R1	R2	R3	R4	R5
reduction	1.5068	1.6442	0.9743	1.0292	1.4664
oxidation	1.4929	1.1215	1.0488	0.9947	1.6059

variables in the $\text{OH}_2(\text{OH}_2)_2$ fragment are, as in all past studies, fixed at the values in the optimized $\text{H}^+(\text{OH}_2)(\text{OH}_2)_2$ structure. There is no good justification for optimizing the fixed structure variables because further hydrogen-bonding interactions with the surrounding medium are absent in the model, and they are expected to provide some constraint, particularly to angular variations. Bond stretches and compressions that are required for electron transfer will be accommodated at low energy cost to the surrounding medium by relatively low-energy angle changes in the medium. Table 1 lists the optimized structure variables for the precursors. The biggest difference is for R2, the H–H internuclear distance, which is large for the reduction precursor, where $\text{H}^+(\text{aq})$ is bonded weakly by 0.33 eV to H on Pt and small for the oxidation precursor, where H_2 is bonded weakly by 0.44 eV to both Pt and O in the water molecule, holding both species to it with a polarization giving the system the charge distribution $\text{Pt}\cdots\text{H}^{\delta-}-\text{H}^{\delta+}\cdots(\text{OH}_2)(\text{OH}_2)_2$. It may also be seen that R5 is shorter for the reduction precursor because of the stronger hydrogen bond between H_2O and the positively charged hydronium ion.

The nonadiabatic electron affinity of the reduction precursor is given by

$$\text{EA} = E(\text{Pt}-\text{H}\cdots\text{H}^+(\text{OH}_2)(\text{OH}_2)_2) - E(\text{Pt}-\text{H}\cdots\text{H}(\text{OH}_2)(\text{OH}_2)_2) \quad (6)$$

where E is internal energy and the structure of the neutral system is the same as that for the charged reduction precursor. The least negative electrode potential for which the reduction precursor can be reduced is then

$$U_{\text{rp}} = ((\text{EA}/\text{eV}) - 4.6) \text{ V} \quad (7)$$

and for the Heyrovsky reaction the value obtained for U_{rp} is -0.86 V . The nonadiabatic ionization potential for the oxidation precursor is given by

$$\text{IP} = E(\text{Pt}\cdots\text{H}-\text{H}^+(\text{OH}_2)(\text{OH}_2)_2) - E(\text{Pt}\cdots\text{H}-\text{H}\cdots\text{OH}_2(\text{OH}_2)_2) \quad (8)$$

where the structure of the charged system is the same as that for the uncharged oxidation precursor. The least positive electrode potential for which the oxidation precursor can be oxidized is then

$$U_{\text{op}} = ((\text{IP}/\text{eV}) - 4.6) \text{ V} \quad (9)$$

and the calculated $U_{\text{op}} = -0.21 \text{ V}$.

Figure 2 shows calculated activation energies as functions of the electrode potential in the range -0.21 to -0.86 V . Additional values are shown outside this range, and they correspond on the right to the Marcus inverted region for oxidation and on the left to the Marcus inverted region for reduction.³¹ It should be noted that the Marcus theory deals with Gibbs activation energies and our theory deals with activation internal energies but the inverted region concept remains the same. The inverted region would be physically relevant on narrow conduction band semiconductors. On metal electrode

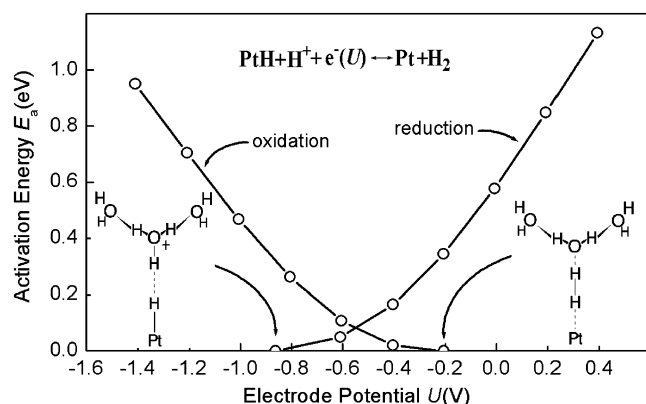
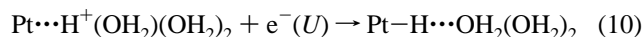


Figure 2. Calculated electrode-potential-dependent activation energies and reduction precursor structure (on the left) and oxidation precursor structure (on the right).

surfaces the activation energies will become zero when the “inverted regions” are entered.

The reversible potential U° is the potential where the activation energies for the forward and reverse reactions are equal, and this is the crossing point in Figure 2, which is -0.55 V. The activation energy at this point is 0.076 eV, in good agreement with the 0.12 eV experimental value from ref 10. The predicted reversible potential is low since the standard reversible potential is 0 V. This inaccuracy stems largely from inaccuracies in the Pt–H bond strength. The calculated value, 3.14 eV,²³ is 0.59 eV greater than the 2.55 eV measured value on Pt electrodes at high coverage.³² It is noted that the 3.14 eV calculated value is from a MP2 calculation for diatomic Pt–H, and the experimental diatomic D_0 value is known only to be ≤ 3.44 eV. Looking at eq 5 it is evident that if the Pt–H bond were 0.59 eV weaker, the electron would have to be 0.59 eV more stable to maintain the equilibrium, and this would mean increasing the electrode potential by 0.59 V. With this correction the calculated reversible potential becomes 0.04 V, in good agreement with experiment. If the ~ 0.14 eV zero-point energy were taken into account, the calculated D_0 would be ~ 3.00 eV, which is only 0.4 eV greater than the high-coverage electrode surface value. However, the diatomic value is not expected to exactly match the surface value, and a perfect match of a predicted reversible potential within the current model, which represents first step in model development, is not generally expected to occur.

Lest the success of the above 0.59 V correction seem fortuitous, another example is given for the case of upd H on Pt electrodes from ref 26. There for the reaction model



the calculated reversible potential for the onset of upd H was 0.85 V, which is ~ 0.45 V higher than the observed onset potential. At low coverage, corresponding to that at the upd onset potential, the measured strength of H bonding to platinum electrodes is 2.75 eV,³² which is 0.20 eV more than the high-coverage value used above. Thus, a 0.39 V correction can be applied in place of the 0.59 V correction used above, yielding a final predicted value of 0.46 V for the onset of upd H deposition on platinum electrodes. This is in good agreement with the experimental value. A full treatment of reversible potentials would require calculations of the free energies of both sides of eqs 5 and 10 as well as the incorporation of additional components of the systems that are being modeled. Further

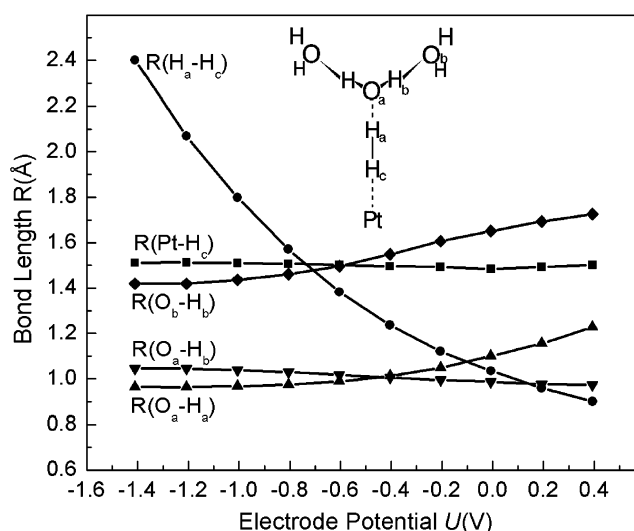


Figure 3. Values of the five bond lengths that were varied when determining $E_a(U)$.

discussion may be found in ref 21. It is noted that, based on the H adsorption bond strengths in ref 32 and these calculations, the reversible potential for adding more H at highest coverage would be 0.26 V. The opd H that is believed to participate in H_2 evolution at potentials < 0 V may be still more weakly bonded, but if it were the calculated reversible potential for H_2 evolution, using eq 5 would become larger. If the opd Pt–H bond strength were assumed to be 0.11 eV weaker at 0 V than was assumed above, the reversible potentials for H_2 evolution and replacement of the H at the surface vacant site thus formed would both be 0.15 V. A goal for the future would be to develop a model that would yield 0 V for this process.

The transition-state structures for the electrode potentials studied are shown in Figure 3, where it can be seen that the H–H bond length is the most sensitive to potential. For oxidation at negative potentials large stretches of the H–H bond are necessary to raise its σ bonding orbital to the point where it becomes oxidized, and for reduction at the same potential a large stretch is needed to lower the σ^* orbital to the point where it can be reduced. At positive potentials the H_2O molecules move away from the hydronium ion because this increases the electron affinity of the reaction center.

Conclusions

This study demonstrates that the Volmer–Heyrovsky mechanism for hydrogen evolution and oxidation is viable near the reversible potential on platinum electrodes. The calculated reversible potentials, with adjustments for Pt–H bond strengths to compensate for some of the limitations of the local reaction center model, 0.04 V for the hydrogen electrode and 0.46 V for the onset potential for under potential deposition of H, are in good agreement with experiment. A future publication will demonstrate how the calculated electrode-potential-dependent activation energies can be used to obtain Tafel plots matching experimental ones from ref 10 for (100) Pt electrodes, further supporting the mechanism assigned by Markovic and co-workers.

Acknowledgment. This research is supported by the National Science Foundation, Grant No. CHE-9982179. Y.C. thanks Lubomir Kostadinov for help with Lagrange multiplier calculations.

References and Notes

- (1) Bockris, J. O'M.; Khan, S. U. M. *Surface Electrochemistry*; Plenum Press: New York, 1993; p 493.
- (2) Tafel, J. Z. *Phys. Chem. (Leipzig)* **1905**, 50A, 641–712.
- (3) Armand, D.; Clavillier, J. J. *Electroanal. Chem.* **1987**, 225, 205–214.
- (4) Nichols, R. J.; Bewick, A. J. *Electroanal. Chem.* **1988**, 243, 445–453.
- (5) Ren, B.; Xu, X.; Li, X. Q.; Tian, Z. Q. *Surf. Sci.* **1999**, 427–428, 157–161.
- (6) Peremans, A.; Tadjeddine, A. J. *Phys. Chem.* **1995**, 103, 7197–7203.
- (7) Conway, B. E.; Jerkiewicz, G. *Electrochim. Acta* **2000**, 45, 4075–4083.
- (8) Barber, J.; Morin, S.; Conway, B. E. *J. Electroanal. Chem.* **1998**, 446, 125–138.
- (9) Tavares, M. C.; Machado, S. A. S.; Mazo, L. H. *Electrochim. Acta* **2001**, 46, 4359–4369.
- (10) Markovic, N. M.; Grgur, B. N.; Ross, P. N. *J. Phys. Chem. B* **1997**, 101, 5405–5413.
- (11) Vermeijlen, J. J. T. T.; Janssen, L. J. J.; Visser, G. J. *J. Appl. Electrochem.* **1997**, 27, 497–506.
- (12) Gennero de Chialvo, M. R.; Chialvo, A. C. *Electrochem. Commun.* **1999**, 1, 379–382.
- (13) Lamy-Pitara, E.; El Mouahid, S.; Barbier, J. *Electrochim. Acta* **2000**, 45, 4299–4308.
- (14) Giorgi, L.; Pozio, A.; Bracchini, C.; Giorgi, R.; Turtu, S. *J. Appl. Electrochem.* **2001**, 31, 325–334.
- (15) Conway, B. E.; Wilkinson, D. P. *Electrochim. Acta* **1993**, 38, 997–1013.
- (16) Gurney, R. W. *Proc. R. Soc. London, Ser. A* **1932**, 134, 137–154.
- (17) Butler, J. A. V. *Proc. R. Soc. London, Ser. A* **1936**, 157, 423–433.
- (18) Krishtalik, L. I. *Russ. J. Phys. Chem.* **1960**, 34, 53–58.
- (19) Dogonadze, R. R.; Kuznetsov, A. M.; Levich, V. G. *Electrochim. Acta* **1968**, 13, 1025–1044.
- (20) Anderson, A. B.; Kang, D. B. *J. Phys. Chem. A* **1998**, 102, 5993–5996.
- (21) Anderson, A. B.; Albu, T. V. *Electrochem. Commun.* **1999**, 1, 203–206.
- (22) Anderson, A. B.; Albu, T. V. *J. Am. Chem. Soc.* **1999**, 121, 11855–11863.
- (23) Anderson, A. B.; Albu, T. V. *J. Electrochem. Soc.* **2000**, 147, 4229–4238.
- (24) Anderson, A. B.; Neshev, N. M.; Sidik, R. A.; Shiller, P. *Electrochim. Acta* **2002**, 47, 2999–3008.
- (25) Sidik, R. A.; Anderson, A. B. *J. Electroanal. Chem.* **2002**, 528, 69–76.
- (26) Anderson, A. B.; Sidik, R. A.; Narayanasamy, J.; Shiller, P. *J. Phys. Chem. B* **2003**, 107, 4618–4623.
- (27) Kostadinov, L. N.; Anderson, A. B. *Electrochem. Solid State Lett.* **2003**, 6, E30–E33.
- (28) This is called the TSOET program, for transition-state optimization for electron transfer, and it uses shell scripts and a C program to control calculations of energies with the Gaussian quantum chemistry software.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (30) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (31) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, 811, 265–323.
- (32) Zolghafhari, A.; Chayer, M.; Jerkiewicz, G. *J. Electrochem. Soc.* **1997**, 144, 3034–3040.