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First principles Tafel kinetics of methanol oxidation on Pt(111)

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ABSTRACT

Electrocatalytic methanol oxidation is of fundamental importance in electrochemistry and also a key reaction in direct methanol fuel cell. To resolve the kinetics at the atomic level, this work investigates the potential-dependent reaction kinetics of methanol oxidation on Pt(111) using the periodic first principles continuum solvation model based on modified-Poisson–Boltzmann equation (CM-MPB), focusing on the initial dehydrogenation elementary steps. A theoretical model to predict Tafel kinetics (current vs potential) is established by considering that the rate-determining step of methanol oxidation (to CO) is the first C–H bond breaking ($CH_3OH_{(aq)} \rightarrow CH_2OH^* + H^*$) according to the computed free energy profile. The first C–H bond breaking reaction needs to overcome a large entropy loss during methanol approaching to the surface and replacing the adsorbed water molecules. While no apparent charge transfer is involved in this elementary step, the charge transfer coefficient of the reaction is calculated to be 0.36, an unconventional value for charge transfer reactions, and the Tafel slope is deduced to be 166 mV. The results show that the metal/adsorbate interaction and the solvation environment play important roles on influencing the Tafel kinetics. The knowledge learned from the potential-dependent kinetics of methanol oxidation can be applied in general for understanding the electrocatalytic reactions of organic molecules at the solid–liquid interface.

1. Introduction

The direct methanol fuel cells (DEFCs) are regarded as a key technology for energy storage and conversion, which features methanol oxidation (MOR) on an anode to deliver clean, abundant and reliable energy ($CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$) [1–5]. The state-of-the-art DMFC anode catalysts are generally Pt-based materials [6–9]. Extensive studies on MOR kinetics have been carried out in the past decades [10–17] with the aim to reduce Pt usages (e.g. alloys or dispersing into nanoparticles) while improving CO tolerance [18–21]. It is generally accepted that methanol could be oxidized to CO_2 via a dual-path mechanism [22–24], namely, the indirect pathway via adsorbed CO and the direct one without the participation of CO. In both pathways, the dehydrogenation reactions (either the C–H or O–H bond breaking) are the initiating steps. To date, the major concern in the catalyst design is to maintain the dehydrogenation efficiency of Pt while reducing its CO poisoning.

From the combined chronoamperometry and mathematical simulation [11,23,25], it was regarded that the C–H bond breakage (e.g. $CH_3OH \rightarrow CH_2OH + H^+ + e$) is the rate-determining step. This is supported by some theoretical calculations [26–32]. For example, Greeley et al. have shown that the initial C–H bond breaking is the rate-determining step for methanol decomposition in vacuum. The reaction barrier of the O–H bond breaking (0.64 eV) is higher than that of the C–H bond breaking (0.51 eV) [33,34]. The kinetic data from the experiment has been utilized to construct the current ~ overpotential ($\log(j) \sim \eta$) plot, known as the Tafel plot. The Tafel equation as shown Eq. (1) is a fundamental equation in the kinetics of electrochemistry, which relates the overpotential $\boldsymbol{\eta}$ with the current density j using the charge transfer coefficient α (i.e. if the rate-determining step involving one electron transfer with the charge transfer coefficient α of ca. 0.5, the Tafel slope $2.3RT/\boldsymbol{\alpha}\mathbf{F}$ should be 118 mV). Interestingly, the measured Tafel slopes of methanol decomposition span in a wide window, from 95 to 440 mV by different experimental groups, e.g. 110 and 95 mV for Pt(554) and Pt(553) [11], 130–140 mV at polycrystalline(pc)-Pt [23] and even ~440 mV at pc-Pt [33]. The large distribution of the Tafel slope obtained from experiment, on the other hand, indicates a complex dehydrogenation kinetics on Pt surfaces, which could be quite sensitive to the catalyst condition and the experimental setups.

$$\boldsymbol{\eta} = \mathbf{a} - \frac{\mathbf{2.3RT}}{\boldsymbol{\alpha}\mathbf{F}} \mathbf{log}(\boldsymbol{j}) \tag{1}$$

Ideally, theoretical kinetic model based on first principles calculations should be utilized to benchmark and rationalize different experimental data, as that was often practiced in heterogeneous catalysis [35,36]. One major concern for current density functional theory (DFT)

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calculations is the lack of proper means to simulate accurately the electrochemical conditions, in particular to treat simultaneously the electrochemical potential, the surface charging and the solid–liquid interface. With the advent of the periodic DFT/CM-MPB method developed recently, the potential dependent kinetics of elementary electrocatalytic reactions can now be investigated in one unified theoretical framework. This work represents a latest application of the DFT/CM-MPB [37–39] method for resolving the puzzles on the Tafel kinetics of MOR and for providing insights into the oxidation mechanism of organic molecules on metal at the atomic level. Multiple reaction pathways for methanol decomposition on Pt(111) surface are investigated in detail and the free energy profiles are computed, based on which the potential dependent kinetics model is established and discussed in the context of experimental findings.

2. Methods

All DFT calculations were performed using the SIESTA package with numerical atomic orbital basis sets [40,41] and Troullier–Martins normconserving pseudopotentials [42]. The exchange-correlation functional utilized was at the generalized gradient approximation level, known as GGA-PBE [43]. The optimized double-ζ plus (DZP) polarization basis set was employed. All transition states (TSs) of the catalytic reaction were searched using our recently-developed methods within the Constrained-Broyden scheme [44–46]. For Pt(111), we utilized p(4 × 4) (16 atoms per layer) six-layer slabs with adsorbates on both surfaces, respectively. The Monkhorst_Pack type of k-point sampling with a (2 × 2 × 1) mesh was used in all calculations, and the denser (4 × 4 × 1) k-point mesh was used to further check the convergence of reaction energetics. The other calculation detail is as those described in our previous work [47,48].

The solid/liquid interface is described using the periodic continuum solvation model based on the modified Poisson–Boltzmann equation (CM-MPB), which can take into account the long-range electrostatic interaction due to the solvation of electrolyte [37,48,49]. The DFT/CM-MPB method has been utilized to calculate the electro-photo catalytic reactions at the solid–liquid interfaces [37,38,49], and compute the fundamental properties of metal surfaces in the solution, such as the potential of zero charge and the differential capacitance, where the calculated values show a good agreement with the available experimental data [48]. For strongly polarized molecules at the solid–liquid interface, such as CH_3OH and the related reaction intermediates, we have to further add explicit H_2O molecules as the first solvation shell within the DFT/CM-MPB framework to compute accurately the energetics, i.e. via a hybrid approach with both explicit and implicit solvation to describe the solvation environment.

It should be noted that the current DFT/CM-MPB method is performed on the basis of the constant-charge framework, in which a surface slab at a fixed net charge (q) can be routinely calculated. As there are two surfaces per slab, the surface net charge Q_{net} equals to half of the total net charge q, $Q_{net} = q/2$. The neutralizing charge ($-q$) is distributed in the vacuum region of the slab following the modified Poisson–Boltzmann equation, mimicking the polarized ionic charge distribution (diffuse layer) in the solution [37]. The constant-charge model in calculation is however not exactly what is operated in the experiment, where the electrode is generally held under a certain potential. We therefore need to convert the kinetic data collected at a certain charge q to that at a certain potential U, which can be summarized briefly as follows.

For an elementary reaction, the free energy barrier $\Delta G_a(q = 0, \theta_i)$ at the potential of zero charge ($q = 0$) condition can be obtained first using Eq. (2),

$$\Delta G_a(q, \theta_i) = G_{TS}(q, \theta_i) - G_{IS}(q, \theta_i) \tag{2}$$

$$\Delta G_a(U, \theta_i) = \Delta G_a(q, \theta_i)|_{q \Leftrightarrow U} \tag{3}$$

where θ_i indicates the surface phase characterized by a particular local coverage i and $G_{TS/IS}$ are the free energies at the TS/IS (IS: initial state). In this work, the coverage of methanol is kept as 0.0625 ML on Pt(111), which corresponds to a typical low coverage condition. This first step ($q = 0$ calculations) involves the location of the relevant TS and ISs at the charge neutral condition, as is typical in standard periodic DFT packages. Next, one needs to establish the linkage between the charge q and the potential U. This is done by carrying out a series of calculations with the variable q and simultaneously measuring the potential U of each q state using DFT/CM-MPB. The absolute electrochemical potential of the system (a surface slab) can be measured by computing the work function in the solution and then referring it to the experimental work function of the standard hydrogen electrode (SHE, 4.4–4.8 from experiment; and 4.6 V utilized in this work). By this way, the free energy barrier at a concerned U can be finally obtained with Eq. (3). The free energy correction (referring to the standard state) to the DFT/CM-MPB total energy can be derived by using the standard thermodynamic equations (see for example ref. [50]). The constant-charge DFT/CM-MPB method for computing the potential dependent kinetics of electrocatalytic reactions has been utilized to resolve the complex reaction network of hydrogen evolution on Pt and Au surfaces recently [51].

3. Results

3.1. CH_3OH adsorption at the interface

To address the kinetics of MOR, it is essential to understand first how methanol molecule adsorbs at the solid/liquid interface, which is the precursor leading to the methanol oxidation. The possible structure of adsorbed CH_3OH on Pt(111) has been explored by using the hybrid explicit/implicit solvation model. The explicit H_2O molecules (at least two molecules) nearby the methanol are found to be important to obtain accurate energetics.

We identified two of the most stable configurations of CH_3OH on Pt(111), namely, the IS-A and IS-B configurations. These two configurations are shown in Fig. 1. In the IS-A configuration (Fig. 1(a)), the O atom of CH_3OH attaches to a surface Pt atom via a O – Pt bond (2.45 Å) together with another adsorbed water molecule; in the IS-B configuration, CH_3OH is hydrogen-bonded (1.51 Å) with the adsorbed H_2O, having no direct contact with the surface. These two structures are quite close to the bilayer structures for H_2O adsorption on metal surfaces as previously found by theory and experiment [52,53]. This may not be surprising considering that the dominant interaction between molecules is the same, i.e. the hydrogen bonding.

$$\Delta E_{ad} = E^{sol}_{CH_3OH\text{-}H_2O/sur} - E^{sol}_{sur} - E^{sol}_{CH_3OH} - 2E^{sol}_{H_2O} \tag{4}$$

The stability of the CH_3OH–H_2O complexes shown in Fig. 1 can be calculated using Eq. (4) by referring to the individual surface or molecules in the bulk water solution, where E_X^{solv} (X = CH_3OH-H_2O/sur, sur, CH_3OH and H_2O) denotes the total energies calculated from the DFT/CM-MPB for system X. We found that the IS-B configuration (−0.74 eV) is slightly more stable compared to the IS-A adsorption configuration (−0.71 eV) (by 0.03 eV), which suggests that the direct interaction between methanol and Pt(111) surface is weak and can be readily influenced by the solvation environment. We noticed that for the adsorbed CH_3OH–H_2O complex, their H-bonding distances are generally shorter (1.51 Å for the IS-B configuration or 1.68 Å for the IS-A) compared to the CH_3OH–H_2O complex in the bulk solution (1.70 Å). This indicates that the molecules upon adsorption are further polarized by the surface through the metal/molecule covalent bonding, which influences the H-bonding interaction at the solid/liquid interface.

To better understand the adsorption strength of the individual methanol molecule, we also compared the ΔE_{ad} for methanol on Pt(111) in vacuum condition and in the CM-MPB solvation condition

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