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Improved oxygen reduction reactivity of platinum monolayers on transition metal surfaces

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ABSTRACT

The catalytic activity of platinum monolayers supported on close-packed transition metal surfaces (Au(111), Pt(111), Pd(111) and Ir(111)) is investigated for the oxygen reduction reaction (ORR) by generating free energy diagrams and performing Sabatier analysis based on periodic, self-consistent density functional theory (DFT) calculations. Three different ORR mechanisms, involving direct or hydrogen-assisted activation of O₂, are considered. At the ORR equilibrium potential of 1.23 V, the reactivity of all surfaces is shown to be limited by the rate of OH removal from the surface. At a cell potential of 0.80 V, the ORR reactivity of different surfaces is dictated by the strength of oxygen adsorption, with OH removal via hydrogenation and O–O bond scission in either O₂, O₂H or H₂O₂ being the rate-limiting steps for surfaces with stronger and weaker oxygen binding, respectively. Among the surfaces studied, Pt monolayer on a Pd(111) substrate shows the highest reactivity and is more active than Pt(111). These results are in excellent agreement with our earlier experimental and theoretical work, which was based on a simpler model for the ORR.

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1. Introduction

Ever-increasing energy demand and simultaneously depleting fossil fuel reserves around the world have inspired numerous studies targeted towards improving the performance of low temperature proton-exchange-membrane fuel cells (PEMFCs) [1]. However, inadequate efficiency of energy conversion and the cost associated with Pt catalysts remain a cause of concern [2,3]. Oxygen reduction reaction (ORR), the reaction taking place at the fuel cell cathode, accounts for a large fraction of the overpotential on the commercial Pt-based catalysts [3]. The all-Pt catalysts also suffer from poisoning by hydroxyl species (OH), which have been shown to inhibit ORR [3,4]. Therefore, it is desirable to design stable catalysts that have higher ORR activity, lower Pt loading, and increased resistance to OH poisoning.

Various experimental [5–8] and theoretical [9–11] studies have been performed to achieve these goals by designing Pt-based alloy electrocatalysts. Indeed, microscopic tailoring of catalysts through a combination of theoretical and experimental techniques has been realized in a few cases over the last few years, and examples of such successes in heterogeneous vapor-phase [12–14] and electrochemical [8,15–18] catalytic systems have been reported in the literature. Although significant progress has been made in understanding the reasons behind the improved performance of

these cathode electrocatalysts, the exact reaction mechanism for ORR on each of these catalysts remains elusive. Despite the simplicity of ORR reactants and products, its reaction mechanism is complex and has continued to be debated on important aspects such as the rate-limiting step and the nature of surface intermediates.

First-principles calculations have been successfully employed for elucidating reaction mechanisms [14,19,20] and also for designing [12,13,21] new alloy catalysts in the field of vapor-phase heterogeneous catalysis. However, the use of these methods has been limited for electrochemical systems, primarily because of the difficulty in accounting for the complicated reaction environment, including electric field and potential effects. Recently, Nørskov and co-workers [10] have proposed a scheme that accounts for a variety of factors, including that of potential bias. They have successfully utilized this approach for studying ORR [10,22], hydrogen evolution reaction [23] and electrochemical water splitting [24], and have established important insights regarding the respective reaction mechanisms.

Using a combination of density functional theory (DFT) calculations and an array of experimental techniques, we recently identified, synthesized and tested successfully, a new class of electrocatalysts for ORR that are based on monolayers of Pt deposited on different late transition metals (Au, Pd, Rh, Ir, Ru) [17]. The reactivity of these catalysts was attributed to the modifications in electronic structure of surface Pt atoms effected by the substrate metal through both geometric and ligand effects. In

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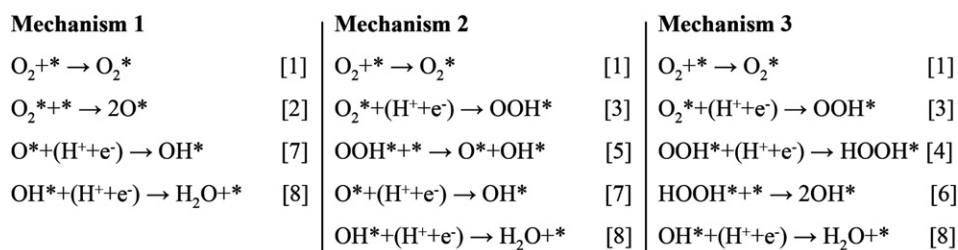


Fig. 1. Three oxygen reduction reaction (ORR) mechanisms.

particular, the center of the d-band (ϵ_d) of surface Pt atoms and the binding energy of atomic oxygen (BE_O) on these surfaces were shown to correlate well with their experimentally measured ORR activity. It was also shown that the kinetics of two key representative reactions, involving a O–O bond scission step and a O–H bond formation step, form the basis for the volcano-type behavior exhibited by these catalysts, whereby a Pt monolayer on Pd (Pt*/Pd) was identified as the best catalyst among the systems studied.

Here, we present an extension of this study, by applying the approach suggested by Nørskov et al. [10] for calculating the free energies of different reaction intermediates on Pt monolayers supported on Au(111), Pt(111), Pd(111) and Ir(111). Subsequently, we construct the hybrid free energy diagrams (FED) by also including the activation energy barriers for different O–O bond scission steps (in O_2 , OOH and HOOH) in the ORR network. Finally, by performing a Sabatier analysis [25], the free energy changes and activation energy barriers for relevant steps are used to estimate the relative activity of these catalysts at two different cell potentials.

2. Methods

Spin-polarized DFT calculations were performed within the generalized gradient approximation (GGA-PW91) using ultrasoft pseudopotentials [26] as implemented in the DACAPO code [27,28]. Detailed calculation parameters have been provided in previous studies [15,17,18]. The platinum monolayer surfaces were modeled by a single layer of platinum placed on top of Au(111), Pd(111) and Ir(111); (111) is dropped hereafter for brevity. Accordingly, the Pt-overlayer adopted the lattice constant of the respective substrate. Each surface was constructed from a (2×2) surface unit cell and consisted of four layers of metal atoms. The top two layers, that is the platinum monolayer and the top layer

of the substrate metal, were relaxed. The binding energies ($BE = E_{\text{total}} - E_{\text{slab}} - E_{\text{gas-phase adsorbate}}$) and geometries of adsorbed species (O, OH, OOH and HOOH), as well as all the O–O bond scission steps in O_2 , O_2H and H_2O_2 were studied on the relaxed surfaces. Minimum-energy paths of the respective reaction steps were calculated using the climbing-image nudged elastic band method [29].

The equilibrium PW91 lattice constants for bulk metals were calculated to be 4.18 (Au), 4.00 (Pt), 3.99 (Pd) and 3.86 Å (Ir), in good agreement with the respective experimental values [30] (4.08 (Au) 3.92 (Pt), 3.89 (Pd) and 3.84 Å (Ir)).

Following the approach proposed by Nørskov et al. [10], the free energies of different reaction intermediates were calculated at 1 bar and 300 K. Zero-point energy (ZPE) and entropic ($T\Delta S$) corrections have been added to the free energies of all reaction intermediates. The Sabatier analysis for ORR was performed as outlined earlier [10,25].

Table 1

Binding energies of different ORR intermediates and transition state energies for O–O bond scission steps

	Pt*/Au	Pt	Pt*/Pd	Pt*/Ir
Strain ^a (%)	4.50	0.00	−0.40	−3.50
ϵ_d (eV)	−1.92	−2.52	−2.36	−3.08
Binding energies in eV				
O	−4.20	−3.88	−3.81	−3.31
OH	−2.17	−2.09	−1.99	−1.90
O_2H	−1.01	−1.09	−1.05	−0.92
H_2O_2	−0.44	−0.42	−0.39	−0.36
Transition state energies in eV				
$TS(O_2 \rightarrow 2O)^b$	−0.04	0.09	0.23	0.75
$TS(O_2H \rightarrow O + OH)^c$	0.23	0.15	0.26	0.40
$TS(H_2O_2 \rightarrow 2OH)^c$	0.11	0.25	0.34	0.45

^a Positive (negative) strain implies expansion (compression) of Pt-monolayer compared to the equilibrium lattice constant of Pt(111).

^b The binding energy of the transition state is defined with respect to gas phase O_2 .

^c The binding energy of transition state is defined with respect to adsorbed initial state.

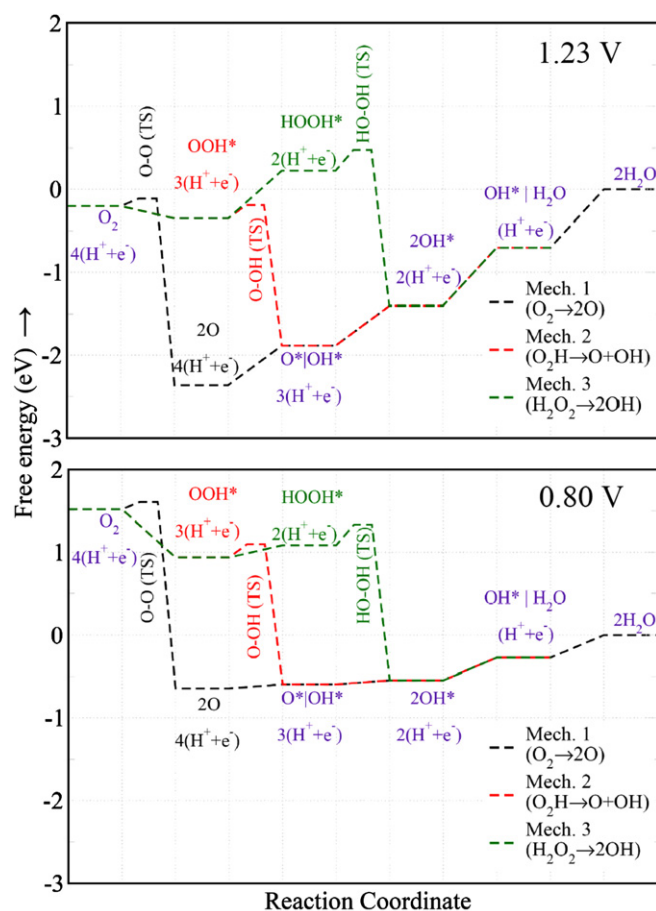


Fig. 2. Free energy diagram for ORR on Pt(111) via three different mechanisms at two different potentials.

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