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Effect of surface hydroxyl coverage on platinum nanoparticles in the oxygen reduction reaction: All-electron density functional theory analysis

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ABSTRACT

Catalysts in commercial proton exchange membrane fuel cells must be optimized for activity and cost, but improvements are hampered for Pt nanoparticles by low activity resulting from extensive OH adsorption. A model system clearly elucidating the impact of OH coverage on Pt nanoparticles was therefore developed. Using first principles calculations, free energies due to changing OH coverage in the oxygen reduction reaction were predicted as functions of electrode potential and local surface structure. Free energy contour plots that considered surface OH coverage were developed. Therefrom, we theoretically predicted the optimum range of operating potentials, yielding design guidelines for catalytic surfaces.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are of great interest because their low temperature and pressure operation, as well as potential in small-scale applications, makes them highly desirable alternatives to existing alkaline fuel cell technologies. Platinum is considered the best catalyst [1,2] for the oxygen reduction reaction (ORR) in PEMFCs, although its high cost and scarcity require increasing its activity and reducing its loading by employing small particles. In this respect, nanoparticles (NPs) are attractive because they provide high specific surface area-to-volume ratios. However, Pt NPs exhibit lower activity than Pt(1 1 1) surfaces because adsorbed OH groups on the NP surfaces block catalytically active sites [3]. To take full advantage of NP activity, studies of site blocking by OH adsorption are necessary to obviate activity losses.

Density functional theory (DFT) calculations have been extensively used to determine the origin of site blocking by OH adsorption, based on the concept of reaction free energy [4–7]. Of the numerous reaction steps in the ORR, the DFT approach has focused mainly on the following elementary step, in which an OH molecule on the surface must be desorbed and simultaneously reduced to water: [4,5]

$$*OH + (H^+ + e^-) \rightarrow H_2O \qquad (1)$$

where * denotes the catalyst surface. In theoretical studies of the adsorption of a single OH moiety on a Pt NP, OH desorption was predicted to be potential-determining [1,7–10]. The large free energy barrier of this endothermic step hinders the overall reaction and is regarded as a serious problem; the sluggish kinetics for removing OH from the surface results in increased OH coverage (Θ_{OH}). There is general agreement that increased Θ_{OH} blocks active sites and results in lower activity at the Pt surface [2,4,11,12].

To improve the activity of Pt NPs in the ORR, solutions to prevent site blocking resulting from increased Θ_{OH} are required. For this, it is necessary to consider the detailed behavior of free energy as a function of Θ_{OH}. Such relationships between free energy and Θ_{OH} have been described extensively and with good agreements to experiments by using the recently proposed methods [4,6,13]. However, these analyses have been applied to bulk surfaces only. Since a detailed analysis for NPs has not been done yet, such studies for the NPs are necessary to inform future catalyst design. Eq. 1, describing a single adsorption, can be extended to the case of multiple adsorptions, as expressed by Eq. (2):

$$*(OH)_N + (H^+ + e^-) \rightarrow *(OH)_{N-1} + H_2O \qquad (2)$$

where N is the number of OH groups on the NP surface. The effect of Θ_{OH} on the free energy can also be described by this equation. As increased surface coverage attenuates the adsorption energy on surfaces, this weakened adsorption energy eases OH desorption (from $*(OH)_N$ to $*(OH)_{N-1}$) by reducing the free energy barrier.

Calculations for multiple adsorptions of OH have only been performed with models describing the surface of bulk Pt [4–6]. Such

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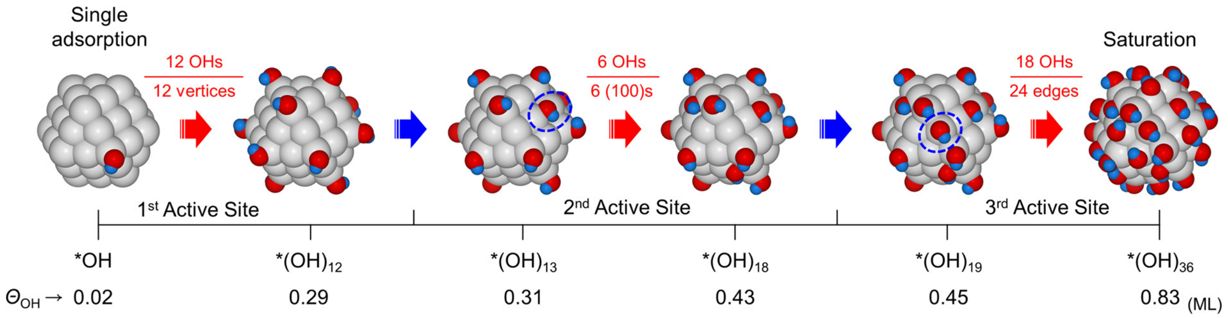

Figure 1. Symmetric filling of identical sites by adsorption of OH moieties (red) on a nanoparticle (NP) surface. The blue dashed lines denote the appearance of new active sites. The asterisk represents the Pt NP surface. Θ_{OH} (ML) is determined as the number of *OH divided by the 42 surface atoms of a Pt_{55} NP. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

models can be applied to the prediction of NP surfaces which contain varied local structures such as vertices, edges and flat sections [14]; furthermore, the convergence of NP's binding energy on the bulk limit was also shown [15]. However, the calculation for directly modeling the NP substrate can provide more useful information; sequence and competition among local structures as the OH coverage changes. Therefore, such calculations for NP surfaces are required. On a NP surface, a single OH is adsorbed at a vertex [7,16]. After all vertices are occupied, subsequent adsorption of OH can occur either at an edge or a flat surface, which naturally have different adsorption strengths than the vertex, and results in a free energy shift. Thus, free energy calculations for multiple OH adsorptions on NPs must include these local structure effects, and will allow the determination of the local structure responsible for site blocking by OH adsorption [17,18]. Then, a strategy to optimize OH desorption during catalytic surface design can also be developed.

The free energy of the ORR has been calculated from relevant electrode potentials (U) [1,5,6], following the report by Nørskov et al. [2]. As the free energy with respect to Θ_{OH} is shifted by U in electrode reactions, Θ_{OH} is also dependent on U [1,4,6]. The value of U is an operating voltage that is controlled during fuel cell operation; by describing Θ_{OH} as function of U, optimized operating voltages for various steps of the ORR have been found through DFT studies of bulk surfaces [4–6]. In addition, experiments to improve activity in the ORR can guide site blocking minimization across a range of suitable operating voltages.

Thus, free energy calculations with respect to Θ_{OH} on a NP can also guide site blocking minimization and OH desorption optimization. The aims of this study were to calculate the OH adsorption energies with increasing surface OH content on 1 nm diameter Pt NPs, and determine the order in which OH is adsorbed on local surface structures such as vertices, edges, Pt(1 0 0) faces, and Pt(1 1 1) faces. The free energies of the OH desorption steps were calculated, and then, free energy surfaces as functions of Θ_{OH} and U were constructed, which were used to explain experimental polarization curves and discuss the optimization of the operating potential and catalytic surfaces for small NPs.

2. Computational details

All calculations employed a revised Perdew–Burke–Ernzerhof [19] exchange-correlation functional. A Fritz Haber Institute ab initio molecular simulation code [20,21], based on a numerical atomic orbital basis set was employed; this set provides better performance than a plane–wave basis set for zero dimensional systems such as NPs [20]. The 'light' default basis set was employed for Pt, O, and H atoms, including a minimal basis with added partial tier 1 functions (s, p, d, f) for Pt, often called "double numerical plus polarization." A scalar relativistic treatment suitable for heavy atoms such as Pt was used, based on the atomic zero-order regular approximation [20,22].

The lattice parameter of face-centered cubic (fcc) bulk Pt was estimated as 3.97 Å, in good agreement with experimental values (3.92 Å, within an error range of +1.3%). Slabs and clusters were generated from the relaxed lattice parameter of bulk Pt. The morphology of the 1 nm diameter Pt_{55} NPs was assumed to be cuboctahedral (COh). In the structure, one Pt atom was placed at the center of the NP and covered by two shells possessing fcc configurations. Two surfaces, the Pt(1 0 0) and Pt(1 1 1) planes, are exposed on such NPs [23–25].

The free energy was calculated using the following equation:

$$\Delta G = \Delta E + \Delta \mathrm{ZPE} - T\Delta S \tag{3}$$

where ΔE is the reaction energy when OH is adsorbed onto the Pt surface, ΔZPE is the difference in zero point energies due to the reaction, T is the temperature, and ΔS is the change in entropy. ΔZPE and $T\Delta S$ were previously reported [1,26–28].

3. Results and discussion

The OH adsorption steps are depicted in Figures 1 and S1 (Supporting Information). Sites at the vertices are predicted as the first active site, in agreement with other reports [16]. At $^*(OH)_{12}$, all the vertices are saturated by 12 OH moieties on the Pt_{55} NP; subsequent OH moieties must then be adsorbed on a new active site. For the $^*(OH)_{13}$ configuration, the unoccupied sites were calculated to compare site preferences (Figure S1). The bridge on the Pt(1 0 0) face was predicted to be the most preferable remaining site. For $^*(OH)_{18}$, one OH per Pt(1 0 0) face was adsorbed and site preferences were calculated again for the remaining unoccupied sites. Edge sites were estimated to be the third active site, to complete the adsorption process by saturation.

As shown in Figure 2, E_{ad} increases weakly with increasing Θ_{OH}. Large differences in E_{ad} are observed when the geometry of the active site changes—e.g., from a vertex to a Pt(1 0 0) face, and from a Pt(1 0 0) face to an edge—resulting in relatively steep slopes. The E_{ad} value noticeably changes by 0.3 eV when the OH adsorption site is changed to a Pt(1 0 0) face from a vertex. For single OH adsorption, the energy difference between the first and the third preferable site was estimated to be 0.38 eV (Figure S1a and c). At low coverage (0.3 mL), saturation of the vertex atoms causes a larger difference in adsorption strength in comparison with the adsorptions on Pt(1 0 0) faces. Because the E_{ad} change from the initial to the final site is 0.64 eV, adsorption energy calculations as a function of increasing coverage are justified.

Our calculations can be used not only for estimating adsorption and desorption energies, but also to predict changes in reaction free energies with respect to coverage (Figure 3). Eq. (2) states that the OH adsorbed on a catalytic surface is desorbed and then reduced to