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A simple method to approximate electrode potential-dependent activation energies using density functional theory

Sneha A. Akhade, Nicole J. Bernstein, Monica R. Esopi, Michael J. Regula, Michael J. Janik*

Department of Chemical Engineering, Fenske Laboratory, Pennsylvania State University,University Park, PA 16802, United States

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ABSTRACT

Density functional theory (DFT) examination of electrocatalytic mechanisms are useful in fuel cell/electrolysis development, but the calculation of potential-dependent activation barriers for elementary steps involving electron and ion transfer remains challenging. A simple and transferable DFT approach to estimate these constant potential barriers for inner sphere electrochemical reactions is presented. The challenge of finding the transition state for an electrochemical reaction step ($A^* + H^+ + e^- \rightarrow AH^*$, where * denotes surface-adsorbed species) is met by using an equivalent analogous non-electrochemical reaction ($A^* + H^* \rightarrow AH^*$). The transition state of the non-electrochemical step is referenced to an equilibrium potential (U^0), at which the analogous non-electrochemical state $\mu(H^*)$ is in equilibrium with its equivalent electrochemical state $\mu(H^+ + e^-)$, allowing for the barrier to be referenced to the chemical potential of the ion in the bulk electrolyte. The potential-dependence is incorporated by extrapolating the activation energy using Marcus theory. The first elementary step of CO_2 electroreduction to $COOH^*$ is used as a detailed example case for illustrating the method. Additional elementary reduction reactions involving C—H, O—H and N—H bond formations are included to demonstrate the transferability of the method. The method is simple and easy to implement to approximate potential-dependent activation energies at the computational cost of a singly hydrogenation barrier calculation and can aid in the development of more active and selective catalysts for electrochemical reactions.

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1. Introduction

With increasing energy demands there is a strong interest in developing efficient and feasible electrochemical energy conversion and storage technologies. Rational design of electrodes for fuel cells and electrolysis units requires mechanism determination for key electrocatalytic reactions including the oxygen reduction reaction (ORR), the carbon dioxide reduction reaction (CO_2 RR) and the hydrogen evolution reaction (HER). A comprehensive mechanism for multi-step electrocatalytic reactions includes knowing the potential-dependent reaction energy and activation energy of every step. These parameters dictate the thermodynamic feasibility and the kinetic rate of the electrocatalytic reaction of interest.

A theoretical description of the electrochemical interface is extremely demanding due to the presence of the electrolyte at the electrode surface and the varying electrical potential of the electrode. The electrified interface has active charge transfer and operates under non-equilibrium conditions when an electrochemical reaction occurs. Density Functional Theory (DFT) based approaches have been developed to incorporate varying complexity towards modeling this interface. In its simplest form, the computational hydrogen electrode (CHE) model uses DFT based evaluation of adsorbate stability at the metal/vacuum interface to provide potential-dependent reaction energies for elementary steps involving transfer of a proton-electron pair. Building from this approach, interfacial solvation (explicit or continuum) [25,30,51,54], applied electric fields [24,39,56] or explicit charging of the electrode [17,31] and inclusion of electrolyte countercharges [3,43,53] can be added to better represent the environment about an adsorbate at the electrode surface. Though these approaches have had significant successes, they have mainly been applied to investigate the thermochemistry and compute elementary reaction free energies and are not trivially transferrable to evaluate transition states and electrochemical kinetic barriers.

In representing potential-dependent reaction free energies, the CHE model takes advantage of the equivalence of the free energies of the proton-electron pair ($G_{H^+ + e^-}$) and hydrogen gas ($0.5\,G_{H2}$) at 0 V to rigorously evaluate the chemical potential of the electrode/electrolyte species [42]. Transferring this computational free energy approach to estimate the electrochemical barriers is

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* Corresponding author.
E-mail address: mjanik@psu.edu (M.J. Janik).

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challenging as this requires tracing the reaction path of the ion-electron pair, for a reduction reaction, from the electrolyte to the surface-adsorbed species. DFT representation of the ion in the bulk electrolyte is difficult due to the limited unit cell size and the use of static solvation models. A few approaches have been previously suggested, all of which place the H^+ in the DFT unit cell, generally in the vicinity of the adsorbed species that it is transferring to, and calculate a local activation barrier of H^+ transfer. Anderson and co-workers proposed a reaction center model [4–6,8] that was used to investigate potential-dependent barriers of elementary steps in the ORR mechanism on Pt (111) [7,12]. Here, the electron transfer between the reaction center and the surrounding electrode took place when the reaction center's electron affinity (EA) or ionization potential (IP) matched the work function of the electrode. The models used, however, are extremely small metal clusters of single metal atoms, and the electron affinity converges to the metal Fermi level for large systems making the suitability of this method for extended electrodes unclear. Neurock and co-workers introduced a double-reference method [17] and applied it to calculate the potential-dependent reaction energy and activation barrier for the reduction of $O_2{}^*$ to OOH^* (where * denotes surface-adsorbed species) at the Pt (111)/water interface surface [23]. The static nature of the electrolyte, finite unit cell size and the use of fully hydrated models, however, makes applying this method computationally challenging for complex reactions and systems. Rossmeisl and co-workers proposed models to estimate the potential-dependent activation energies of elementary steps in the HER mechanism on Pt (111) by varying the concentration of surface-adsorbed hydrogen and solvated protons in the double layer [53]. To account for unrealistic H^+ concentrations in small unit cells, the electrochemical barriers were extrapolated using multiple larger unit cells making the method prohibitively expensive for complex reaction mechanisms [46]. Nørskov and co-workers apply this method to evaluate the activation barriers for elementary electrochemical reactions in the CO_2 reduction pathway, however, the computed barriers are not referenced to a specific potential scale and are subject to the size of the unit cell size and the water structure used in the models [52]. All these approaches are challenged by the improper referencing of energies to an arbitrary initial state with H^+ in small DFT unit cells and/or difficulty in assigning a meaningful potential-dependence to the calculated barrier.

Two more recent developments in DFT approaches to estimating electrokinetic barriers present further options. Chan and Nørskov recently proposed a charge-extrapolation technique that has been applied to calculate the electrokinetics of hydrogen evolution on Pt (111) [13,14] and CO reduction on Cu (100) surfaces [15]. This technique conveniently allows estimation of potential-dependent activation energies using a single DFT calculation and the charges of the surface species, however, it relies on the choice of initial state and the use of interfacial charges that are sensitive to charge delocalization and partitioning schemes. Recently, Head-Gordon and co-workers examined the energetics of C—C bond formation during electrochemical CO_2 RR using an elegant constant potential self-consistent field procedure [18]. The scheme self-consistently solves for the charge density of an implicit solvent and electrolyte at constant potential, thereby incorporating explicit treatment of the electrochemical potential, electrolyte, solvent and electric fields. However, each energy calculation is reported to be three times more expensive computationally than potential-free DFT calculations, and a series of energy calculations are needed to give potential-dependent values. Both of these new approaches, as presented, lead to local barriers that reference an initial state with the transferring ion in the unit cell rather than a state with the chemical potential of the ion in the bulk electrolyte.

In this study, we illustrate a simple method to approximate elementary electrochemical barriers that are potential-dependent and can be referenced to the bulk electrolyte. In this method, potential-dependent activation energies ($\Delta G^{ACT}(U)$) are extrapolated from non-electrochemical hydrogenation/dehydrogenation reactions to their equivalent electrochemical redox reactions. Since the elementary reaction rate depends on the electrocatalyst, we presume these are inner sphere reactions, wherein we expect the highest energy state along the reaction path to be local to the electrocatalyst surface, allowing for the use of localized models of the surface-adsorbed species and ion transfer [5,6]. The activation energy for the non-electrochemical reaction ($\Delta G^{ACT}(U^0)$), computed using well-established DFT models [20,21], is assigned to an appropriate equilibrium potential (U^0) at which the analogous non-electrochemical state, $\mu(H^*)$, is in equilibrium with its equivalent electrochemical state, $\mu(H^+{}_{(aq)} + e^-)$. By referencing to the chemical potential of ion in the bulk electrolyte, we ensure that the calculated transition state is referenced back to its equivalent electrochemical reactant state regardless of the nature of the analogous non-electrochemical model used. This method allows for the potential-dependence to be referenced to a useful potential scale (NHE/RHE). Effects of solvation and interfacial electric fields are neglected herein but can be included within the same framework. The activation energy is then extrapolated to other potentials using Marcus Theory wherein varying the potential from U_1 to U_2 shifts the relative free energies of the reactant and product states (and consequently the activation barrier) of an elementary redox reaction by $\beta(U)\ (U_2 - U_1)$ [33,35]. Here, $\beta(U)$ is a reaction symmetry factor, typically measured and reported in literature to vary between 0.3 and 0.7 [10,50]. Collectively, the method presented provides an approximate barrier at any electrode potential at the computational expense of a DFT evaluation of a single hydrogenation barrier.

We have previously applied the method presented herein to examine the elementary barriers of carbon dioxide electroreduction [3,40,41] and borohydride oxidation [36,47] reactions. This method has helped explain the overpotentials, selectivity and electrolytic ion effects on the CO_2 electroreduction reaction on Cu (111) [3,40,41]. Linear sweep voltammograms for the kinetic regime of borohydride oxidation over Au (111) were previously simulated with elementary rate constants derived using this approach [47]. In these previous studies, the reaction symmetry factor (β) was presumed to be constant and approximately 0.5. In the present work, we further develop the method to approximate potential-dependent activation energies by demonstrating two approaches that allow us to better estimate the potential dependence of barriers, improving on the previous assumption of β being a constant near 0.5. The electroreduction of CO_2 to $COOH^*$ on Cu (111) via a solvation assisted proton-shuttling mechanism is used as the primary reaction for illustrating our approach. Additional elementary electrochemical reactions including C—H, O—H and N—H bond formation on Cu (111) and Pt (111) surfaces are considered to exhibit the general applicability and transferability.

In the following sections, we show how the challenge of finding a transition state for an elementary electrochemical reaction is met by using an equivalent analogous non-electrochemical reaction. We then illustrate how Marcus Theory can be used to calculate the intersection point between the reactant and product free energy parabolas that shift continuously with potential U. We consider multiple definitions of the reaction coordinate to construct the free energy parabolas using (i) Bader charges and (ii) the geometric bond distances between the reactant, transition and product states and compute potential-dependent activation energies ($\Delta G^{ACT}(U)$). Section 3 shows the application of our approach to examining the elementary electrokinetics of CO_2 to $COOH^*$ electroreduction on Cu (111). The last section evaluates the transferability of the method to alternate elementary electrochemical reactions. We find that the partitioning of charges in the Bader scheme limits its use as a

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