



Theoretical modeling of electrode/electrolyte interface from first-principles periodic continuum solvation method

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ABSTRACT

It has been a long challenge to understand the equilibrium and the dynamic phenomena (e.g. chemical reactions) at the electrode/electrolyte interface in a unified theoretical framework. Here periodic first-principles calculations integrated with modified-Poisson–Boltzmann electrostatics are utilized to provide the atomic level insight into the nature of electrochemical double layer and the catalytic reaction at the interface. The double layer properties of a series of metal electrodes and CO-covered Pt electrode, such as the potential of zero charge and the differential capacitance, are calculated from theory and a good agreement between theoretical values and experimental data is achieved. The theoretical method is also applied to understand the mechanism of CO electrooxidation on Pt. By comparing CO + O and CO + OH reaction channels, we show that CO + OH is the major mechanism for CO electrooxidation. It is observed that the barriers of these surface association reactions are weakly dependent on the potential. The theoretical results presented here demonstrate that first-principles periodic continuum solvation method is a practical and general-purpose theoretical tool for studying electrochemical phenomena occurring at the electrode/electrolyte interface.

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1. Introduction

The electronic and geometrical structure of the electrode/electrolyte interface lies at the heart of the electrochemical processes. The current knowledge on the electrochemical double layer originates mainly from the measurement of the macroscopic, equilibrium properties of the interface, such as surface tension, work function and interfacial capacitance [1–6], and also the simplified theoretical model based on classical Poisson–Boltzmann electrostatics from Gouy–Chapmann and Stern [7–9] (GCS model). Due to the electrochemical adsorption, the redox reactions involving water and electrolyte, and the surface structural reconstruction (defect creation), especially on active transition metals, it is generally difficult to measure accurately the double layer properties. For instance, for the typical catalyst in fuel cell, Pt electrode, the potential of zero charge (pzc) and differential capacitance (C_d) have been measured with different experimental methods and the reported values span a certain range (pzc: 0.2–0.4 V and C_d : 14–20 $\mu\text{F}/\text{cm}^2$ [10–12]). In line with this, the understanding for the electrocatalytic reactions that occur at the electrode/electrolyte interface is much poorer compared to those for the solid–gas reactions, not

least because of the complexity of the electrode/electrolyte interface. New experimental and theoretical techniques are urgently required to decouple the many-body problem associated with the electrode/electrolyte interface, where the electrochemical potential, the adsorbate, the surface structure and the solution are the key factors.

Recent years have seen a great progress in understanding electrochemical phenomena using theoretical methods, such as Canonical Monte Carlo [13], Wertheim–Lovett–Mou–Buff integral equation [14,15], modified Poisson–Boltzmann (MPB) [16–18] and molecular dynamics [19–22]. As one of the major progress, the solid–liquid interface can now be studied with the state-of-the-art quantum mechanics approaches, such as the large-scale density functional theory (DFT) calculations [23–25]. Neurock and coworkers proposed a double-reference method to describe the metal/water interface, in which the water layers outside the metal surface are explicitly included with the ice-like structure and the counter charge of electrolyte is described by the homogeneously distributed background charge [24,26]. Using Cu(1 1 1) in contact with water as the model, they calculated pzc (0.6 ± 0.1 V vs. SHE, cf. exp. -0.01 V [27]) from the double-reference method [28], but there are still obvious difference between theory and experimental values. By fitting the curvature of the parabola of free energy versus potential, Norskov group [25] calculated C_d of Pt(1 1 1) with a few layers (1–3) explicit water included and the calculated value 23 $\mu\text{F}/\text{cm}^2$

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is somewhat larger than the reported experimental value [10–12]. They also investigated hydrogen oxidation and evolution reaction with a water bi-layer model by adding protons into the first water layer [25]. Recently, a periodic continuum-solvation method based on the modified-Poisson–Boltzmann theory [16] has been implemented in DFT framework (DFT/CM-MPB) for modeling the electrode/solution interface [29,30]. Jinnouchi and Anderson analyzed the pzc of Pt(1 1 1) with different water coverage and water orientation with the values from -0.35 to 0.74 V [29,31]. They found that the exact water orientation can affect greatly the pzc. This is consistent with the conclusion obtained from other research groups with water bilayer on metals: it was found that the work function difference between the H-down and H-up water bilayer structure on Pt(1 1 1) can be as large as 2.6 eV [25]. By focusing on the dynamic aspects of the reaction, our group recently investigated water splitting on RuO₂ and TiO₂ under electrochemical and photocatalytic conditions [30,32].

To date, it remains unclear whether it is possible to treat the static/equilibrium (such as pzc, C_d) and the dynamic properties (chemical reactions) of the electrode/electrolyte interface in a unified theoretical framework. One may be able to predict the static properties of the interface via heavy demanding computational techniques such as first principles molecular dynamics, but these methods are not practical in general for studying the rare dynamic event (reactions) under electrochemical condition. In this work, we demonstrate that the theoretical approach based on periodic DFT/CM-MPB calculations can be utilized to model electrochemical interface and the effects due to the solvation and the electrochemical potential can be included straightforwardly. We calculate the equilibrium properties of the double layer of a series of metal electrodes and CO-covered Pt electrode. We also apply the method for understanding a typical reaction on Pt electrode, i.e. CO oxidation. The results from theory are compared thoroughly with those from the experimental measurement.

2. DFT calculation detail

All DFT calculations were performed using SIESTA package with numerical atomic orbital basis sets and Troullier–Martins norm-conserving pseudopotentials [33–35]. The exchange–correlation functional utilized was at the generalized gradient approximation level, known as GGA-PBE [36]. The optimized double- ζ plus polarization basis (DZP) set was employed routinely for total energy calculations and the diffuse basis (e.g. 7s for Au) was also added in calculating work function of metal surfaces [37]. The orbital-confining cutoff was determined from an energy shift of 0.010 eV. The energy cutoff for the real space grid used to represent the density was set as 250 Ry. The Quasi-Newton Broyden method was employed for geometry relaxation until the maximal forces on each relaxed atom were less than 0.1 eV/Å. Transition states (TSs) of the catalytic reaction were searched using our recently developed Constrained-Broyden–Minimization [38] and the Constrained-Broyden–Dimer methods [39]. In all calculations, the rectangular $p(4 \times 2\sqrt{3})$ symmetric six-layer slab was utilized routinely for modeling the (1 1 1) surfaces and the middle two layers were fixed at the bulk-truncated position. The adsorbates were added symmetrically on both sides of the slab. To compute Pt(1 1 1) at various CO coverage conditions and the CO oxidation reaction, both $p(2 \times 2\sqrt{3})$ and $p(4 \times 2\sqrt{3})$ unit cells were utilized.

3. Periodic continuum-solvation method based on modified Poisson–Boltzmann equation

In our previous work, we have developed a Gaussian-plane-charge method for the calculation of charged surfaces [40]

(the counter-charge is distributed in a Gaussian-plane several angstroms away from the surface), which considers the surface polarization explicitly due to the surface charging. However, because of the lack of solvation and the unrealistic ionic charge distribution, the Gaussian-plane-charge method is not ideal for an accurate description of electrocatalytic reaction. Recently, we replace the Gaussian-plane charge distribution by a point-charge distribution in the continuum dielectric medium throughout the entire vacuum region (at the grid points in DFT calculations), which mimics the real ionic distribution of electrolyte [41]. This approach is introduced below.

3.1. Continuum solvation

The continuum dielectric medium is introduced via a parameterized smooth dielectric function $\epsilon(r)$ (Eq. (1)) as proposed by Fattebert and Gygi [42],

$$\epsilon(\rho(r)) = 1 + \frac{\epsilon_\infty - 1}{2} \left[1 + \frac{1 - (\rho(r)/\rho_0)^{2\beta}}{1 + (\rho(r)/\rho_0)^{2\beta}} \right] \quad (1)$$

which approaches to ϵ_∞ (e.g. 78.36 for water at room temperature) asymptotically in the regions where electron density is low, and 1 in the regions where it is high. In the equation, ρ_0 and β are the only two parameters: ρ_0 is the threshold of electron density $\rho(r)$ to adjust the size of the cavity, whereas β determines the smoothness of the transition from 1 to ϵ_∞ . According to Fattebert and Gygi, these two parameters can be chosen by fitting the experimental solvation energy value for the systems of interest (e.g. water) and the values utilized in this work is 5.5 e/bohr³ for ρ_0 and 1.3 for β . For $\rho(r)$, we utilize the pseudoatomic charge distribution according to the pre-defined atomic configuration of the element and it is then fixed during the self-consistent loop. A fixed $\epsilon(r)$ during the self-consistent field calculation is found to be essential to speed up the convergence, especially for metallic system. The atomic configuration of the element acts as a convenient way to tune the solvation radius of the element, similar to that utilized in traditional continuum solvation method [43]. The continuum solvation model enables the band structure alignment between different surfaces with the same solution level (i.e. the potential zero defined in the middle of the vacuum of slab where the dielectric function approaches to 78.36), and more importantly, it corrects the DFT energy with the long-range electrostatic interaction due to solvation.

For example, the typical distribution of $\epsilon(r)$ for a metal surface (Pt(1 1 1)) at different atomic configurations are shown in Fig. 1a, where the dielectric function increases from 1 (metal bulk) to 78.36 (water solution) within a thickness of ~ 3 Å from the surface plane. By changing the atomic configuration, the distribution of dielectric function $\epsilon(r)$ is also modified: as seen in Fig. 1a, with the gradual depopulation of electrons in 5d, the solution ($\epsilon = 78.36$) will be pushed away from the surface. Consistently, we found that the potential of zero charge (pzc) will increase gradually. The calculated pzc are 0.31, 0.50, 0.60, 0.71 with the Pt atomic configuration $5d^{10}6s^0$, $5s^96s^1$, $5s^86s^2$, $5d^76s^26p^1$, respectively (see Section 4.1 for more detail), indicating that the pzc is very sensitive to the exact solvation radius of the element.

3.2. MPB implementation in slab calculations

We utilize the MPB equation as shown in Eq. (2) [16,18] to determine the total electrostatic potential, where k is the Boltzmann constant, T is the absolute temperature, and $v = 2a^3c_b$ (a is the effective ion size and c_b is the bulk concentration of the electrolyte). The technique detail for the implementation of the numerical PB solver in periodic slab calculations was described in our previous work

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