

# Electrochemical reactions at the electrode/solution interface: Theory and applications to water electrolysis and oxygen reduction

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Theoretical simulations on complex electrochemical processes have been developed on the basis of the understanding in electrochemistry, which has benefited from quantum mechanics calculations. This article reviews the recent progress on the theory and applications in electrocatalysis. Two representative reactions, namely water electrolysis and oxygen reduction, are selected to illustrate how the theoretical methods are applied to electrocatalytic reactions. The microscopic nature of these electrochemical reactions under the applied potentials is described and the understanding of the reactions is summarized. The thermodynamics and kinetics of the electrochemical reactions affected by the interplay of the electrochemical potential, the bonding strength and the local surface structure are addressed at the atomic level.

**density functional theory, electrode/solution interface, water electrolysis, oxygen reduction reaction, review**

## 1 Introduction

The first-principles methods have been widely utilized to describe and predict significant quantities in chemistry, e.g. the geometrical structure, the bonding energy and the reaction barrier of elementary reactions. Much progress has been made in the understanding of catalytic reactions at the solid/gas interface [1–3]. Electrocatalysis at the solid/liquid interface remains a highly challenging field where the first-principles simulation is increasingly utilized. Despite the intrinsic complexity of the many-body problem in electrocatalysis (water, ions, adsorbates and electrodes), theoretical simulation methods based on first-principles theory have been developed for investigating the reactions under electrochemical conditions [4–7]. This review aims to summarize the theoretical models and their applications in typical electrochemical reactions.

Electrocatalysis is closely related to new energy generation [8–11], necessitating an atomic-level understanding of

the reactions at the electrode/solution interface. The conventional theories in electrochemistry [12], such as Gouy-Chapman theory, Nernst equation and Butler-Volmer model, often meet difficulties in rationalizing the microscopic mechanism in electrocatalysis, not least because of the complex nature of the geometrical and electronic structure of the electrode and solution. Advances in both computational facilities and theoretical methods [13, 14] have enabled the quantum mechanics (QM) treatment of the electrochemical interface in a much more realistic way, where the electrochemical potential, the water environment and the electrode are all taken into account explicitly. The combination of the modern experimental techniques with the theoretical modeling made it possible to reveal the atomic-level details of the reaction at the electrode/solution interface.

With the aim to establish a predictive basis for the design and optimization of electrocatalysts, a number of elementary electrochemical reactions have been studied utilizing first principles density functional theory (DFT) calculations. Among those reactions, water electrolysis and oxygen reduction reaction (ORR) perhaps have been most frequently

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studied because of their relevance to fuel cell applications. The former is an oxidation reaction occurring on an anode, and the latter is a reduction process occurring on a cathode. These two reactions provide insights on how the current theoretical framework is applied for understanding electrocatalytic reactions in general.

## 2 General background on DFT methods for simulating reactions

An accurate description of molecule-surface interaction is the first step toward a fundamental understanding of reactions on an electrode surface. The modeling of the surface using the first-principles methods was, however, a formidable task for many years [15], and a breakthrough was only made with the advent of DFT and powerful computers in the late 1980s [16]. In general, DFT starts with a consideration of the entire electron density of the system based on the foundation work of Hohenberg and Kohn [17, 18], in which the ground-state total electronic energy is demonstrated to be a function of the electron density. In the framework of DFT, the non-classical part of electron-electron interaction energy, namely electron-electron exchange and correlation, is expressed as a unified function of a single variable, i.e. the total electron density, which is much simpler compared with the conventional Hartree-Fock approach. Although the exact form of the exchange-correlation functional is yet unknown, many approximate functionals have been proposed in practice, such as local density approximation (LDA) and its derived version of generalized gradient approximation (GGA) [19, 20]. It has been demonstrated that GGA reproduces satisfactory structures up to the experimental accuracy and bond energies with errors within a few percents compared with experimental results [21].

To model extended surface systems, two different models, the cluster and the supercell, were often utilized. While the cluster approach could be treated with highly accurate QM methods beyond DFT, the cluster size is often limited and the metal surface is often represented by dozens of atoms. The supercell approach [22] developed in the 1980s is based on Bloch's theorem [23] in solid physics, in which the delocalized wavefunction is split into a local part (Bloch function) and a plane-wave part. By integrating DFT, Bloch's theorem, and many other elegant methods/algorithms, such as the ultrasoft pseudopotential method [24], the iterative minimization scheme [22], and Broyden's method for density mixing [25], the state-of-the-art computational package is able to efficiently solve the electronic structure of systems up to hundreds of atoms.

Using DFT, the forces on atoms are evaluated based on the Hellmann-Feynman theorem. The structure optimization techniques, such as BFGS method [26], molecular dynamics [22], and transition state (TS) search techniques are utilized to determine the possible states along a reaction

pathway, e.g. the initial state (IS), TS and the final state (FS)). The calculated pathways and energetics provide significant information on the reaction kinetics. The TS is of particular significance for kinetics as it determines the barrier height of the reaction. Several methods have been utilized to locate the TS for heterogeneous catalytic reactions, e.g. constrained minimization method [27–29], nudged elastic band method [30] and the dimer method [31, 32].

## 3 Theoretical methods for electrochemical reactions

The electrode/solution interface phenomena have been a hot subject of theoretical simulations, to which various theoretical approaches based on classical mechanics have been applied, such as Canonical Monte Carlo [33, 34], Wertheim-Lovett-Mou-Buff (WLMB) integral equation [35, 36], modified Poisson-Boltzmann [37–39], and molecular dynamics [40, 41]. Using these approaches, some features of the electrode/solution interface, such as the dynamic ordering of the interfacial water [41, 42] and the structure of the electrochemical double layer, [33] have been elucidated. However, they are unsuitable for electrochemical reactions which are sensitive to both the atomic structure of electrodes and the distribution of solutions and charges at the interface as influenced by the applied potential. The rigorous QM treatment is essential for obtaining the reliable energetics for electrochemical reactions. Some theoretical methods based on first-principles calculations have been developed to treat the electrochemical interface, and their applications for understanding the mechanism of electrocatalytic reactions have been reported. The details of these methods will be elaborated as follows.

To correctly describe the electrochemical environment, the effect of the electrochemical potential is first taken into account. A direct approach to model the induced electric field in electrochemistry is via the addition of a homogeneous external field perpendicular to the surface in simulation. This is implemented straightforwardly by adding an extra potential term to the Hamiltonian. The potential is tuned by changing the strength of the external field. This technique has been widely adopted to investigate the electric field dependence of adsorption, such as CO/Pt(111) by van Santen [43], H<sub>2</sub>O and OH/Ag(111) by Patrito [44, 45]. The oxygen-related electrochemical reaction, e.g. oxygen reduction, has also been studied by directly applying the electric field [46–48]. This approach is simple to be implemented, however, it is not straightforward to quantitatively correlate the applied field with the electrochemical potential induced by the charged electrode and the counter ions in solution.

An alternative way of modeling potential-dependent interface developed by Anderson and coworkers involves a semiempirical Atom-Superposition and Electron-Delocali-

zation Molecular Orbital theory (ASED-MO) [49, 50]. In the approach, the electrochemical potential is calculated with a band shift method by relating the diagonal element of Hamiltonian matrix of the metal with the applied potential. Later Anderson's group developed a charge self-consistent model to describe the reversible potentials and the reaction energies for electrochemical redox reactions [4, 51–58]. They utilized a small cluster to represent the reaction center (as shown in Figure 1(a)). Two approaches to calculate the reversible potential have been implemented. In the first approach, the reversible potential ( $U^0$ ) is calculated by using the equation  $\Delta G^0 = -nFU^0$ , where the free energy change  $\Delta G^0$  is obtained by the reaction energy between reactants and products. The second approach is more complex, involving the calculation of the ionization potential (IP) and the electron affinity (EA) of the reaction system, where both the reaction coordinates and the charge of the system vary during the oxidation/reduction. Using this method, the potential and potential-dependent activation energy are estimated. This model is the first major step towards understanding the elementary electrocatalytic reaction under the electrochemical potential. The contribution from the electrolyte has been reported [4, 57–59] by incorporating into Hamiltonian a Madelung sum over the assumed average point-charge ions. The major limitation of the approach is that the metal electrode is solely modeled by one or two atoms, which is not valid for addressing the effects of surface structure and composition.

Norskov and coworkers have explored the thermodynamics of electrochemical reactions via a simple approach [6, 60–62]. Their method takes advantage of the equality of the free energy of a gas phase hydrogen molecule with that of a proton and an electron at standard conditions. In this way, the free energy for the reaction  $*\text{AH} \rightarrow \text{A} + \text{H}^+ + \text{e}^-$  is transferred as the free energy of the reaction  $*\text{AH} \rightarrow \text{A} + 1/2\text{H}_2$ . The presence of the potential  $U$  could shift the free energy of a state by  $-neU$  magnitude ( $\Delta G_U$ ). By combining the thermodynamics with the DFT calculations, the free energy of each intermediate becomes comparable after correcting the energy of extra protons, electrons and water. The solvation interaction was modeled by including 2/3 monolayer of water (hexagonal ring structure) on the metal surface as suggested by Ogasawara [63]. A simple estimate of the effect of electric field  $\Delta G_{\text{field}}$  was considered [48, 64] by calculating the coupling between the dipole moment of the adsorbed state and the average electric field just outside the surface. Finally, the free energy of the reaction is derived as  $\Delta G(U, \text{pH}, p_{\text{H}_2} = 1 \text{ bar}, T) = \Delta G_0 + \Delta G_{\text{w}} + \Delta G_U + \Delta G_{\text{pH}} + \Delta G_{\text{field}}$ , where  $\Delta G_{\text{w}}$ ,  $\Delta G_U$ ,  $\Delta G_{\text{pH}}$  and  $\Delta G_{\text{field}}$  are respectively the effects of water, potential, pH and external electric field, as determined by DFT calculations.

The first practical scheme for performing DFT calculations for a charged slab was developed by Lozovoi *et al.* [65, 66], in which a reference electrode is introduced in the supercell to compensate the charge. The solvation effects

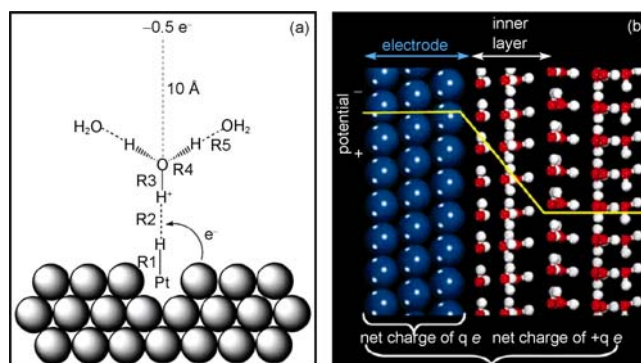
have not been considered. Neurock and coworkers proposed a double-reference method to describe the metal/water interface (Figure 1 (b)), in which the water layers outside the metal surface are explicitly included [7, 67–71]. The electrode surface is represented by the standard slab model, while several layers of water molecules fill the vacuum gap in between the slabs. The metal/water interface is polarized by altering the number of electrons included in the simulation cell, and the overall charge neutrality is maintained with a homogeneous background countercharge, whose contribution to the total energy and potential is subtracted afterwards. The double reference approach has been used to describe the potential dependence of various elementary reactions in fuel cell applications.

We developed a more simple approach based on the periodic DFT calculation [72], which is described in detail as follows. As shown in Figure 2, the metal slab is placed in the center of the cell and a 30 Å vacuum is introduced along the  $z$  direction. The adsorbed species and water layers, if any, are added/subtracted symmetrically on both sides of the slab. The slab is charged by adding or subtracting a predetermined number of electrons. Since there are two symmetric surfaces in the slab, excess charges are evenly divided onto two surfaces ( $Q/2$ ). To balance the excess charge  $Q$ , the counter charge is added as two charge planes in the form of Gaussian distribution along the  $z$  direction, each with  $-Q/2$ . One plane is near the top surface, and the other is near the bottom surface. The Gaussian charge plane centers are either at the first water layer (with water) or at a fixed  $z$ -height (typically about 3 Å) away from the outmost surface atom (without water). In order to calculate the electrochemical potential ( $U$ ) of a system, the following eqs. (1) and (2) are used according to the definition of the absolute electrochemical potential [73].

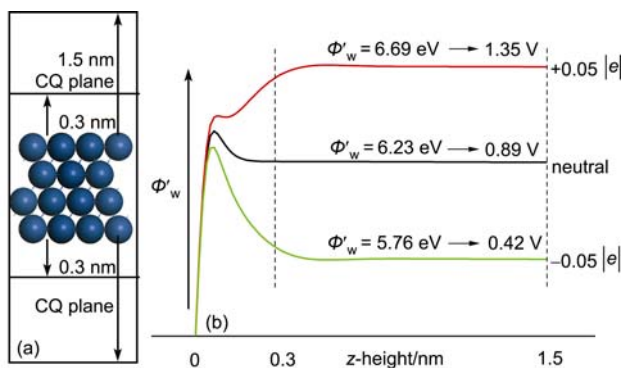
$$U/V = (\Phi_{\text{w}} - 4.6)/\text{eV} \quad (1)$$

$$\Phi_{\text{w}} = \Phi_{\text{ref}} - \Phi_{\text{f}} \quad (2)$$

$\Phi_{\text{w}}$  is the work function, which is related to the electro-



**Figure 1** Illustration of the reaction center model, Pt-H... H<sup>+</sup>(OH<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub> for H<sub>2</sub> formation (a), the periodic slab employed with the double-reference method to determine the potential (b). (a) and (b) are respectively from refs. [59] and [69].



**Figure 2** (a) Symmetric slab model with the counter charge (CQ) plane in vacuum; (b) electrostatic potential averaged in the  $xy$  plane above Pt(111) surface ( $z$ -height = 0) for systems with different charges per  $p$  ( $\sqrt{3} \times \sqrt{3}$ ) unit cell. The workfunction  $\Phi'_w$  and the electrochemical potential are subsequently obtained.

chemical potential by eq. (1) considering that the typical hydrogen electrode (NHE) has a measured work function of  $\sim 4.6$  eV experimentally [74]. In theory, the workfunction  $\Phi_w$  is obtained by measuring the difference between  $\Phi_f$ , the Fermi level of system, and a pre-defined reference level of zero potential, i.e. the potential level in solution far away from the surface. However, it is practically impossible for first principles calculations to obtain the accurate reference level because of the difficulty in treating the long-range screening effect of water and counter ionic charge in solution. However, we could adopt an indirect approach, in which the experimental value for the potential of zero charge (pzc) is used to correct the calculated workfunction  $\Phi'_w$  to yield a more reasonable  $\Phi_w$ , as described by eq. (3).

$$\Phi_w = \Phi'_w - (\Phi'_{w\text{pzc}} - \Phi_{\text{pzc}}^{\text{exp}}) \quad (3)$$

where the  $\Phi_{\text{pzc}}^{\text{exp}}$  is the average experimental pzc value for Pt(111), which is about 4.85 eV (0.25 V NHE) [75, 76].  $\Phi'_{w\text{pzc}}$  is the theoretical workfunction for neutral Pt(111) at the approximated reference level. For example, we could calculate a finite layer of  $\text{H}_2\text{O}$  covered Pt(111) surface and use its workfunction as  $\Phi'_{w\text{pzc}}$ . Alternatively, we may totally omit the  $\text{H}_2\text{O}$  layer, i.e. the largest approximation, and use the calculated workfunction of Pt(111) as  $\Phi'_{w\text{pzc}}$  ( $\sim 5.5$  eV from DFT, consistent with experimental values [77, 78]). For any other systems (charged or neutral), the similar condition as utilized in calculating  $\Phi'_{w\text{pzc}}$  is used to obtain  $\Phi'_w$  and subsequently U (NHE).

To compare the total energy of phases with different charges, the DFT-calculated energy is corrected following eq. (4). As suggested previously by Neurock's group [7], two extra energy contributions are removed from DFT total energy, i.e. (i) the energy of the countercharge itself ( $E_{\text{CQ}}$ ) and its electrostatic interaction with the charged-slab

( $E_{\text{CQ-slab}}$ ) and (ii) the energy of the excess charge in the slab ( $n_{\text{Q}}E_{\text{F}}$ ). This is expressed as

$$E_{\text{corrected}} = E_{\text{DFT}(n_{\text{Q}}, n_{\text{CQ}})} - (E_{\text{CQ}} + E_{\text{CQ-slab}}) - n_{\text{Q}}E_{\text{F}} \quad (4)$$

Using the method, we have investigated the mechanism of oxygen evolution on differently structured Pt surfaces.

To better account for the solvation energy, Anderson's [79, 80] group and our group [81] further implemented a continuum-solvation method based on the Poisson-Boltzmann (PB) theory [37] to model the electrode/solution interface. Different from previous theoretical models, the continuum-solvation approach describes the distribution of the diffuse ionic charges close to the interface and obtains more accurate solvation energy by fitting parameters of PB equation. A smooth dielectric model function [82] is utilized in solving the Poisson-Boltzmann equation numerically. With the empirical models, Anderson's group took into account the finite size effect of the ions and the nonelectrostatic solute-solute and solute-electrode interactions. Using the modified PB theory, Anderson's group have analyzed the potential of zero charge on Pt(111) and the redox potentials of hydrogen oxidation reaction (HOR) and ORR [79, 80]. Our group [81] utilized this approach to study the formic acid decomposition on Pt surface under electrochemical conditions, where the solvation energy's contribution to the reaction barrier is corrected by solving the PB equation.

## 4 Applications of the theoretical methods

### 4.1 Water electrolysis

Water splitting in electrochemistry is one of the most significant anodic reactions involved in many applications concerning energy storage/conversion [83, 84]. Because the reaction causes the major energy loss, the mechanism of the electrochemical process has been consistently pursued for years [85–87] with the aim to design better catalysts. The oxidative species, such as  $\text{OH}_{\text{ad}}$  and  $\text{O}_{\text{ad}}$  from  $\text{H}_2\text{O}$ , appear on the electrode at certain positive potentials. By further increasing the potential,  $\text{O}_2$  was generated from these surface oxidative species. However, the detailed mechanism for water electrolysis on the electrode falls far short of expectation. The aforementioned theoretical methods have been utilized to shed light on the microscopic nature of the process.

Anderson and coworkers made the first attempt to simulate the dissociation of water on small metal clusters [88–92]. The formation energy of the adsorbed OH ( $\text{OH}_{\text{ad}}$ ) and its activation energy on Pt have been studied using the semiempirical ASED-MO model. They concluded that the  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}_{\text{ad}} \rightarrow \text{OH}_{\text{ad}} + \text{H}_{\text{ad}}$ ) and OH ( $\text{OH}_{\text{ad}} \rightarrow \text{O}_{\text{ad}} + \text{H}_{\text{ad}}$ ) homolytic cleavage is unlikely to occur below 0.6 V due to the high reaction barrier (1.35 eV) [88]. They utilized the local reaction center model to investigate the  $\text{OH}_{\text{ad}}$  formation in the acid and base solutions [57, 93]. In the latter, water split

to hydroxyls through an oxidative deprotonation pathway:  $\text{H}_2\text{O}_{\text{ad}} \rightarrow \text{OH}_{\text{ad}} + \text{H}^+ + \text{e}^- (\text{U})$  [57]. Such a pathway for the dissociation of  $\text{H}_2\text{O}_{\text{ad}}$  has a lower activation energy above 0.57 V than that of the homolytic cleavage pathway. In addition,  $\text{OH}_{\text{ad}}$  formation on the Fe and alloy surface, i.e.  $\text{Pt}_3\text{Cr}(111)$ ,  $\text{Pt}_3\text{Co}(111)$ , was calculated [92, 94–96], which showed that the oxidative deprotonation pathway on these surfaces is favored.

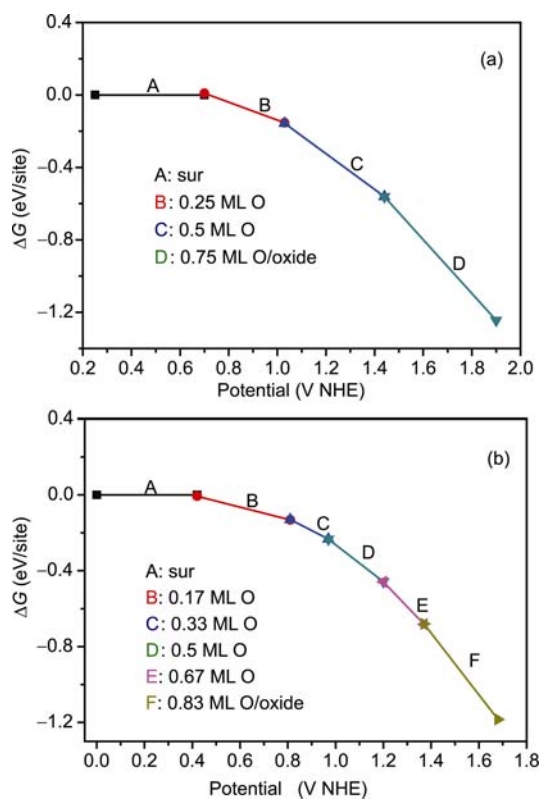
By applying an excess of charges to the periodic slab, Neurock's group investigated the electrochemical response of water and its derived products. Filhol and Neurock considered  $\text{H}_2\text{O}$  interaction with  $\text{Pd}(111)$  based on the double reference method [7] and determined the phase-diagram which correlates the surface species with the applied electrochemical potential. At strong positive potentials, water molecules tend to align with their oxygen ends towards the surface. Above 1.1 V (experimental value 0.7–0.9 V), the free energy of the hydroxide phase becomes lower than that of the water phase, which leads to a phase change. By contrast, at low potentials the hydrogen end of water points toward the surface. The change from the water phase to the hydride phase is calculated to occur at 0.5 V (experimental value  $\sim 0.4$  V [97, 98]). The same approach was later extended to investigate the phase diagram over different metal substrates including  $\text{Cu}(111)$  [99],  $\text{Ni}(111)$  [68] and  $\text{Pt}(111)$  [64]. The results show that the phase diagrams have the same trend with that of Pd. Water is activated to form adsorbed hydroxyls, oxygen and finally a surface oxide layer. In addition, the geometric changes were observed with the change of the electrochemical potential. For example, the bond length between the oxidative species (oxygen on water, hydroxyls and oxygen atoms) and metal surface ( $\text{Cu}(111)$  and  $\text{Ni}(111)$ ) decreases as the surface gets more positively charged.

Nørskov's group focused on the thermodynamic aspects of the electrochemical reactions, in which the effect of the electrochemical potential is simplified and taken into account by the equation  $\Delta G_{\text{U}} = -neU$ . They explored the thermochemistry of water splitting as a function of potential bias on a series of surfaces including metal surfaces and oxide surfaces [61, 62, 64, 100]. The solvation effect of water was simplified and modeled by covering the surface with a few water molecules. The methods from Neurock and Nørskov yield consistent phase diagrams for Pt in contact with  $\text{H}_2\text{O}$ : the adsorbed hydrogen formation occurs at 0.09 V and the oxidative species formation starts at 0.8 V. The calculated phase transition potentials are in agreement with experiment observation [60, 101]. According to thermodynamics, they proposed that the difficult step in the water splitting process is the formation of superoxy-type (OOH) species on the surface, which may be formed by the dissociation of a water molecule on top of an adsorbed oxygen atom. They further proposed a linear relationship between the catalytic activity of the electrode and the binding energy of oxygen ( $\Delta E_{\text{O}}$ ). With this simple descriptor for

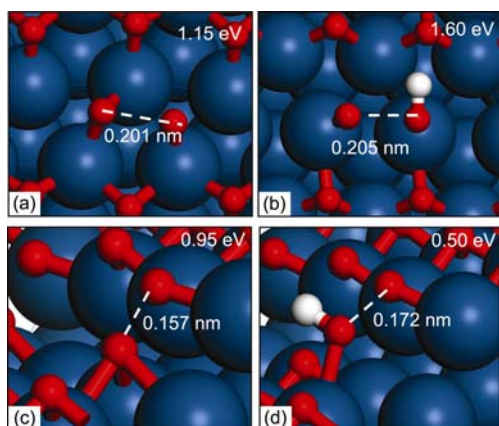
the activity, it is expected that better anode materials may be designed and optimized.

Focusing on the oxygen coupling kinetics, we utilized the Gaussian-charge-plane model to understand the oxygen evolution process [72], where the effects due to the surface structure, the electrochemical potential and the solvation are considered. The surface phase diagrams for the  $\text{Pt}(111)$  and the stepped (211) surfaces were determined, as shown in Figure 3. The phase-diagrams show that stepped surface sites better accumulate oxidative species (O and OH), which leads to higher local O coverage compared with terrace sites at the same potential condition. The effect of the water environment on surface phase diagram is quantitatively evaluated and found to be small. All oxygen coupling reaction channels on Pt surfaces at different potentials were examined. It is shown in Figure 4 that the local surface coverage and the surface structure are much more significant. At low potentials the oxygen coupling reaction is the rate-determining step and an  $\text{O} + \text{OH} \rightarrow \text{OOH}$  reaction eventually occurs at a high local coverage of the stepped sites (at  $\sim 1.4$  V, when the oxidation of the metal surface starts to evolve) with the calculated barrier lower than 0.7 eV (Figure 4). By contrast, no facile O coupling channels exist on  $\text{Pt}(111)$  as the barriers are no less than 1 eV.

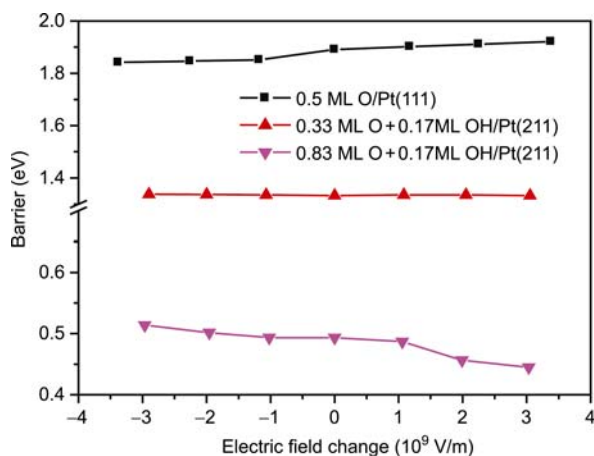
We have shown that the variation of the electric field (the charged surface) only marginally influences the barrier of oxygen coupling reactions. As shown in Figure 5, the effect of the electric field induced by the excess surface charges



**Figure 3** Surface phase diagram of  $\text{Pt}(111)$  (a) and  $\text{Pt}(211)$  (b).



**Figure 4** Located TS structures and the calculated barrier on Pt(111) for (a) O+O reaction at 0.75 ML O coverage; (b) O+OH reaction at 0.75 ML O+0.0625 ML OH coverage; (c) O+O reaction at 0.83 ML O coverage; (d) O+OH reaction at 0.83 ML O+0.17 ML OH coverage.



**Figure 5** Oxygen coupling barrier on charged surfaces as influenced by the change of the electric field. The zero in the  $x$ -axis corresponds to the neutral situations.

on the barrier is below 0.1 eV per change of  $10^9$  V/m. This is consistent with the results of other theoretical studies showing that the barrier of oxygen reduction reaction is slightly affected by electric fields [48, 61]. Considering that the electric field at the anode is typically in the range of  $10^8$ – $10^{10}$  V m $^{-1}$ , we concluded that the shift of the electrochemical potential does not significantly change the reaction barrier in a direct manner. Instead, the potential variation could adjust the surface coverage of oxidative species, which effectively reduces/increases the barrier of oxygen coupling reactions.

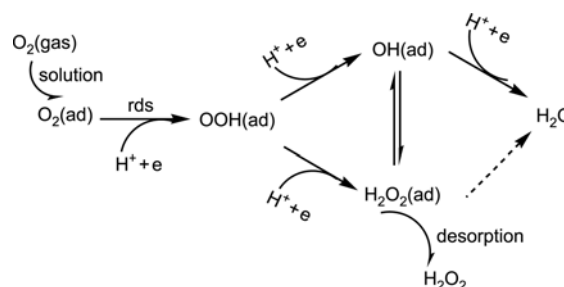
Through theoretical analyses, we outlined two factors affecting the electrocatalytic activity for water electrolysis: (i) the adsorption energy of oxidative species, and (ii) the surface local structure. We showed that Pt surface has a strong oxygen bonding ability at low coverages. The overpotential is required for increasing the surface coverage and reducing the adsorption energy of oxidative species. The

adsorption energy of oxidative species is thus the essential thermodynamic factor. Perhaps more significantly, an optimum surface structure was found to be essential for oxygen coupling reaction kinetically. Provided with the similar O adsorption energy, stepped surface sites facilitate the coupling between O and OH, largely due to the fact that the oxygen atom on (111) surface shifts from its original fcc hollow site to the atop site in order to couple with another O or OH species, which induces a significant energy cost.

## 4.2 Oxygen reduction reaction

The oxygen reduction reaction (ORR) is a key step in hydrogen fuel cells [102, 103]. However, the ORR at the cathode requires a high overpotential (i.e.  $\sim 300$  mV on Pt-based electrocatalysts), which is one of the major obstacles hindering practical applications of fuel cells [9, 104]. To improve the cathode's catalytic efficiency, fundamental research has been carried out to elucidate the mechanism and the origin of the overpotential [47, 105, 106]. Although there is no consensus on the exact ORR mechanism [107–109], the reaction was generally believed to follow roughly the path shown in Scheme 1, where the four-electron transfer occurs stepwisely. In the reaction, the OOH intermediate is a key reaction intermediate, the formation of which might be the rate-determining step on Pt [48, 53, 54, 101, 110–112]. However, according to the Sabatier principle the rate-determining step is not always unchanged on different materials. For metals which strongly bind oxygen, the electrochemical removal of O or OH could take over to be the rate-determining step. A good catalyst needs to have desirable oxygen binding ability. Since most theoretical studies focused on the Pt electrode, which is one of the most efficient metals for the ORR reaction, our brief review will concentrate on the understanding concerning Pt surfaces.

The first QM analysis of the oxygen reduction process at applied potentials was performed by Anderson and Albu using their reaction center model [52]. They studied the unsupported, single Pt atom supported and dual-Pt supported oxygen reduction at potentials from 0 to 2 V (SHE) by considering all possible intermediate species ( $O_2$ ,  $HO_2$ ,  $H_2O_2$ , and OH) in contact with a hydronium ion solvated with two water molecules [53, 54, 58]. Compared with the unsupported case, the presence of Pt decreases the reduction



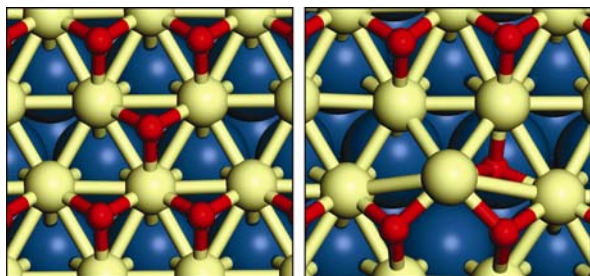
**Scheme 1** Possible mechanism of oxygen reduction reaction.

activation energies for  $O_2$  and  $H_2O_2$ . They found that  $O_2$  bound to a  $Pt_2$  site does not dissociate before the first electron and proton transfer to form OOH. The step to form OOH has the highest activation barrier and thus is the rate-determining step, in agreement with the proposed kinetic model in the literature [113, 114].

Norskov and coworkers have compared the thermodynamics of the dissociative and associative reaction paths [6, 61]. The dissociative path refers to the combination of the adsorbed atomic oxygen, originated from molecular oxygen dissociation, with the proton/electron to form  $OH_{ad}$  and further  $H_2O$ . The associative path is the direct channel in which the proton/electron transfer to the adsorbed molecular oxygen before its dissociation ( $O_{2(ad)} + H^+ + e^- = HO_{2(ad)}$ ). They found that both pathways are possibly thermodynamic, but the increase of the local electric field [48] would favor the associative path. The initial stages of oxygen reduction at the Pt(111)/water interface were also investigated by Neurock's group with the double-reference method. They suggested that the reaction is through (i) the electron transfer to the adsorbed molecular oxygen and (ii) the addition of protons which are diffused toward the electrode to form  $OOH^*$  [112].

On the basis of the mechanism on Pt(111), Norskov *et al.* calculated the adsorption energies of the surface intermediates, such as the oxygen atom, over a number of metal substrates and utilized this database to predict the rate of the cathodic reaction. Their investigation showed that Pt and Pd are the best pure metal catalysts for oxygen reduction [6, 48]. They pointed out that metals or alloys with a slightly lower oxygen binding energy than Pt could have the highest rate for oxygen reduction. In combination with experimental studies, it was found that the Pt-skin alloys between Pt and 3d late transition metals or early transition metals have much higher activity [115, 116] than pure Pt metal.

In addition to the catalytic activity, the cathode stability is another key issue concerned for oxygen reduction reaction. The high concentration of surface OH or O species has vital destructive effect on the Pt electrode [117, 118], which leads to the dissolution (loss) of Pt due to the corrosion.



**Figure 6** Identified most stable structures for the surface adsorption phase and subsurface O phase for the 0.75 ML O covered Pt(111) surface. It was shown [72] that at such a high coverage, equivalent to 1.4 V vs. NHE, the (111) surface already prefers the oxidation as evidenced by the subsurface O formation. Large ball: subsurface Pt atoms; small yellow ball: top layer Pt atoms; small red ball: O atoms.

Although at low O coverages there is a high kinetic barrier for atomic O to penetrate into the subsurface ( $\leq 0.25$  ML) [119], theoretical studies indicated that high surface coverages are more relevant to surface oxidation at high electrochemical potentials [72]. By exploring the possible subsurface O phases, where an oxygen atom per cell sits at the subsurface, and subsequently comparing their stability with that of the surface O phases, we showed that the O subsurface phase is already slightly stable at the stage of 0.75 ML O (by 0.79 eV) and 0.75 ML O + 0.0625 ML OH (by 0.31 eV) coverage of Pt(111). The structure of 0.75 ML O and the subsurface O is shown in Figure 6. This implies that the surface oxidation on (111) terraces is already thermodynamically favored at about 1.4 V. Pt surface oxidation has been observed by Jerkiewicz *et al.* and Tian *et al.*, which showed that the oxidation of Pt occurs at about 1.2 V [8, 117].

Norskov and coworkers found that many Pt alloys which have high predicted activity for the ORR were thermodynamically unstable at high potentials associated with the ORR. Only the Pt and Pd bulk alloys' "skin" structure may be active and stable for the ORR [120]. However, it was reported that after 4000 CV cycles, the CV measurement showed a loss of 30% in the electrochemically active surface area for the Pt-Pd electrode [9]. Alternatively, Zhang *et al.* demonstrated that the Pt electrode for the ORR becomes much more anti-corrosive after the deposition of Au clusters [102].

## 5 Concluding remarks

This paper reviews the progress on the theoretical simulation of electrochemistry based on first-principles methods. The understanding of the microscopic mechanisms of two key reactions in electrocatalysis, i.e. water splitting and oxygen reduction reaction, is summarized. The key points are summarized as follows.

(1) The electrochemical potential strongly affects the surface coverage of oxidative species, which effectively changes the barrier of surface reactions.

(2) The electric field induced by the excess surface charges plays a minor role in influencing the barrier of surface coupling reactions.

(3) It is possible to identify a simple descriptor to describe the catalytic activity, which is particularly useful for designing new electrocatalysts. For example, in oxygen reduction reactions, an appropriate oxygen binding energy is essential to achieve a high activity.

(4) The surface local structure could be significant for the electrocatalytic activity.

(5) The Pt surface electrochemical corrosion occurs with high O coverage, accompanied with the oxygen reduction reaction. The anti-corrosion ability of the electrode material needs to be explicitly considered in order to optimize the ORR activity of electrocatalysts.

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- 1 Hammer B, Norskov JK. Theoretical surface science and catalysis - Calculations and concepts. *Adv Catal*, 2000, 45: 71-129
- 2 Liu ZP, Hu P. CO oxidation and NO reduction on metal surfaces: density functional theory investigations. *Top Catal*, 2004, 28: 71-78
- 3 Studt F, Abild-Pedersen F, Bligaard T, Sorensen RZ, Christensen CH, Norskov JK. Identification of non-precious metal alloy catalysts for selective hydrogenation of acetylene. *Science*, 2008, 320: 1320-1322
- 4 Anderson AB, Neshev NM. Mechanism for the electro-oxidation of carbon monoxide on platinum, including electrode potential dependence-Theoretical determination. *J Electrochem Soc*, 2002, 149: E383-E388
- 5 Schweiger H, Vayner E, Anderson AB. Why is there such a small overpotential for O-2 electroreduction by copper laccase? *Electrochem Solid-State Lett*, 2005, 8: A585-A587
- 6 Norskov JK, Rossmeisl J, Logadottir A, Lindqvist L, Kitchin JR, Bligaard T, Jonsson H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J Phys Chem B*, 2004, 108: 17886-17892
- 7 Filhol JS, Neurock M. Elucidation of the electrochemical activation of water over Pd by first principles. *Angew Chem Int Ed*, 2006, 45: 402-406
- 8 Tian N, Zhou ZY, Sun SG, Ding Y, Wang ZL. Synthesis of tetrahexahedral platinum nanocrystals with high-index facets and high electro-oxidation activity. *Science*, 2007, 316: 732-735
- 9 Lim B, Jiang MJ, Camargo PHC, Cho EC, Tao J, Lu XM, Zhu YM, Xia YA. Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. *Science*, 2009, 324: 1302-1305
- 10 Imai H, Izumi K, Matsumoto M, Kubo Y, Kato K, Imai Y. *In situ* and real-time monitoring of oxide growth in a few monolayers at surfaces of platinum nanoparticles in aqueous media. *J Am Chem Soc*, 2009, 131: 6295-6302
- 11 Di Blasi A, D'Urso C, Baglio V, Antonucci V, Arico A S, Ornelas R, Matteucci F, Orozco G, Beltran D, Meas Y, Arriaga LG. Preparation and evaluation of RuO<sub>2</sub>-IrO<sub>2</sub>, IrO<sub>2</sub>-Pt and IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> catalysts for the oxygen evolution reaction in an SPE electrolyzer. *J Appl Electrochem*, 2009, 39: 191-196
- 12 Bard AJ, Faulkner LR. *Electrochemical Methods Fundamentals and Applications*. 2nd ed. New York: John Wiley & Sons Inc, 2001. 1-400
- 13 Darling GR, Holloway S. The dissociation of diatomic molecules at surfaces. *Rep Prog Phys*, 1995, 58: 1595-1672
- 14 Hammer B, Norskov JK. Electronic factors determining the reactivity of metal surfaces. *Surf Sci*, 1995, 343: 211-220
- 15 Brivio GP, Trioni MI. The adiabatic molecule-metal surface interaction: Theoretical approaches. *Rev Mod Phys*, 1999, 71: 231-265
- 16 Parr P, Yang W. *Density Functional Theory of Atoms and Molecules*. Oxford: Oxford University Press, 1989. 3-281
- 17 Hohenberg P, Kohn W. Inhomogeneous electron gas. *Phys Rev B*, 1964, 136: B864-&
- 18 Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. *Phys Rev*, 1965, 140: 1133-&
- 19 Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*, 1996, 77: 3865-3868
- 20 Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C. Atoms, molecules, solids, and surfaces-applications of the generalized gradient approximation for exchange and correlation. *Phys Rev B*, 1992, 46: 6671-6687
- 21 Ge QF, Kose R, King DA. Adsorption energetics and bonding from femtomole calorimetry and from first principles theory. *Adv Catal*, 2000, 45: 207-259
- 22 Payne MC, Teter MP, Allan DC, Arias TA, Joannopoulos JD. Iterative minimization techniques for *ab initio* total-energy calculations-molecular-dynamics and conjugate gradients. *Rev Mod Phys*, 1992, 64: 1045-1097
- 23 Ashcroft NW, Mermin ND. *Solid State Physics*. Philadelphia: Holt Saunders, 1976
- 24 Vanderbilt D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys Rev B*, 1990, 41: 7892-7895
- 25 Johnson DD. Modified broyden method for accelerating convergence in self-consistent calculations. *Phys Rev B*, 1988, 38: 12807-12813
- 26 Fletcher. *Practical Methods of Optimization*. 2nd ed. Chichester: John Wiley, 1987
- 27 Hammer B, Jacobsen KW, Norskov JK. Dissociation path for H<sub>2</sub> on Al(110). *Phys Rev Lett*, 1992, 69: 1971-1974
- 28 Alavi A, Hu PJ, Deutsch T, Silvestrelli PL, Hutter J. CO oxidation on Pt(111): An *ab initio* density functional theory study. *Phys Rev Lett*, 1998, 80: 3650-3653
- 29 Wang HF, Liu ZP. Comprehensive mechanism and structure-sensitivity of ethanol oxidation on platinum: New transition-state searching method for resolving the complex reaction network. *J Am Chem Soc*, 2008, 130: 10996-11004
- 30 Henkelman G, Uberuaga BP, Jonsson H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J Chem Phys*, 2000, 113: 9901-9904
- 31 Kaestner J, Sherwood P. Superlinearly converging dimer method for transition state search. *J Chem Phys*, 2008, 128: 014106
- 32 Henkelman G, Jonsson H. A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. *J Chem Phys*, 1999, 111: 7010-7022
- 33 Yang KL, Yiacoumi S, Tsouris C. Monte Carlo simulations of electrical double-layer formation in nanopores. *J Chem Phys*, 2002, 117: 8499-8507
- 34 Yang KL, Yiacoumi S, Tsouris C. Canonical Monte Carlo simulations of the fluctuating-charge molecular water between charged surfaces. *J Chem Phys*, 2002, 117: 337-345
- 35 Vossen M, Forstmann F. The structure of water at a planar wall-an integral-equation approach with the central force model. *J Chem Phys*, 1994, 101: 2379-2390
- 36 Kramer A, Vossen M, Forstmann F. The influence of image interactions on the structure of water and electrolytes in front of a metal surface. *J Chem Phys*, 1997, 106: 2792-2800
- 37 Borukhov I, Andelman D, Orland H. Steric effects in electrolytes: A modified Poisson-Boltzmann equation. *Phys Rev Lett*, 1997, 79: 435-438
- 38 Abrashkin A, Andelman D, Orland H. Dipolar Poisson-Boltzmann equation: Ions and dipoles close to charge interfaces. *Phys Rev Lett*, 2007, 99: 077801
- 39 Kilic MS, Bazant MZ, Ajdari A. Steric effects in the dynamics of electrolytes at large applied voltages. II. Modified Poisson-Nernst-Planck equations. *Phys Rev E*, 2007, 75: 021503
- 40 Spohr E, Heinzinger K. Computer-simulations of water and aqueous-electrolyte solutions at interfaces. *Electrochim Acta*, 1988, 33: 1211-1222
- 41 Halley JW, Mazzolo A, Zhou Y, Price D. First-principles simulations of the electrode vertical bar electrolyte interface. *J Electroanal Chem*, 1998, 450: 273-280
- 42 Spohr E. Molecular dynamics simulation studies of the density profiles of water between (9-3) Lennard-Jones walls. *J Chem Phys*, 1997, 106: 388-391
- 43 Koper MTM, van Santen RA. Electric field effects on CO and NO adsorption at the Pt(111) surface. *J Electroanal Chem*, 1999, 476: 64-70
- 44 Olivera PP, Ferral A, Patrito EM. Theoretical investigation of hydrated hydronium ions on Ag(111). *J Phys Chem B*, 2001, 105: 7227-7238
- 45 Patrito EM, Paredes-Olivera P. Adsorption of hydrated hydroxide and hydronium ions on Ag(111). A quantum mechanical investigation. *Surf Sci*, 2003, 527: 149-162
- 46 Hyman MP, Medlin JW. Theoretical study of the adsorption and dissociation of oxygen on Pt(111) in the presence of homogeneous electric fields. *J Phys Chem B*, 2005, 109: 6304-6310
- 47 Panchenko A, Koper MTM, Shubina TE, Mitchell SJ, Roduner E. *Ab*



- initio* calculations of intermediates of oxygen reduction on low-index platinum surfaces. *J Electrochem Soc*, 2004, 151: A2016–A2027
- 48 Karlberg GS, Rossmeisl J, Norskov JK. Estimations of electric field effects on the oxygen reduction reaction based on the density functional theory. *Phys Chem Chem Phys*, 2007, 9: 5158–5161
- 49 Anderson AB. Derivation of extended huckel method with corrections—one electron molecular-orbital theory for energy-level and structure determinations. *J Chem Phys*, 1975, 62: 1187–1188
- 50 Anderson AB. Electron-density distribution-functions and the ased-mo theory. *Int. J Quantum Chem*, 1994, 49: 581–589
- 51 Anderson AB, Kang DB. Quantum chemical approach to redox reactions including potential dependence: Application to a model for hydrogen evolution from diamond. *J Phys Chem A*, 1998, 102: 5993–5996
- 52 Anderson AB, Albu TV. *Ab initio* approach to calculating activation energies as functions of electrode potential—Trial application to four-electron reduction of oxygen. *Electrochem Commun*, 1999, 1: 203–206
- 53 Anderson AB, Albu TV. *Ab initio* determination of reversible potentials and activation energies for outer-sphere oxygen reduction to water and the reverse oxidation reaction. *J Am Chem Soc*, 1999, 121: 11855–11863
- 54 Anderson AB, Albu TV. Catalytic effect of platinum on oxygen reduction—An *ab initio* model including electrode potential dependence. *J Electrochem Soc*, 2000, 147: 4229–4238
- 55 Albu TV, Anderson AB. Studies of model dependence in an *ab initio* approach to uncatalyzed oxygen reduction and the calculation of transfer coefficients. *Electrochim Acta*, 2001, 46: 3001–3013
- 56 Anderson AB. O-2 reduction and CO oxidation at the Pt-electrolyte interface. The role of H<sub>2</sub>O and OH adsorption bond strengths. *Electrochim Acta*, 2002, 47: 3759–3763
- 57 Anderson AB, Neshev NM, Sidik RA, Shiller P. Mechanism for the electrooxidation of water to OH and O bonded to platinum: quantum chemical theory. *Electrochim Acta*, 2002, 47: 2999–3008
- 58 Sidik RA, Anderson AB. Density functional theory study of O-2 electroreduction when bonded to a Pt dual site. *J Electroanal Chem*, 2002, 528: 69–76
- 59 Cai Y, Anderson AB. The reversible hydrogen electrode: Potential-dependent activation energies over platinum from quantum theory. *J Phys Chem B*, 2004, 108: 9829–9833
- 60 Norskov JK, Bligaard T, Logadottir A, Kitchin JR, Chen JG, Pandelov S. Trends in the exchange current for hydrogen evolution. *J Electrochem Soc*, 2005, 152: J23–J26
- 61 Hansen HA, Rossmeisl J, Norskov JK. Surface Pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni(111) surfaces studied by DFT. *Phys Chem Chem Phys*, 2008, 10: 3722–3730
- 62 Rossmeisl J, Logadottir A, Norskov JK. Electrolysis of water on (oxidized) metal surfaces. *Chem Phys*, 2005, 319: 178–184
- 63 Ogasawara H, Brena B, Nordlund D, Nyberg M, Pelmenchikov A, Pettersson LGM, Nilsson A. Structure and bonding of water on Pt(111). *Phys Rev Lett*, 2002, 89: 276102
- 64 Rossmeisl J, Norskov JK, Taylor CD, Janik MJ, Neurock M. Calculated phase diagrams for the electrochemical oxidation and reduction of water over Pt(111). *J Phys Chem B*, 2006, 110: 21833–21839
- 65 Lozovoi AY, Alavi A, Kohanoff J, Lynden-Bell RM. *Ab initio* simulation of charged slabs at constant chemical potential. *J Chem Phys*, 2001, 115: 1661–1669
- 66 Lozovoi AY, Alavi A. Reconstruction of charged surfaces: General trends and a case study of Pt(110) and Au(110). *Phys Rev B*, 2003, 68: 245416
- 67 Taylor CD, Neurock M. Theoretical insights into the structure and reactivity of the aqueous/metal interface. *Curr Opin Solid State Mater Sci*, 2005, 9: 49–65
- 68 Taylor C, Kelly RG, Neurock M. First-principles calculations of the electrochemical reactions of water at an immersed Ni(111)/H<sub>2</sub>O interface. *J Electrochem Soc*, 2006, 153: E207–E214
- 69 Janik MJ, Taylor CD, Neurock M. First principles analysis of the electrocatalytic oxidation of methanol and carbon monoxide. *Top Catal*, 2007, 46: 306–319
- 70 Taylor C, Kelly RG, Neurock M. Theoretical analysis of the nature of hydrogen at the electrochemical interface between water and a Ni(111) single-crystal electrode. *J Electrochem Soc*, 2007, 154: F55–F64
- 71 Cao D, Lu GQ, Wieckowski A, Wasileski SA, Neurock M. Mechanisms of methanol decomposition on platinum: A combined experimental and *ab initio* approach. *J Phys Chem B*, 2005, 109: 11622–11633
- 72 Fang YH, Liu ZP. Surface phase diagram and oxygen coupling kinetics on flat and stepped Pt surfaces under electrochemical potentials. *J Phys Chem C*, 2009, 113: 9765–9772
- 73 Tsipalakes D, Archonta D, Vayenas CG. Absolute potential measurements in solid and aqueous electrochemistry using two Kelvin probes and their implications for the electrochemical promotion of catalysis. *Top Catal*, 2007, 44: 469–479
- 74 Reiss H, Heller A. The absolute potential of the standard hydrogen electrode—a new estimate. *J Phys Chem*, 1985, 89: 4207–4213
- 75 Cuesta A. Measurement of the surface charge density of CO-saturated Pt(111) electrodes as a function of potential: the potential of zero charge of Pt(111). *Surf Sci*, 2004, 572: 11–22
- 76 Iwasita T, Xia XH. Adsorption of water at Pt(111) electrode in HClO<sub>4</sub> solutions. The potential of zero charge. *J Electroanal Chem*, 1996, 411: 95–102
- 77 Ranke W. Low-temperature adsorption and condensation of O<sub>2</sub>, H<sub>2</sub>O and NO on Pt(111), studied by core level and valence band photoemission. *Surf Sci*, 1989, 209: 57–76
- 78 Kiskinova M, Pirug G, Bonzel HP. Adsorption and decomposition of H<sub>2</sub>O on a K-covered Pt(111) surface. *Surf Sci*, 1985, 150: 319–338
- 79 Jinnouchi R, Anderson AB. Aqueous and surface redox potentials from self-consistently determined Gibbs energies. *J Phys Chem C*, 2008, 112: 8747–8750
- 80 Jinnouchi R, Anderson AB. Electronic structure calculations of liquid-solid interfaces: Combination of density functional theory and modified Poisson-Boltzmann theory. *Phys Rev B*, 2008, 77: 245417
- 81 Wang HF, Liu ZP. Formic Acid oxidation at Pt/H<sub>2</sub>O interface from periodic DFT calculations integrated with a continuum solvation model. *J Phys Chem C*, 2009, 113: 17502–17508
- 82 Fattebert JL, Gygi F. Density functional theory for efficient *ab initio* molecular dynamics simulations in solution. *J Comput Chem*, 2002, 23: 662–666
- 83 Beni G, Schiavone LM, Shay JL, Dautremontsmith WC, Schneider B S. Electrocatalytic oxygen evolution on reactively sputtered electrochromic iridium oxide-films. *Nature*, 1979, 282: 281–283
- 84 Bockris JOM. Hydrogen economy in the future. *Int J Hydrogen Energy*, 1999, 24: 1–15
- 85 Damjanov A, Dey A, Bockris JOM. Kinetics of oxygen evolution and dissolution on platinum electrodes. *Electrochim Acta*, 1966, 11: 791–814
- 86 Trasatti S. Electrocatalysis in the anodic evolution of oxygen and chlorine. *Electrochim Acta*, 1984, 29: 1503–1512
- 87 Marshall AT, Sunde S, Tsykin A, Tunold R. Performance of a PEM water electrolysis cell using IrxRuyTazO<sub>2</sub> electrocatalysts for the oxygen evolution electrode. *Int J Hydrogen Energy*, 2007, 32: 2320–2324
- 88 Anderson AB. Reactions and structures of water on clean and oxygen covered pt(111) and fe(100). *Surf Sci*, 1981, 105: 159–176
- 89 Anderson AB, Grantscharova E. Potential dependence of co(ads) oxidation by oh(ads) on platinum anodes—molecular-orbital theory. *J Phys Chem*, 1995, 99: 9143–9148
- 90 Anderson AB, Grantscharova E. Catalytic effect of ruthenium in ruthenium-platinum alloys on the electrooxidation of methanol—molecular-orbital theory. *J Phys Chem*, 1995, 99: 9149–9154
- 91 Anderson AB, Grantscharova E, Seong S. Systematic theoretical study of alloys of platinum for enhanced methanol fuel cell performance. *J Electrochem Soc*, 1996, 143: 2075–2082
- 92 Seong S, Anderson AB. Water dissociation on Pt(111) and (100) anodes: Molecular orbital theory. *J Phys Chem*, 1996, 100: 11744–11747
- 93 Cai Y, Anderson AB. Calculating reversible potentials for Pt-H and Pt-OH bond formation in basic solutions. *J Phys Chem B*, 2005, 109: 7557–7563

- 94 Roques RM, Anderson AB. Theory for the potential shift for OHads formation on the Pt skin on Pt<sub>3</sub>Cr(111) in acid. *J Electrochem Soc*, 2004, 151: E85–E91
- 95 Roques J, Anderson AB. Electrode potential-dependent stages in OHads formation on the Pt<sub>3</sub>Cr alloy (111) surface. *J Electrochem Soc*, 2004, 151: E340–E347
- 96 Roques J, Anderson AB, Murthi VS, Mukerjee S. Potential shift for OH( ads) formation on the Pt skin on Pt<sub>3</sub>Co-(111) electrodes in acid. *J Electrochem Soc*, 2005, 152: E193–E199
- 97 Bolzan AE, Chialvo AC, Arvia AJ. Fast faradaic processes observed during the potentiodynamic polarization of polycrystalline palladium in acid electrolyte. *J Electroanal Chem*, 1984, 179: 71–82
- 98 Tateishi N, Yahikozawa K, Nishimura K, Takasu Y. Hydrogen electrode-reaction on electrodes of glassy carbon-supported ultrafine pd particles in alkaline media. *Electrochim Acta*, 1992, 37: 2427–2432
- 99 Taylor CD, Kelly RG, Neurock M. A first-principles analysis of the chemisorption of hydroxide on copper under electrochemical conditions: A probe of the electronic interactions that control chemisorption at the electrochemical interface. *J Electroanal Chem*, 2007, 607: 167–174
- 100 Rossmesl J, Qu ZW, Zhu H, Kroes GJ, Norskov JK. Electrolysis of water on oxide surfaces. *J Electroanal Chem*, 2007, 607: 83–89
- 101 Markovic NM, Ross PN. Surface science studies of model fuel cell electrocatalysts. *Surf Sci Re*, 2002, 45: 121–229
- 102 Zhang J, Sasaki K, Sutter E, Adzic RR. Stabilization of platinum oxygen-reduction electrocatalysts using gold clusters. *Science*, 2007, 315: 220–222
- 103 Xiao L, Zhuang L, Liu Y, Lu J, Abruna HD. Activating Pd by morphology tailoring for oxygen reduction. *J Am Chem Soc*, 2009, 131: 602–608
- 104 Rossmesl J, Norskov JK. Electrochemistry on the computer: Understanding how to tailor the metal overlayers for the oxygen reduction reaction (A perspective on the article, “Improved oxygen reduction reactivity of platinum monolayers on transition metal surfaces”, by AU Nilekar and M. Mavrikakis). *Surf Sci*, 2008, 602: 2337–2338
- 105 Wang JX, Uribe FA, Springer TE, Zhang JL, Adzic RR. Intrinsic kinetic equation for oxygen reduction reaction in acidic media: the double Tafel slope and fuel cell applications. *Faraday Discuss*, 2008, 140: 347–362
- 106 Nilekar AU, Xu Y, Zhang JL, Vukmirovic MB, Sasaki K, Adzic RR, Mavrikakis M. Bimetallic and ternary alloys for improved oxygen reduction catalysis. *Top Catal*, 2007, 46: 276–284
- 107 Clouser SJ, Huang JC, Yeager E. Temperature-dependence of the tafel slope for oxygen reduction on platinum in concentrated phosphoric-acid. *J Appl Electrochem*, 1993, 23: 597–605
- 108 Li X, Gewirth AA. Oxygen electroreduction through a superoxide intermediate on Bi-modified Au surfaces. *J Am Chem Soc*, 2005, 127: 5252–5260
- 109 Anderson AB, Roques J, Mukerjee S, Murthi VS, Markovic NM, Stamenkovic V. Activation energies for oxygen reduction on platinum alloys: Theory and experiment. *J Phys Chem B*, 2005, 109: 1198–1203
- 110 Damjanovic A, Sepa DB. An analysis of the pH-dependence of enthalpies and gibbs energies of activation for O<sub>2</sub> reduction at Pt electrodes in acid-solutions. *Electrochim Acta*, 1990, 35: 1157–1162
- 111 Grgur BN, Markovic NM, Ross PN. Temperature dependent oxygen electrochemistry on platinum low index single crystal surfaces in acid solutions. *Can J Chem*, 1997, 75: 1465–1471
- 112 Janik MJ, Taylor CD, Neurock M. First-principles analysis of the initial electroreduction steps of oxygen over Pt(111). *J Electrochem Soc*, 2009, 156: B126–B135
- 113 Anderson AB, Cai Y, Sidik RA, Kang DB. Advancements in the local reaction center electron transfer theory and the transition state structure in the first step of oxygen reduction over platinum. *J Electroanal Chem*, 2005, 580: 17–22
- 114 Damjanov.A, Brusic V. Electrode kinetics of oxygen reduction on oxide-free platinum electrodes. *Electrochim Acta*, 1967, 12: 615–&
- 115 Stamenkovic V, Mun BS, Mayrhofer KJJ, Ross PN, Markovic NM, Rossmesl J, Greeley J, Norskov JK. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. *Angew Chem Int Ed*, 2006, 45: 2897–2901
- 116 Greeley J, Stephens IEL, Bondarenko AS, Johansson TP, Hansen HA, Jaramillo TF, Rossmesl J, Chorkendorff I, Norskov JK. Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. *Nature Chem*, 2009, 1: 552–556
- 117 Jerkiewicz G, Vatankhah G, Lessard J, Soriaga MP, Park YS. Surface-oxide growth at platinum electrodes in aqueous H<sub>2</sub>SO<sub>4</sub> Reexamination of its mechanism through combined cyclic-voltammetry, electrochemical quartz-crystal nanobalance, and Auger electron spectroscopy measurements. *Electrochim Acta*, 2004, 49: 1451–1459
- 118 Komanicky V, Chang KC, Menzel A, Markovic NM, You H, Wang X, Myers D. Stability and dissolution of platinum surfaces in perchloric acid. *J Electrochem Soc*, 2006, 153: B446–B451
- 119 Gu ZH, Balbuena PB. Absorption of atomic oxygen into subsurfaces of Pt(100) and Pt(111): Density functional theory study. *J Phys Chem C*, 2007, 111: 9877–9883
- 120 Greeley J, Norskov JK. Combinatorial density functional theory-based screening of surface alloys for the oxygen reduction reaction. *J Phys Chem C*, 2009, 113: 4932–4939