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Probing the edge effect on the ORR activity using platinum nanorods: A DFT study

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ABSTRACT

The overall activity of the oxygen reduction reaction (ORR) over multifaceted nanoparticles is typically interpreted as a linear combination of the ORR activity of different facets and surface site-types present on these particles. It is thus implicitly assumed that (i) edge effects are local phenomena and (ii) different facets are kinetically isolated, i.e. transfer of adsorbates over the edge is kinetically limited. Here we use rhombic nanorod models and density functional theory, with atomic O as a probe, to investigate these assumptions. The adsorption energy of atomic O was found to be virtually independent of the distance from the nanorod edge beyond the edge atomic row, indicating a localized edge effect. A kinetic connection between two adjacent facets however cannot be ruled out. The connection between the adjacent Pt{100} and Pt{111} facets, through atomic O diffusion, is kinetically more favorable at 1.0 ML edge coverage compared to 0.5 ML edge coverage as a result of repulsive lateral interactions between co-adsorbed O atoms and the corresponding flattening of the potential energy surface.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are an attractive technology for e.g. mobile applications [1,2], since they have higher theoretical efficiencies compared to Carnot engines. Platinum-based catalysts have been shown to be highly active for the oxygen reduction reaction (ORR), which occurs at the cathode electrode of a PEMFC [1]. However, to make this technology commercially attractive for application in the automotive industry, a 4- to 10-fold reduction in platinum loading is required without decreasing power density [1].

The overall fuel cell reaction can theoretically generate a potential difference of 1.23 V at 298.15 K, but the experimentally obtained potential difference is lowered due to the current drawn from the cell. This lowering of the obtained potential has been ascribed to reaction activation, proton-electron transport resistance and gas transport losses [1,3]. Hence, state-of-the-art PEMFCs only achieve efficiencies in practice between 45 % and 55 % [2], with two-thirds of the potential loss in platinum-based fuel cells due to kinetic losses mostly due to the sluggish kinetics of the ORR [1]. Hence, there is a need to understand the ORR with a view to increase its mass-specific activity.

Different Pt surface terminations are exposed on equilibrated platinum nanoparticles [4,5]. Experimental electrochemical studies have been used to investigate the ORR activity over these different Pt surfaces, making use of single crystals with well-defined and polished surface orientations [6–10]. In $HClO_4$ and KOH the ORR activity increases in the order Pt(100) < Pt(110) < Pt(111), whereas in H_2SO_4 the order is reversed, with the activity over the Pt(110) surface two orders of magnitude higher than that on Pt(111) [8]. The different order in the activity over low Miller index surfaces in various electrolytes may be a consequence of anion adsorption [8]. On more complex platinum surfaces such as Pt(111) surfaces terminated by periodic Pt (111) or Pt(100) steps, i.e. n(111) × (100) and n(111) × (111), the surface area specific activity for the ORR has been reported to increase with an increase in the density of steps for $n > 4$ [9,10]. Bandarenka *et al.* [10] verified the existence of a well-defined Sabatier-type correlation between the measured ORR activity over these stepped surfaces and the corresponding adsorption strength of OH*. They proposed that the destabilization of OH*, responsible for the improvement in activity with increasing step density, was due to decreased solvation of OH* as a result of step edges [10].

Density functional theory (DFT) has also been used to study the ORR activity over different Pt surface terminations [11–19]. In summary, the activity is thought to increase in the order Pt(210) < Pt(110) < Pt (100) < Pt(111) based on calculated adsorption and activation energies [12,18]. Further analysis of the activity of the ORR for each individual surface termination requires a detailed microkinetic model [11,20,21]. For a multifaceted nanoparticle with i facets each with an area specific current density of j_i and a relative surface fraction of facet

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iof χ_i, the overall ORR area specific activity ($J_{overall}$) is modeled as [12,22–25]:

$$J_{overall} = \sum_{i}^{N} x_i \cdot j_i \tag{1}$$

The relative fraction of different crystallite surfaces is dependent on the particle shape and size. The relationship in Eq. (1) presumes that (i) edge effects are a local phenomenon and (ii) the diffusion of ORR intermediates from one facet to another facet is kinetically limited. The latter may occur if adsorption on edge sites is much stronger than on the facets, as indicated by DFT calculations on stepped surfaces [12,26] and small platinum clusters (38–201 atoms) [27–29].

In this study, we use nanorod models [30,31] to simulate the edge between {111} and {100} facets on a nanoparticle. Nanorod models can isolate edge and near-edge regions. They are computationally less demanding than calculations using larger nanoclusters. At the same time, nanorod models can be computationally more expensive than modeling stepped surfaces. Recently, Badan et al. [32] and Ogawa et al. [26,33] independently and respectively reported an appreciable influence of the (111) terrace length and (100) step height on adsorption energies of oxygen-containing species, i.e. O, O_2, and H_2O. Here we report the adsorption energies of atomic O on various Pt{111} and Pt{100} nanorod facet sites to probe the local nature of the edge effect. We chose to use nanorod models, instead of stepped surfaces, in order to isolate the edge region by eliminating the influence of the bottom step/step height on the edge adsorption properties. Furthermore, since the dissociation of O_2 has been reported to be more energetically facile on a Pt(100) surface than on a Pt(111) surface [16,17,20] it is of some interest to investigate the diffusion of atomic O from the Pt{100} facet towards the Pt{111} facet. Therefore, we further report on the diffusion barriers and rate constants for the migration of an O-adatom from the Pt{100} facet towards the Pt{111} facet over the edge. Overall, we highlight some of the limitations of the current approach to model the overall ORR activity over multifaceted nanoparticles.

Although the ORR has been reported to go via an associative reaction pathway over a Pt(111) surface [14,16,19], over a Pt(100) surface a dissociative mechanism has been argued to be dominant [17,19]. Moreover, since even the associative ORR mechanism does result in O* generation via OOH* dissociation[13], O* remains an interesting reaction intermediate. This is especially true when considering a model consisting of both a Pt{111} and Pt{100} facet. In the present study O* is investigated as a probe intermediate. The general approach presented here can be extended to OH*, which is also an important ORR intermediate [17,19].

2. Computational methods

Periodic DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [34–37]. A generalized gradient approximation exchange-correlation functional, the Perdew, Burke and Ernzerhof (PBE) functional [38], was used with the projector augmented wave (PAW) method [39,40]. Spin polarization was considered in all calculations. A plane-wave basis set with a 400 eV kinetic energy cut-off was used. All relaxed atoms were optimized by minimizing the Hellman-Feynman forces to below 0.02 eV/Å. For the electronic self-consistent iteration, the energy was converged within 10^{-5} eV/unit cell. The description of the electronic structure optimization was based on the Methfessel-Paxton scheme with a smearing width of 0.1 eV for adsorbed states, whilst Gaussian smearing with a smearing width of 0.01 eV was used for gas phase O_2 molecules. In both cases, adsorbed states and O_2 gas, the total energies were extrapolated to 0 K.

The climbing image nudged elastic band (CI-NEB) method [46] was used together with the fast-inertial relaxation engine (FIRE) optimizer [41,42] to determine the transition states for diffusion of atomic O. The force components perpendicular to the tangent of the diffusion pathway were optimized to within 0.05 eV/Å. Stable adsorption geometries and transition states were verified using vibrational analyses. For all stable geometries, it was observed that all vibrational modes were real, indicative of a local minimum on the potential energy surface, whilst for all transition states only one imaginary vibrational frequency was obtained.

For all nanorod models an optimized k-point grid of 1 × 5 × 1 was used, with more points along the nanorod axis. A minimum vacuum spacing of 12 Å between nanorod surfaces in adjacent periodic cells was maintained. Slab models of Pt(111), Pt(100) and Pt(211) surfaces, and 147-atom and a 309-atom cuboctahedral nanoparticles were also used for comparison purposes. For nanoparticle models, we used a k-point grid of 1 × 1 × 1 and ensured a > 12 Å vacuum spacing between nanoparticle surfaces on surrounding periodic cells. Two supercells, p(2 × 2) and p(2 × 4) were used for the Pt(111) and Pt(100) slab surfaces each with 6 atomic layers–the bottom 3 layers were fixed in all calculations. The k-point grids used for the p(2 × 2) and p(2 × 4) supercells were 5 × 5 × 1 and 5 × 3 × 1 respectively. For the Pt(211)-p(1 × 2) stepped surface, a 4 × 5 × 1 k-point grid was used. In all slab models, the vacuum spacing between periodic slabs was set to 12 Å. The adsorbates were then introduced only on the relaxed side of the slab models.

All slab calculations included the application of a dipole moment correction, along the surface normal/z-direction, and spin polarization. For nanorod models we observed only a 2 meV change in the total energy when the nanorod was rotated relative to the lattice cell keeping the dipole correction in the z-direction. We then considered a correction only the z-direction and only one orientation of the nanorod, with the Pt{111} or Pt{100} surface normal aligned with the z-direction. We do not include dispersion effects in our calculations as these do not change the relative energies and shape of the potential energy surfaces (PES). We observe in test calculations that when van der Waals interactions are included only the absolute adsorption energies become more exothermic whilst the relative differences remain relatively unchanged (Fig. 1s, Supporting Information)

The adsorption energy of atomic O ($E_{ads,O}$) was defined as follows:

$$E_{ads,O} = E_{O@NR} - E_{NR} - \frac{1}{2}E_{O_2} \tag{2}$$

$E_{O@NR}$ and E_{NR} are the total energies of an O atom covered and clean nanorod model, respectively – E_{O_2} is the total energy of an O_2 molecule in a vacuum. The Gibbs free energy barriers ($\Delta G^{\ddagger}_{Act}$) were calculated as the difference between the Gibbs free energy of the transition state (G_{TS}) and initial state (G_{IS}). The Gibbs free energies were calculated using statistical thermodynamics and a set of equations taken form the *MOPAC* Manual [43]. The hopping frequency (k_{hop}, [s^{-1}]) was calculated as a function of temperature (T) and Gibbs free energy barrier ($\Delta G^{\ddagger}_{Act}$) and is given by Eq. (3) below:

$$k_{hop} = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}_{Act}}{k_B T}\right) \tag{3}$$

where k_B and h are Boltzmann and Planck constants.

3. Results and discussion

Using periodic DFT we calculate the adsorption energy of atomic O over various adsorption sites on a Pt(mNR)-[7(111) × 5(100)] (Model 1A) and Pt(mNR)-[5(111) × 7(100)] (Model 1B) nanorod model (shown in Fig. 1). A Pt(mNR)-[*m*(111)x*n*(100)] nanorod model is rhombic in shape with *m* and *n* atomic rows along the Pt{111} and Pt{100} nanorod facets, respectively.

The adsorption energy of atomic O on an edge-bridge site (EB) is calculated to be −1.59 eV/½O_2 and −1.54 eV/½O_2 over Model 1A and 1B, respectively. The latter compares reasonably well with −1.56 eV/½O_2 and −1.62 eV/½O_2 over EB sites of a 147-atom and 309-atom cuboctahedral nanoparticle, respectively.