Theoretical Trends in Particle Size Effects for the Oxygen Reduction Reaction

By J. Greeley 1,2,* J. Rossmeisl 1, A. Hellman 1, and J. K. Nørskov 1

1 Center for Atomic-scale Materials Design, NanoDTU, Dept. of Physics, Technical Univ. of Denmark, DK-2800 Kongens Lyngby, Denmark
2 Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA

Dedicated to Prof. Dr. Dieter M. Kolb on the occasion of his 65th birthday

(Received June 14, 2007; accepted July 23, 2007)

A simple, first principles-based model of the oxygen reduction reaction (ORR) is used to determine ORR kinetics on the (111), (100), and (211) facets of eleven transition metals (Au, Ag, Pt, Pd, Ir, Cu, Rh, Ni, Ru, Co, Fe). For most metals, the unreconstructed (100) facets are found to have an activity comparable to, or slightly higher than, the (111) facets. In contrast, (211) steps are found to be significantly less active than the terraces, with the exception of the most noble metals. These results are combined with simple models of the geometries of catalytic nanoparticles to estimate the average ORR activity of Pt and Au nanoparticles of various sizes. On Pt, a modest decrease in the activity with decreasing particle size is predicted, while for Au, the opposite trend is found.

1. Introduction

The oxygen reduction reaction (ORR) is among the most important and well-studied reactions in electrochemistry. As the primary chemical reaction occurring on the cathodes of low temperature polymer electrolyte membrane (PEM) fuel cells, the kinetics and thermodynamics of the ORR exert a substantial influence on overall fuel cell performance. As such, one of the most important goals of current fuel cell research is to find active, stable, and inexpensive catalysts for this reaction [1–3].

* Corresponding author. E-mail: jgreeley@anl.gov
One of the major areas of study in fundamental ORR research has been the so-called particle size effect. As the name implies, this effect, which is closely linked to the structure sensitivity of the ORR, can lead to significant changes in catalytic activity as a function of particle size; these changes, in turn, may have significant implications for the economics of PEM fuel cells. If, for example, the loading of precious metals on fuel cell cathodes could be reduced by decreasing the size of the catalytic particles without sacrificing activity, then significant economic savings could be realized [3].

The majority of experimental studies of the particle size effect have focused on platinum, the canonical PEM fuel cell cathode; recently, similar studies have been performed on gold nanoparticles [4]. Both the magnitude and the direction of the effect on platinum have been extensively debated; some researchers have observed essentially no effect of particle size on ORR activity [5], but a majority have measured a decrease in specific activity as the particle size is decreased [3, 6, 7]. The explanation for this decrease is not fully understood, but there is some speculation that defects on smaller catalytic particles are less active for the ORR than are well-defined, low-index crystal planes; as the Pt particles become smaller, the concentration of defects increases, and the average particle activity drops.

Although a variety of experimental studies of the particle size effect have been performed, to our knowledge, few theoretical studies exist. To begin to develop theoretical analyses of this effect, it is clearly necessary to model ORR chemistry on transition metal nanoparticles; such models might provide, for example, important insights into the role that particular surface features play in determining the particle size effect. In particular, first principles-based computations are well-suited to studying the effect of nanoscale structural features on catalytic activity [8], and we focus on such calculations in the following.

In this study, we present a simple model of oxygen reduction reaction kinetics on transition metal nanoparticles. We study the structure sensitivity of ORR kinetics on the (111), (100), and (211) crystal facets of a variety of metals, and using simple assumptions about the equilibrium nanoparticle geometries, we determine average ORR rates as a function of particle size. We find that the average reaction rate on platinum nanoparticles will decrease as the particle diameter is decreased, but on gold, we find the opposite trend. Consistent with various experiments, the results imply that significant reduction of platinum loading on fuel cell cathodes cannot be achieved by simply reducing the size of Pt particles indefinitely without sacrificing activity.

2. Methods

DACapo, the total energy calculation code [9], is used in this study. For all calculations on (111) and (100) surfaces, a four-layer slab, periodically
repeated in a super-cell geometry with at least five equivalent layers of vacuum between any two successive metal slabs, is used. $(2 \times 2)$ unit cells are employed, and the top two layers of the slab are allowed to relax. Details of the calculations for the (111) surfaces can be found in [10]; as is described in that reference, a few calculations on these surfaces (involving the effect of adsorbed water bilayers) are also performed on $(3 \times 2)$ unit cells (see also discussion below). For the (100) surfaces, all elements are constrained to the fcc crystal system, and a $4 \times 4$ Monkhorst–Pack $k$-point grid is used. Adsorption is allowed on only one of the two surfaces exposed, and the electrostatic potential is adjusted accordingly [11]. Ionic cores are described by ultrasoft pseudopotentials [12], and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energy below 340 eV; a density cutoff of 500 eV is used. For the (211) surfaces, a $(3 \times 2)$ unit cell is employed; additional details of these calculations can be found in Ref. [13]. For all surfaces, convergence of the total energy with respect to the $k$-point set and with respect to the number of metal layers included is confirmed. The exchange-correlation energy and potential are described self-consistently within the generalized gradient approximation (GGA-RPBE) [9]. The self-consistent RPBE density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density [14]. All total energies are extrapolated to $k_B T = 0$ eV.

To determine the effect of water on the binding energies (B.E.’s) of O, OH, and OOH on the (100) surface of platinum, we use a $(3 \times 2)$ surface unit cell; such a cell permits the formation of a pseudo-hexagonal water bilayer, similar to that observed on Pt(111) [15]. In contrast to the situation on Pt(111), however, the bilayer is not in perfect registry with the underlying Pt surface lattice.

Nanoparticle shapes are determined using Wulff constructions; surface energies used in the constructions are taken from Vitos et al. [16]. Only (111) and (100) facets are used in the determination of the Wulff particles, and the particle diameters are taken to be the distance between (111) facets on opposite sides of the respective particles. It is assumed that atoms on all of the edges on the nanoparticles (that is, the atoms at the intersections between the various crystal facets) are unstable and will be lost in solution, thus resulting in the formation of steps; this assumption has been verified in the case of Ru nanoparticles [17]. We assume that each atom on the appropriate steps or facets is an active site, and we average the activity according to the number of atoms of the various steps/facets on the particles. Hence, we assume that the various particle facets are independent of one another, and we neglect any sort of communication (for example, adsorbate diffusion) between the facets.
3. Results and discussion

3.1 Review of oxygen reduction reaction volcano on (111) surfaces

A basic model for the ORR on the (111) surfaces of various transition metals has been previously presented [10, 18]. In brief, this model is based upon analyses of two mechanisms that are often discussed for the ORR, the dissociative and associative mechanisms. The reaction energies of the elementary steps in these mechanisms are determined with DFT, and simple corrections for solvent, zero-point energy, and entropy effects are added to these values to obtain the free energies of reaction. Using the normal hydrogen electrode (NHE) as a reference, the free energies of each step in which electron transfer occurs are then corrected for the effect of changing electrode potential. The various free energies are determined as functions of the adsorption energies of O, OH, and OOH, together with the activation barrier for dissociation of molecular oxygen. By combining these results with simple correlations between the adsorption energies of the various species and a Brønsted–Evans–Polanyi relationship that relates the O₂ dissociation energy to the adsorption energy of atomic oxygen [19, 20], the free energies of each elementary reaction step are expressed as approximate functions of the oxygen adsorption energy.

The above relations are combined with Sabatier analysis [13] to determine the rate-limiting steps (RLS’s) and ORR activities for a range of values of the oxygen adsorption energy (Fig. 1). For metals that bind oxygen quite strongly,
Table 1. Binding energies of O, OH, and OOH on transition metal (100) and (211) surfaces. All energies are calculated assuming H₂O dissociative adsorption from the gas-phase; a stoichiometrically appropriate amount of gaseous H₂ is also assumed to be produced. For the (211) surfaces, all adsorbates are at a coverage of 1/6 ML; the corresponding coverage on the (100) surfaces is 1/4 ML. For the (100) calculations, all metals are constrained to the fcc crystal system. The (211) data for O and OH are taken from Ref. [13] (additional computational details can be found in that reference). OOH data for the (211) surface are only reported for metals where OOH formation might be rate-limiting (i.e., for metals on the right-hand side of the volcano curve). The metals are listed in their order on the periodic table.

<table>
<thead>
<tr>
<th>Metal</th>
<th>O</th>
<th>OH</th>
<th>OOH</th>
<th>O</th>
<th>OH</th>
<th>OOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(211)</td>
<td></td>
<td>(100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>−0.80</td>
<td>−0.86</td>
<td>−</td>
<td>−0.76</td>
<td>−0.63</td>
<td>2.86</td>
</tr>
<tr>
<td>Co</td>
<td>−0.18</td>
<td>−0.65</td>
<td>−</td>
<td>−0.37</td>
<td>−0.29</td>
<td>3.02</td>
</tr>
<tr>
<td>Ni</td>
<td>0.4</td>
<td>−0.49</td>
<td>−</td>
<td>0.10</td>
<td>−0.08</td>
<td>3.11</td>
</tr>
<tr>
<td>Cu</td>
<td>1.10</td>
<td>−0.07</td>
<td>−</td>
<td>0.72</td>
<td>0.19</td>
<td>3.42</td>
</tr>
<tr>
<td>Ru</td>
<td>0.04</td>
<td>−0.64</td>
<td>−</td>
<td>−0.11</td>
<td>−0.39</td>
<td>2.72</td>
</tr>
<tr>
<td>Rh</td>
<td>0.34</td>
<td>−0.27</td>
<td>−</td>
<td>0.38</td>
<td>−0.02</td>
<td>3.15</td>
</tr>
<tr>
<td>Pd</td>
<td>1.75</td>
<td>0.36</td>
<td>−</td>
<td>1.54</td>
<td>0.64</td>
<td>3.88</td>
</tr>
<tr>
<td>Ag</td>
<td>2.03</td>
<td>0.52</td>
<td>4.03*</td>
<td>1.74</td>
<td>0.53</td>
<td>3.79</td>
</tr>
<tr>
<td>Ir</td>
<td>0.03</td>
<td>−0.35</td>
<td>−</td>
<td>0.45</td>
<td>−0.06</td>
<td>3.17</td>
</tr>
<tr>
<td>Pt</td>
<td>1.27</td>
<td>0.25</td>
<td>3.58</td>
<td>1.61</td>
<td>0.56</td>
<td>3.80</td>
</tr>
<tr>
<td>Au</td>
<td>2.62</td>
<td>0.92</td>
<td>4.38</td>
<td>2.79</td>
<td>1.09</td>
<td>4.39</td>
</tr>
</tbody>
</table>

* This value is estimated from a linear interpolation based on the O and OOH binding energies on Au and Pt.

the electrochemical hydrogenation of O or OH is the rate-limiting step, and for weak-binding metals, the RLS becomes the hydrogenation of O₂ to produce OOH radicals. At potentials near the equilibrium potential (1.23 V vs. NHE), a third regime appears; O₂ dissociation becomes rate-limiting for metals of intermediate oxygen binding strength [10]. Metals that bind oxygen with intermediate strength are found to have the highest activity for the ORR; consistent with experimental evidence, platinum shows the highest activity of the pure metals.

3.2 ORR activity analysis on (100) and (211) surfaces

To estimate the ORR activities on the (100) and (211) surfaces of various metals, we follow a very similar approach to that used to develop activity relationships on the (111) surfaces. The first step is to calculate the binding energies of O, OH, and OOH on the surfaces of interest; the appropriate energies are reported in Table 1.

The second step is to correct the calculated binding energies for coverage effects and for the effect of coadsorbed water bilayers. The corrections are
explicitly evaluated on Pt(100), and it is assumed that they will be roughly constant for the other metals. The corrections for the (100) surfaces differ from those on the (111) surfaces; neither O, OH, nor OOH species are stabilized by water adlayers on (100) surfaces (the coverage of the indicated species is 1/6 ML). This result stems from the geometrical mismatch between the rectangular (100) surfaces and the preferred hexagonal arrangement of water in bilayers; on Pt(111), there is a near-perfect registry between these geometries, but on Pt(100), the registry is broken, thereby significantly limiting the ability of water bilayers to stabilize adsorbed species. This result is also consistent with the fact that, to our knowledge, no highly ordered overlayers of water have ever been observed on (100) crystal planes [21]. For the hydroxyl species, we do find a lowering of the binding energy due to coverage effects; hydrogen-bonded networks of OH lead to a reduction of the binding energy per OH of $\sim 0.1$ eV. On the (211) surfaces, where the terrace geometry is identical to the hexagonal arrangement of (111) terraces, the coverage and water corrections are determined to be very similar to the (111) corrections.

The next step is to determine the transition state energies and activation barriers for O$_2$ dissociation on (100) surfaces; these barriers are of relevance to the dissociative ORR mechanism, and they have already been evaluated on the (211) surfaces [20]. On (100) surfaces, it turns out that the only metals for which O$_2$ dissociation can be competitive are Au and Ag; on those metals, we determine transition state energies of 0.50 and 0.06 eV (these energies are referenced to the appropriate clean slab surfaces and to O$_2$(g), where the O$_2$ energy is corrected to give the correct free energy of formation of liquid water – see Ref. [10] for details). On these two surfaces, we generally find facile O$_2$ dissociation.

Next, we perform Sabatier analysis to estimate ORR activities for the (100) and (211) surfaces of the various transition metals, assuming the same prefactors as are used in the previously published analysis for (111) surfaces [10]. From this analysis, we produce volcano plots as a function of the oxygen binding energy on the various facets; such plots are shown for the (111), (100), and (211) facets in Fig. 2. Approximate linear relationships are seen to exist between the calculated activities and the oxygen binding energy (BE$_O$) across a broad range of BE$_O$'s. This phenomenon is simply a result of the fact that many of the key catalytic parameters that determine the activity (e.g., the O, OH, and OOH BE's) correlate linearly with the BE$_O$; such correlations are shown for the (100) surfaces in Fig. 3.

The kinetic trends shown in Fig. 2 indicate that, in general, steps (i.e., (211) surfaces) are significantly less active for the ORR than are perfect (111) terraces; in effect, the maximum of the volcano is shifted towards more noble metals on the steps. This result indicates that O and OH species poison the steps on most metals; they are bound so strongly that it becomes energetically prohibitive to activate these species to form water. On Au, however, where the rate-limiting step is hydrogenation of O$_2$ to form OOH, the increased binding
at the steps makes OOH formation more favorable than it is on (111) terraces, thus leading to a higher rate of reaction. Unfortunately, it is somewhat difficult to find clear experimental evidence of activity differences between steps and terraces. Feliu et al. [22] have performed studies of the ORR on Pt(111) and Pt(211); in perchloric acid, they found small differences in activity between the two surfaces. This result is somewhat surprising, given the considerations mentioned above. Presumably, the (111) terraces between the steps are controlling the activity in the experiments, but a small cooperative effect may exist that slightly enhances the (111) rate beyond that found on defect-free (111) terraces [23].

Interestingly, the trends in Fig. 2 also suggest that (100) facets are, for the most part, of comparable activity to (111) facets. Although somewhat counter-intuitive, given the different geometries of these facets, the result is consistent with recent results in alkaline solution and in weakly adsorbing perchloric acids on Pt(111) and Pt(100) [24–26]. On Au and Ag surfaces, however, the (100) facets show somewhat higher activity than do the close-packed (111) facets; these increased activities are due, in part, to changes in the rate-limiting steps of the reactions on the respective facets (for Au, the RLS changes from $O_2$ dissociation to $O_2$ hydrogenation in going from the (100) to the (111) facet, and on Ag, the corresponding change is from OH hydrogenation to $O_2$ hy-
Fig. 3. Binding energy correlations on the (100) surfaces of transition metals. All binding energies are referenced to appropriate stoichiometries of gaseous water and gaseous \textit{H}_2. The specific correlations shown are (a) OH vs. O binding energies and (b) OOH vs. O binding energies. The correlations are $\text{BE}_{\text{OH}} = 0.48\text{BE}_0 - 0.21 \text{eV}$ and $\text{BE}_{\text{OOH}} = 0.47\text{BE}_0 + 3.05 \text{eV}$, respectively. Figure 3a is adapted from Ref. [19].

drogenation). We note that previous measurements and analyses have shown a relatively high activity for Au(100) compared to Au(111) [27]. We finally note that, in the present analysis, we have not considered the famous “hex” re-
Our theoretical results suggest that the ORR should exhibit non-negligible particle size effects on some metals. In general, smaller nanoparticles are expected to exhibit a higher concentration of edges and, assuming that the edge atoms are removed (see Methods section), steps. Thus, we might expect that nanoparticles of metals where the steps are more active than the terraces (e.g.,...
Au nanoparticles) would show increasing ORR activity as the particle size is decreased. Nanoparticles of metals where the steps are less active, however, might actually show decreasing activity with decreasing particle size, since the percentage of active terraces on small particles would be decreased compared to larger particles.

To quantify these speculations, we average the ORR activity over all relevant surface features for two transition metals and for a variety of nanoparticle diameters; the results are shown in Fig. 4. As expected, the average activity of Au nanoparticles increases as the particle diameter is decreased. This result is consistent with the fact that extensive particle size effects for Au have been documented for other important catalytic reactions [29]. A recent study by Guerin et al. suggests that our prediction is correct down to particle diameters of a few nanometers on titania supports. For even smaller particles, the average measured activity of the Au nanoparticles rapidly decreases to zero [4]. The discrepancy between the calculations and the experimental results for such small particles might be explained by changes in the Au nanoparticle shape due to adsorbate effects; it may also be that the smallest Au particles experience finite size-related electronic structure effects that are not treated in our model.

In contrast to our predictions of particle size effects on Au, we find that the activity for Pt nanoparticles is predicted to decrease as the particle diameter decreases. Although there is some controversy over particle size effects on Pt in the experimental literature [3, 5–7], there appears to be a general consensus that decreasing Pt particle diameters do, in fact, lead to decreased inherent catalytic activity. For example, Mayrhofer et al. [6] found substantial decreases in activity for particles with diameters decreasing from 30 to 5 nm, in good qualitative agreement with our results. We note that the magnitude of the decrease measured by those authors is larger than the decrease predicted in our model, suggesting that effects beyond simple changes in the number of defects may also be significant in those experiments.

4. Conclusions

A simple, first principles-based model of the oxygen reduction reaction (ORR) has been used to estimate ORR kinetics on the (111), (100), and (211) facets of eleven transition metals (Au, Ag, Pt, Pd, Ir, Cu, Rh, Ni, Ru, Co, Fe). A major conclusion of the study is that, for nearly all of the studied metals, (211) steps have lower ORR activity than do the more planar terraces; in effect, O and OH radicals are bound too strongly to the steps, thus increasing the barrier to form water on these defect sites. A significant exception to this trend is found for Au; on that metal, stronger binding of O and OH actually leads to increases in the ORR activity. These results, combined with Wulff-type nanoparticle models, suggest that the average ORR activity of Au nanoparti-
cles will increase as the particle size is decreased; Pt nanoparticles, on the other hand, are predicted to show a decrease in ORR activity with decreasing particle size.

Acknowledgement

This manuscript is submitted on the occasion of Professor Dieter Kolb’s 65\textsuperscript{th} birthday. J. Greeley acknowledges a H. C. Ørsted Fellowship from the Technical University of Denmark. We acknowledge computational resources through the Danish Center for Scientific Computing. The Center for Atomic-scale Materials Design is supported by the Lundbeck Foundation. The work at the Center for Nanoscale Materials/Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

References