Surface Science 602 (2008) 3415–3423

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Bonding of Pt/Fe overlayer and its effects on atomic oxygen chemisorption from density functional theory study

Mary Clare Sison Escaño, Tien Quang Nguyen, Hiroshi Nakanishi, Hideaki Kasai *

Department of Precision Science and Technology and Applied Physics, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

ARTICLE INFO

Article history:
Received 21 May 2008
Accepted for publication 16 September 2008
Available online 20 September 2008

Keywords:
Density functional calculations
Chemisorption
Oxygen
Metal–metal interfaces
Bimetallic surfaces
Pt metal overlayer

ABSTRACT

First principles spin-polarized total energy calculations using density functional theory (DFT) within generalized gradient approximation (GGA) were performed to investigate the electronic structure of Pt monolayer on Fe(001) and the bonding at Pt–Fe and its effect on O atom chemisorption. Layer by layer density of states (DOS) for Pt/Fe(001) against the reference systems, unreconstructed Pt(001) and Fe(001) show a peak of Pt d states at the Fermi level and a spin polarization of Pt d_{zz} states. Charge redistribution at Pt–Fe interface shows charge transfer from the Pt and Fe atom sites towards the Pt–Fe bonds verifying strong bimetallic bonding. Similar charge redistribution is observed for Pt(001) with increase in charges at surface Pt–Pt bonding sites. Binding energies of adsorbed O on the three high symmetry sites follow the order: top < hollow < bridge. The efficiency of Pt d-electron back donation to adsorbed O on bridge is driven by a more localized bonding of O atom on this site. This mechanism of electron back donation may also be utilized in rationalizing the observed weakened binding of O on Pt/Fe system as compared to clean Pt(001) along with the d-band center model.

1. Introduction

Polymer electrolyte fuel cell (PEFC) offers a promising alternative to conventional power generation systems for both stationary and mobile applications because of its high efficiency, low temperature operation, fuel flexibility and zero-emission. It is known that the major drawbacks in PEFC are the slow kinetics of oxygen reduction in the cathode and the high cost of platinum used to catalyze the reaction [1]. Tuning Pt surface electronic and chemical properties to achieve high activity and selectivity have therefore become very attractive. To date, Pt-alloy systems such as Pt_3M (M = 3d transition metal) have been recognized in terms of their much improved catalytic activity for oxygen reduction reaction (ORR) than pure Pt [2–4]. Stamenkovic et al. in their combined experimental and theoretical studies, have explained the volcano-shape dependence of specific activity of Pt_3M electrodes across the late transition metals (Ni → Ti) in terms of oxygen chemisorption energy resulting to a correlation between catalytic activity for ORR with variation in surface electronic structure [5]. One non-trivial concern however for Pt_3M would be the small reduction in Pt content compared to standard Pt loading as such Pt-based alloy systems are still generally rich in Pt. The goal of significantly lowering Pt content in fuel cell cathode catalyst has attracted researchers to consider adlayer structures on less expensive metal substrates [6–8]. Very recently, Pt monolayer on Pd(111) was found to show increased catalytic activity than Pt bulk and Pt nanoparticles while lowering Pt loading up to 90% [6]. The observed favorable catalytic activity is partly ascribed to decreased PtOH formation as a result of changes in the d-band properties of Pt due to its interaction with Pd. Sasaki et al. reported increase in d-band vacancy of the deposited Pt submonolayer on Ru electrocatalyst caused by Pt–Ru interaction [7]. Bimetallic systems such as metal overlayers have therefore shown increasing catalytic importance in fuel cell research [1,9,10]. Aside from significantly lowering Pt content, ultra thin bimetallic films exhibit modified surface electronic structure towards favorable catalytic property due to interfacial interactions [11] and strain effects [10,12]. However, many details of electrocatalytic behavior of such Pt overlayer systems still remain to be clarified. Theoretical studies have proposed the change in the electronic properties of the metal adlayer which in turn results to a change in its reactivity to be attributable to the formation of surface metal–metal bond which include shifts of core levels due to charge transfer between monolayer and the substrate [13]. Others include change in density of states near the Fermi level [14], and change in d-band occupancy and electronegativity [15]. Since both critical factors, strain effects and interfacial interaction, occur simultaneously in bimetallic systems, models with very small lattice mismatch between components may be good starting points. It has been reported that Pt/Fe(001) films grow in layer by layer fashion at room temperature and epitaxial growth is ensured up to 5 Pt atomic layers (∼10 Å) on

---

* Corresponding author. Tel.: +81 6 6879 7857; fax: +81 06 877 2900.
E-mail address: kasai@dyn.ap.eng.osaka-u.ac.jp (H. Kasai).

0039-6028/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2008.09.019

the basis of low-energy-electron diffraction (LEED) study [16–18]. Our previous spin-polarized density functional theory calculations on atomic structure of Pt monolayer on Fe(001) referenced to the clean Fe(001) surface [19], show a very small (0.5%) lattice mismatch between Pt and Fe. This allows focus of changes in Pt electronic surface structure solely on metal–metal interaction. So far, no *ab initio* study on electronic structure and bonding of Pt/Fe overlayer has been conducted probably due to the fact that most systems considered (even for high-density magnetic storage devices) are Fe/Pt(001) multilayers [20,21]. Hence, in this paper, we begin with a detailed analysis of electronic structure of Pt atomic layer on Fe(001) with reference to unreconstructed Pt(001) and Fe(001) surfaces. Adsorption characteristics of atomic oxygen for Pt/Fe(001) as compared to Pt(001) are also explored. In the last sections, we show how the change in Pt electronic structure accounts for atomic oxygen chemisorption properties. It is true that this adsorption model represents single crystal surfaces exposed to gas-phase oxygen, and not to the fuel cell operating conditions. Nevertheless, the paper presents significant information on bimetallic surface oxidation which may form basis for further gas-surface interaction studies.

2. Computational method

Spin-polarized total energy calculations using Projector Augmented Wave (PAW) method [22,23] and plane–wave basis set were performed within density functional theory (DFT) framework using Vienna *ab initio* simulation program (VASP) [24–27]. The spin-polarized version of the program accounts for the magnetic moment of O and ferromagnetic character of Fe. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) was used for the exchange-correlation functional [28,29] as GGA is known to predict the correct ground state of Fe than local density approximation (LDA) [30,31]. Also, calculations using GGA gave reliable descriptions of total energy for chemisorption systems while LDA calculations tend to exaggerate adsorbate binding [32]. The PAW method was used instead of pseudopotential technique because ultrasoft pseudopotentials (USPPs) are known to produce the wrong ordering of magnetic states of bulk Fe [30]. Brillouin-zone integrations were performed on a grid of $(11 \times 11 \times 1)$ Monkhorst–Pack *k*-points using Methfessel–Paxton smearing [33] of $\sigma = 0.2$ eV. The substrate is modeled by a five-layer slab in a (1×1) unit cell with Pt atom pseudomorphically laid on the Fe substrate and with each slab separated by $\sim$12.0 Å of vacuum. For the chemisorption models, we used a (2×2) unit cell, large enough to avoid O–O interactions while a grid of $(4 \times 4 \times 1)$ Monkhorst and Pack [34] special *k*-points is used for Brillouin-zone integration to lower computational cost. The Pt, Fe and O PAW–PBE potentials were all tested for bulk Pt, Fe and oxygen molecule. The GGA (PBE) calculated lattice parameter for Pt and Fe with 300 eV energy cutoff are 3.980 Å and 2.834 Å respectively, in excellent agreement with other DFT–GGA calculations [25,35]. For atomic and molecular oxygen, a 400 eV cutoff energy yields a O_2 bond length of 1.235 Å and a dissociation energy of 5.67 eV, also in good agreement with experiment [36] and other DFT calculations[4,37].

3. Results and discussions

3.1. Pt overlayer relaxation

The top layer relaxation for unreconstructed Pt(001) was calculated using four-layer slab in a (1×1) unit cell. The Pt atoms from the second to the bottom layers were fixed at their bulk positions. The slabs are separated by $\sim$12.0 Å thick of vacuum layer. The optimized structure is shown in Fig. 1a. Calculated interlayer distance between the first and second layer is 1.93 Å, in general agreement with other DFT calculation [37]. The Pt–Pt bond length in the first interlayer is 2.77 Å. For the Pt monolayer on Fe(001), also in a (1×1) unit cell, Fe atoms from the 3rd Fe layer (designated by Fe–III in Fig. 1b) down to the bottom layer are fixed at bulk positions. Pt–Fe bond length is 2.50 Å which gives a significant contraction with respect to the Pt–Pt bond length in Pt(001). The desorption energy (defined as energy needed for 1 Pt atom vacancy formation) per Pt atom in both systems is

$$E_{\mathrm{des}} = E_{\mathrm{Pt}^{*}/\mathrm{slab}} - [E_{\mathrm{slab}} + E_{\mathrm{Pt}}] \qquad (1)$$

where E_{slab} is the total energy of the slab, E_{Pt} is the total energy of isolated Pt atom and $E_{\mathrm{Pt}^{*}/\mathrm{slab}}$ is the total energy of the Pt/slab system with one surface atom vacancy. The results show a marked difference between two systems with Pt monolayer on Fe(001) greater by 0.18 eV. Such result may contribute significant insights in rational cathode catalyst design under stability arguments.

3.2. Electronic structure

Since total charge density has been the starting point in modern density functional theory for discussing bonding, we used charge density difference obtained by subtracting the valence charge density of the clean Fe substrate from that of Pt adlayer system and the Pt substrate from that of the four-layer Pt(001) slab for Pt/Fe(001) and Pt(001) systems, respectively. Fig. 2 shows the redistribution of charges at Pt–Pt (left figure) and at Pt–Fe (right figure) regions as depicted by contours on a vertical plane which directly cuts through the surface Pt atom. Such plane is chosen to determine the difference in charge distribution above and around the surface Pt between the two systems. First, we note similar accumulation of charges within the Pt–Pt and Pt–Fe regions and we as well note that the increase in charge is more pronounced at the bonding sites. While in both systems, depletion of charges from vacuum

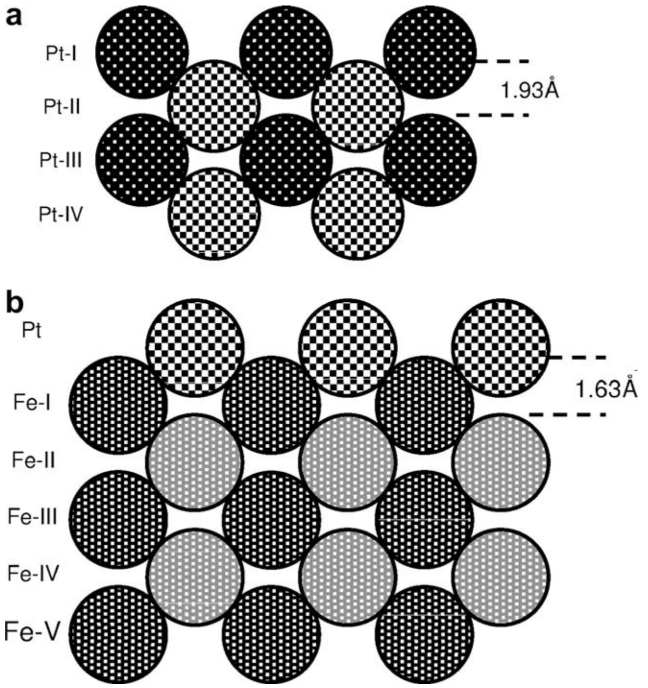

Fig. 1. Optimized structure for (a) unreconstructed Pt(001) viewed along [010] direction and (b) Pt monolayer on Fe(001) viewed along [100] direction, where the first interlayer distances are shown. The layers of (a) pure Pt slab and (b) Fe slab are labeled accordingly.