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DFT study of high performance Pt_3Sn alloy catalyst in oxygen reduction reaction

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ABSTRACT

The oxygen reduction reaction (ORR) is a multi-step catalytic process occurring at the cathode in fuel cells. As an alternative to a conventional Platinum catalyst, PtSn-based alloy catalyst experimentally presents an enhanced ORR activity compared with pure Pt catalysts. However, how the ORR reaction proceeds on PtSn is not yet well understood. On this context, a systematic study of O_2 reduction on the (1 1 1) facets of Pt_3Sn based on periodic density functional theory (DFT) calculation is presented. With the charge transfer from Sn to Pt, *d*-band center shifts away from the Fermi level, the electronic structure thoroughly differs from that of pure Pt thus producing ligand (electronic) effect. The ORR intermediates (H, O, OH, O_2, OOH, H_2O_2, and H_2O) species preferred site, adsorption configuration, binding energies, active barriers, rate constants, equilibrium constant are studied. Additionally, the corresponding transition states in seven elementary reactions are confirmed using the climbing image nudged elastic band (CI-NEB) method, and the thermodynamic and dynamic property in each reaction step are evaluated. Herein, the DFT results imply that on both the Pt_3Sn(1 1 1) and Pt(1 1 1) surfaces, the ORR share the same mechanism following OOH_{ad} dissociation pathway ($O_{2ad} \rightarrow OOH_{ad} \rightarrow O_{ad} \rightarrow OH_{ad} \rightarrow H_2O_{ad}$). The rate-determining step of the ORR on the (1 1 1) surfaces is found to be the O_{ad} hydrogenation reaction which requires activation barrier of 0.66 eV on the Pt_3Sn(1 1 1) surface and 0.77 eV on the pure Pt(1 1 1) surface, indicating the introduction of Sn significantly decreases the activation energy barrier. As the same temperature, the reaction rate of ORR on the Pt_3Sn(1 1 1) surface is faster than that on the pure Pt(1 1 1) surface. Our thermodynamic and kinetic results verify the important role of tin in improving the catalytic activity of ORR.

1. Introduction

The oxygen reduction reaction (ORR) is the most important reaction in energy conversion systems such as fuel cells [1,2]. The sluggish reaction kinetics of ORR requires an effective electrocatalyst to make fuel cell reach a practical level [3]. Although platinum (Pt) is the foremost electrocatalyst for the ORR [4], its high overpotential in the low current [5] and its high cost [6] have hampered the large-scale practical application in fuel cell. Over the past half a century, therefore, a big portions of investigation in this area is devoted to the alternative ORR electrocatalysts which satisfy both electrochemical stability and catalytic activity, including advanced Pt alloys [7,8], core-shell structured catalysts [9,10], non-noble metal composite catalysts [11,12], and nitrogen group-doped metal free catalysts [13]. Compared to monometallic catalysts, bimetallic catalysts have received great scientific interest due to their outstanding reactivity and high selectivity [14,15]. Generally, doping and alloying are the conventional methods to design bimetallic catalysts, which can significantly alter the chemical properties over either of the pure metal.

Among the above mentioned protocols, alloying Pt with a secondary nonprecious metal such as PtSn [16–19], PtNi [20,21], PtCo [22,23], and PtTi [24,25] can reduce the usage of scarce Pt while simultaneously improve ORR performance as compared with that of pure Pt on mass activity [4,7,8,26–29]. The additives in these alloys can well adjust the oxophilicity of Pt through strain (geometric) and ligand (electronic) effects [30,31]. The strain effect occurs when the Pt overlayer is laterally strained, e.g. by placing it on top of a core with a different lattice parameter, while the ligand effect arises due to subsurface alloying: the electronic structure of Pt is altered by nearby subsurface atoms with a different atomic number [32,33]. Specifically, Tin (Sn) is a good choice to alloy with Pt and has exhibited significantly higher catalytic activity as a cathodic catalyst [34–36], although SnO_2 itself suffers from poor stability at potentials relevant to the ORR because it can dissolve under acidic solution [37]. Carbon supported PtSn electrocatalyst prepared by alcohol reduction process at pH = 12 presented 1.34 times higher ORR activity as compared to commercial Pt/C catalyst after 500 cycles [17].

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PtSn alloy catalyst prepared by Bönnemann colloidal synthesis method exhibited a higher ORR activity owing to the presence of optimal amount of Sn oxides [18]. Further study confirmed that in PtSn/C catalyst, the SnO_2 nano-islands on Pt nanoparticle surfaces prevented the Pt cathode surface layers from being over-oxidized [38].

Besides all experimental works mentioned above, density functional theory (DFT) calculations have been widely employed to study the reaction and establish the correlation between surface composition and ORR catalytic activities in a micro level so as to rationally design and predict cost-effective, highly active and durable Pt alloy catalysts for ORR [39,40]. Pt-alloys Pt_3M (M = As, Sb, Ni, Co, Fe, Ti, V) led to 'volcano-type' electrocatalytic behavior [26,41,42]. The maximum in the catalytic activity in Pt_3M alloys is due to the interplay between the adsorption energy of reactive intermediates and the efficiency of the electron transfer to adsorbates. However, the DFT information on the PtSn alloy concerning ORR activity is very limited [43], except that the theoretical study on $Pt_3Sn(1\,1\,0)$ surface [16] revealed Sn in the PtSn alloy could change a relevant shift of *d*-band centers with respect to clean Pt. Although the kinetic calculation has envisaged that oxygen reduction could occur over PtSn alloy through the production of both H_2O_2 and H_2O [44], the detailed computational screening of ORR proceeding on PtSn is so far not clear.

On this point, the present work is contributed to understanding the advantageous ORR catalytic activity of PtSn alloy. DFT calculations were conducted to study pure and Sn modified Pt catalysts. First, the preferable adsorption sites of the ORR intermediates on the $Pt_3Sn(1\,1\,1)$ and Pt(1 1 1) surfaces were investigated. Second, the positive role of Sn in the $Pt_3Sn(1\,1\,1)$ was estimated in terms of the geometric and electronic properties. Third, the potential energy surfaces for three possible ORR mechanisms were sketched based on the reaction energies and activation barriers in all elementary reactions. Besides, the equilibrium constant of the rate-determining step in the feasible ORR pathway was calculated. The systematic DFT calculated values revealed that addition of Sn to Pt improved the electrocatalytic activity toward ORR.

2. Computational methods

In this paper, all DFT calculations were performed with the DMol^3 program from Materials Studio [45,46]. Spin-polarization was considered in all DFT calculations. Meanwhile, the exchange-correlation functional was developed by the generalized gradient approximation (GGA) of the Perdew, Burke, and Ernzerhof (PBE) used for the nonlocal corrections [47]. In our simulations, DFT Semi-core Pseudopots (DSPP) [48] was implemented to treat the core treatment for relativistic effects and Double numerical plus (DNP) polarization functions was used as the basis set. The global orbital cutoff was assigned to be 4.9 Å to ensure high quality in the calculations. The Brillouin zone was sampled at $5 \times 5 \times 1$ Monkhorst-Pack grid for K-space integration through the slab simulation. Electronic orbital occupancy was employed to use a Fermi smearing of 0.005 Hartree. For the geometry optimization, the convergence tolerance of energy, maximum force, maximum displacement and SCF were set as 1×10^{-5} Hartree, 0.002 Hartree per Å, 0.005 Å, and 1×10^{-6}, respectively. Complete linear and quadratic synchronous transit (LST/QST) method [49] was used to search for transition states (TS). The climbing image nudged elastic band (CI-NEB) method [50,51] was used to conform the lowest curvature mode of the transition states. All saddle points in our model were identified by frequency calculations and each saddle point was confirmed that there was only one imaginary vibrational frequency.

The (1 1 1) surfaces of Pt (Fig. 1a) and Pt_3Sn (Fig. 1b) were modeled by a periodic four-layer slab with a p (2×2) unit cell, with four atoms per surface layer. The surface coverage here was 1/4 ML which was enough to avoid irrelevant cross cell interaction. A vacuum layer of 12 Å thick was added in the initial slab cell, in order to avoid the artificial interactions between the distinct slabs. Bulk Pt has a faced-centered cubic (fcc) crystal structure and the lattice constant was calculated to be 4.00 Å in this work, which is in good consistent with the reported theoretical value of 3.99 Å [21] and experimental value of 3.924 Å [18]. Ordered Pt_3Sn bimetallic alloy employs $L1_2$ fcc-type structure, in which the Pt atoms lie at the face-centered positions and the Sn atom occupies the corner of the unit cell. The DFT calculated lattice parameter of the Pt_3Sn ($L1_2$) crystal structure is 4.08 Å, which is consistent with the theoretical study of 4.01 Å [52] and the experimental estimate of 4.00 Å [53]. For the structural optimization calculations of Pt(1 1 1) and $Pt_3Sn(1\,1\,1)$ surface, the adsorbate and the uppermost two layers were relaxed, while the remaining two bottom layers were fully fixed in a bulklike positions: interatomic distance of 2.833 Å for the Pt(1 1 1) and 2.891 Å for the $Pt_3Sn(1\,1\,1)$, which is in good agreement with a previous DFT calculation of 2.812 Å for the Pt (1 1 1) and 2.876 Å for the $Pt_3Sn(1\,1\,1)$ [54]. In addition, the Sn atom has a slight upward relaxation (0.16–0.26 Å) in the same plane with Sn and Pt atoms on the surface layer.

The above employed model of $Pt_3Sn(1\,1\,1)$ was experimentally verified to be stable in the electrochemical environment [55]. The microscopic analyses for the $Pt_3Sn(1\,1\,1)$ surface by a combination of ex-situ low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and low-energy ion scattering (LEIS) unanimously revealed the clean-annealed $Pt_3Sn(1\,1\,1)$ surface in ultrahigh vacuum produced a p(2×2) LEED pattern with 25 at.% Sn. Furthermore, in-situ surface X-ray scattering (SXS) results showed that the p(2×2) structure remained stable in 0.5 M H_2SO_4 upon repeated potential cycling from 0.05 to 0.8 V [56].

The surface binding energy (E_b) or adsorption energy (E_{ads}) of an adsorbate is defined as:

$$E_b = E_{adsorbate/catalyst} - E_{adsorbate} - E_{catalyst} \quad (1)$$

where $E_{adsorbate/catalyst}$, $E_{adsorbate}$, and $E_{catalyst}$ correspond to the total energy of interacting system of catalyst and adsorbate, the total energy of an isolated adsorbate and the total energy of bare catalyst in vacuum, respectively. Negative E_b indicates an attractive interaction between the adsorbate and the surface. Therefore, $E_b < 0$ is favorable for the elementary reaction over the catalysts' surface.

The reaction energy (ΔE) is defined as the energy difference in a chemical reaction between the initial state (IS) and the final state (FS). The activation barriers (E_a) refers to the energy difference of a chemical reaction between the initial state (IS) and the transition state (TS). In our DFT study, ΔE and E_a were all corrected with zero-point energy (ZPE). Transition state theory [57] was used to calculate the rate constant and equilibrium constant in the elementary step. The rate constant (κ) and equilibrium constant (K_e) are given as:

$$\kappa = \frac{\kappa_B T}{\hbar}\frac{Q_{TS}}{Q_{IS}}\exp\left(\frac{-E_a}{RT}\right) = A^0\exp\left(\frac{-E_a^0}{RT}\right) \quad (2)$$

$$K_e = \exp\left(\frac{-(\Delta E_b - T\Delta S)}{\kappa_B T}\right) = \frac{k_r}{k_{-r}} \quad (3)$$

where κ_B is the Boltzmann constant, $\hbar$ is Planck's constant, A^0 is the pre-exponential factor, R is the gas constant, T is 300 K which is the temperature of Pt-based catalysts following the experimental conditions. E_a^0 and E_a are activation energies with and without zero-point energy (ZPE) corrections, respectively. Q_{IS} and Q_{TS} are the partition functions at the initial state (IS) and the transition state (TS), respectively. ΔE_b is the minus binding energy of ORR and ΔS is the entropy change of ORR induced by adsorption. k_r and k_{-r} are the forward reaction rate constant and reverse reaction rate constant, respectively.

The *d*-band center is an important surface descriptor to explain the chemical reactivity of transition-metal surfaces and their alloy. The value of *d*-band center with relative to the Fermi energy refers to the center value of the density of states (DOS).