New Mechanism for the Enhancement of the Oxygen Reduction Reaction on Stepped Platinum Surfaces

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Article

New Mechanism for the Enhancement of the Oxygen Reduction Reaction on Stepped Platinum Surfaces

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Abstract

It has long been recognized that the oxygen reduction reaction occurs more readily on Pt(111) surfaces that include steps, both (111) and (100), than on near-perfect Pt(111). Theoretical models were developed involving the water structure in the electric double layer and its interactions with adsorbed OH, with the actual O_2 reduction occurring on the (111) terraces adjacent to the steps. However, the present density functional theory (DFT) calculations confirms that O_2 adsorbs strongly at the steps and can undergo dissociation aided by adjacent water molecules to produce adsorbed OH. OH produced at the steps can move to the (111) terraces, where it can be more readily reduced to H_2O and desorbed. This model avoids the scaling relation, which predicts that all oxygen-containing reactants and intermediates are proportional to each other on any given surface. Efforts to develop new O_2 reduction catalysts have been hampered by this assumption, which supposes that the reaction rate can be increased by decreasing OH adsorption strength, even though decreased OH adsorption strength is accompanied by decreased O_2 adsorption strength. This proposed model can explain the experimental results on stepped surfaces and may also be important for the development of Pt nanoparticle catalysts.

Keywords: density functional theory; oxygen reduction; fuel cell catalysts

1. Introduction

There has been an intensive search for ways to increase the activity of catalysts for the oxygen reduction reaction (ORR) in order to decrease the catalyst cost in H_2-O_2 fuel cells, which are an integral component of the much-anticipated hydrogen energy economy. Much research has been devoted to fine-tuning the adsorption of reactants and intermediates in order to reach the summit of the famed volcano plot, in which reaction rate is plotted versus the adsorption strength of oxygenated species, OH for example. The adsorption strength of most oxygenated species, including O_2, O, OH, HO_2 all appear to be proportional to each other, the so-called scaling relationship [1]. Thus, if it is assumed that OH adsorption should be weakened, O_2 adsorption would also be weakened. This is a dilemma that has been largely ignored thus far. Nevertheless, it has been found experimentally that the use of Pt alloys such as Pt-Co with decreased OH adsorption strength has resulted in increased ORR rates. Interestingly, no Pt alloys have been reported for which O_2 adsorption is too weak, even though theoretical results show that adsorption on Pt-covered Pt-Fe should be very weak indeed, on the order of -0.15 to -0.20 eV, which should in principle have a detrimental impact upon O2 capture [2-4]. At this point, O_2 must compete with water for adsorption sites, as shown later. Clearly, this approach has its limits, since eventually O_2 adsorption would be impaired.

One key to this puzzle has been the recognition that platinum surfaces based on Pt(111) that include steps, either (110) or (100), can have increased ORR activity based on area, usually with a maximum activity being observed at intermediate terrace widths [5-8]. Early theoretical work predicted that stepped surfaces would be less active than Pt(111), based on the strong adsorption of OH at steps [9]. Bandarenka et al. proposed that the maximum in ORR activity at intermediate step density is due to a trade-off between OH removal and OH formation rates, based on H-bonded water

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network stabilization of OH [10]. Subsequently, Jinnouchi et al. have similarly explained the presence of a maximum in the ORR activity at intermediate step widths based on the trade-off between destabilization of OH and stabilization of HO_2 adsorbed on (111) terraces by water molecules [11]. In contrast, Hoshi and coworkers have argued that, since the step structures differ between (110) and (100) steps, with the activities being similar, the steps themselves cannot be the active sites, which are proposed to be the (111) terraces immediately adjacent to the steps [8]. Subsequently, Kodama et al. reported that a variety of Pt stepped surfaces in which the steps are capped with gold are still active for the ORR [12]. This result seems to strongly suggest that the steps themselves are not the active sites, based on the assumption that gold is inactive for the ORR, at least in acid electrolytes, although high activity can be observed in alkaline electrolytes [13,14].

The present work aims to take into account the clearly observed experimental results that the ORR activity in acid electrolyte mainly increases with step density, both (110) and (100) steps on Pt(111) surfaces except for very narrow (111) terraces. The simplest assumption is that the steps have an increased adsorption strength for O_2 so that the ORR current is proportional to the O_2 coverage at the step. Using DFT calculations, we have found that indeed the O_2 adsorption strength is significantly higher at steps compared with the terraces. In addition, we have found that water molecules adsorbed on either side of the bridging O2 can assist in its dissociation, creating 4 OH, and the activation energies are much smaller at both types of steps than on the (111) terrace. Thus, water is being used as a proton donor, which has been shown to be important for alkaline electrolytes but not thus far for acid [13].

In principle, these results can help to escape the scaling relation dilemma by the use of Pt alloys on which OH adsorption on (111) terraces is weak, but the O_2 adsorption at steps is still strong enough so that the overall reaction rate is enhanced. Rurigaki et al. have studied PtNi alloy stepped surfaces experimentally and have found some deviations from the trends observed for pure Pt surfaces, however [15]. Nevertheless, we believe that the present model may be useful in the search for more active ORR catalysts.

2. Results

O_2 has been found to be relatively stable on Pt(111) and has been observed directly with STM [16] [17]. Its adsorption energy is compared on these surfaces in Table 1. The adsorption energies for O2 adsorption on the (100) edge of Pt(533) and the (110) edge are quite similar, -1.96 and -1.86 eV, respectively, far larger than that on Pt(111), -0.89 eV. The presence of water stabilizes O2 on both steps slightly but destabilizes that on Pt(111). The adsorption energies of O2 on the (111) terraces of Pt(533) and Pt(553) are also similar to those on Pt(111) itself. Thus, O_2 is expected to adsorb at the steps rather than on the terraces, as long as the latter are not covered with OH, which adsorbs strongly. However, it must be kept in mind that the adsorption energy for OH is referred to gas-phase OH and thus is misleadingly large.

To get a more realistic idea of the first steps in the ORR, the energies of the O_2-$2H_2O$ system have been plotted as the O-O bond is stretched in ca. 0.2 Å increments on Pt(533), Pt(553) and Pt(111) (Fig. 1), in much the same way as was done for O2 dissociation on Pt(111), Pt(211) and Pt(221) in a UHV study by Gambardella et al. [17]. As with the latter study, the behavior on the two stepped surfaces is somewhat similar, but the activation energy E act is somewhat smaller on Pt(533), 0.21 vs. 0.28 eV (Table 2). Both energies are far smaller than that on Pt(111), 0.55 eV. In contrast, Gambardella calculated values of 0.9 eV for O_2 dissociation energies on three surfaces, Pt(111), Pt(211) and Pt(221) using DFT. However, Gee and Hayden found O_2 to be dissociated more readily on Pt(533) than Pt(111) in UHV [18]. The corresponding atomic models for the overall process are shown in Figures 2, 3 and 4 for Pt(111), Pt(533) and Pt(553), respectively.

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Table 1. Experimental and calculated adsorption energies for O2, H2O, OH on Pt surfaces.

Surface	**O_2**	**O-O, Å**	**OH**	**H_2O**	**Reference**
Pt(111) exp.	-0.35 ~ -0.38				[19,20]
Pt(111) calc.	-045 ~ -0.81				[2-4, 21-23]
Pt(111) calc.				-0.46	[24]
Pt(111) calc.	-0.89	1.370	-2.75	-1.41	pw
Pt(111)/H_2O calc.	-0.81	1.399			pw
Pt(533) calc.	-1.96	1.375	-3.24	-1.64	pw
Pt(533)/H_2O calc.	-2.05	1.414			pw
Pt(553) calc.	-1.86	1.378	-3.33	-1.81	pw
Pt(553)/H_2O calc.	-2.13	1.408			pw

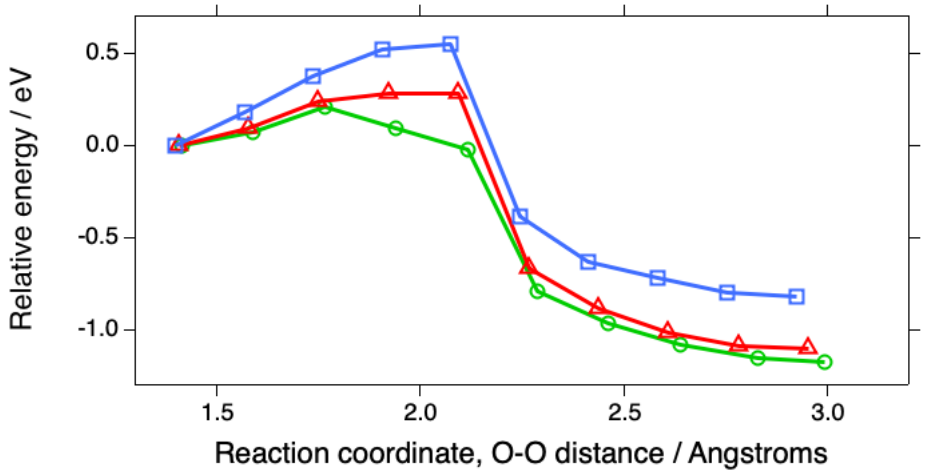

Figure 1. Reaction profiles for the first steps in the ORR involving O_2 adsorbed in the bridging configuration at (100) steps on Pt(533) (green circles), at (110) steps on Pt(553) (red triangles), and on Pt(111) (blue squares)..

Table 2. Calculated kinetic parameters for water-assisted O_2 dissociation.

Surface	**E_{act}, eV**	**O-O, TS, Å**	**ΔE, eV**
Pt(111)	0.55	2.075	-0.82

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Pt(533)	0.21	1.766	-1.17
Pt(553)	0.28	1.923 ~ 2.094	-1.11

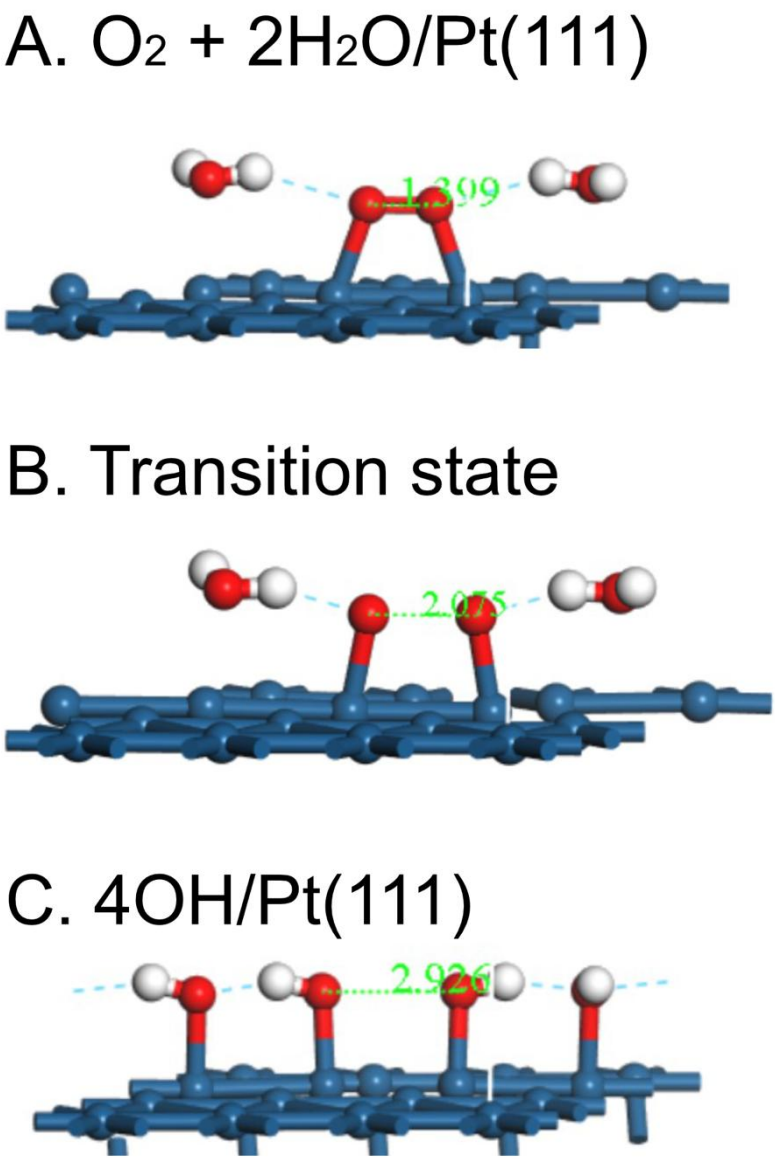

Figure 2. Initial state, transition state and final state for the reaction $O_2 + 2H_2O \rightarrow 4OH$ on Pt(111).

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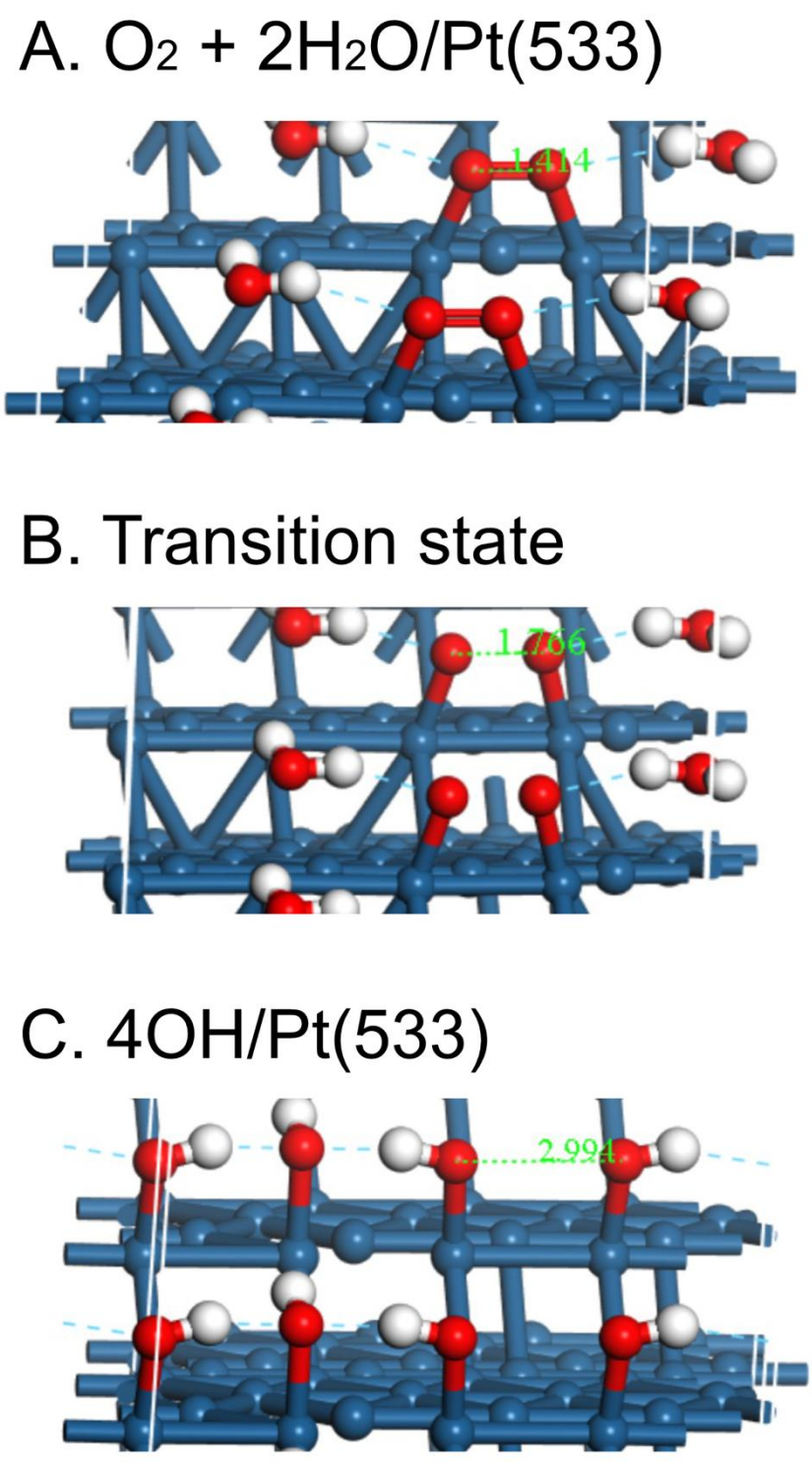

Figure 3. Initial state, transition state and final state for the reaction $O_2 + 2H_2O \rightarrow 4OH$ on Pt(533).

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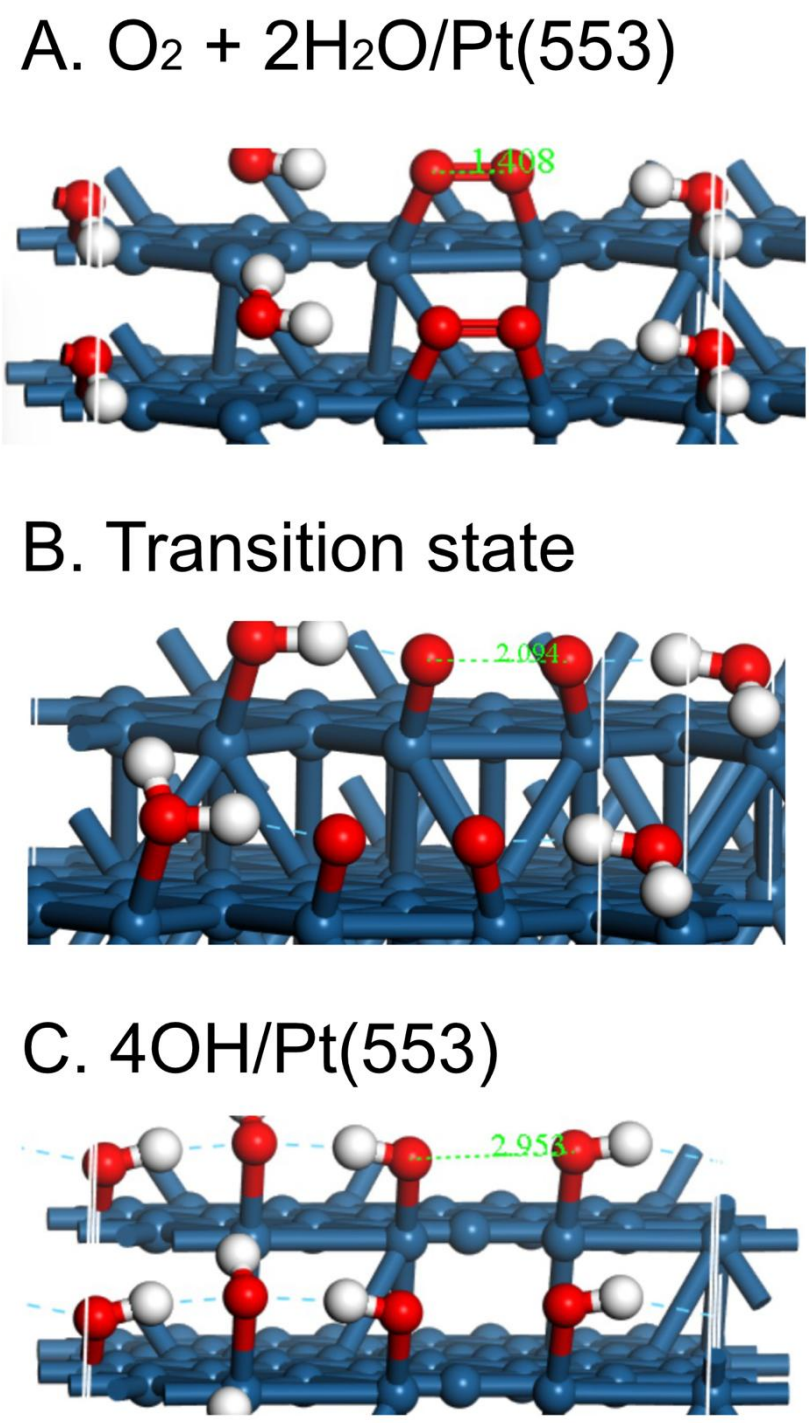

Figure 4. Initial state, transition state and final state for the reaction $O_2 + 2H_2O \rightarrow 4OH$ on Pt(553).

The reasons for the great differences in E_{act} are proposed to involve both the stronger adsorption of O_2 but also that of H_2O, which is ca. 0.75 eV stronger at the steps than on the (111) terrace. Thus, the reactants are held in place firmly during the overall reaction. Even more importantly, O_2 adsorbs more strongly at the steps than does water, in contrast to the situation on Pt(111), on which water is calculated to adsorb more strongly than O_2, which would lead to an impairment of the ORR activity. This is a result that has not been reported thus far to our knowledge. It should also be noted that water adsorption does not follow the usual scaling relations, so that it is possible for water to adsorb more strongly than O_2.

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The overall reaction can also be plotted to show the differences in the initial O_2 adsorption energies (Fig. 2). This representation emphasizes the great advantage of the stepped surfaces in terms of capturing O_2 from solution. These reaction profiles follow the well-known BEP relation, which predicts that, for dissociation reactions, the activation energy should decrease as the energy of the products is decreased, as long as the activated state is similar to the product state [25].

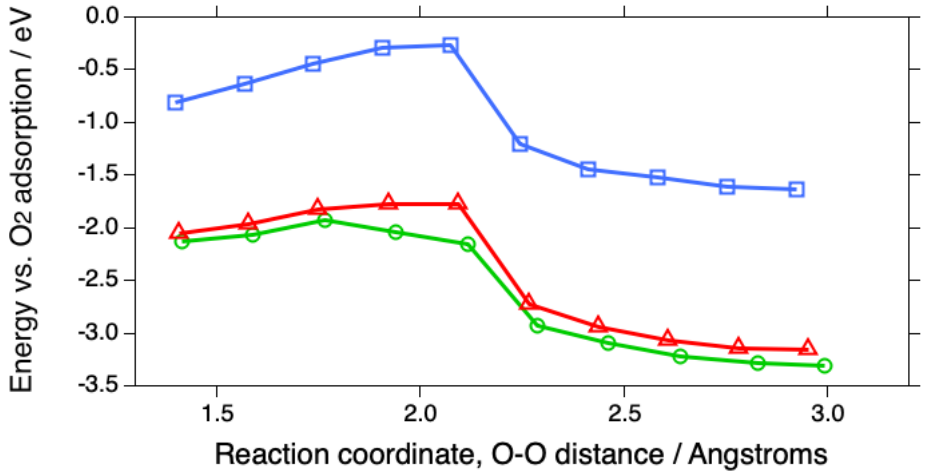

Figure 5. Reaction profiles for the first steps in the ORR involving O_2 adsorbed in the bridging configuration at (100) steps on Pt(533) (green circles), at (110) steps on Pt(553) (red triangles), and on Pt(111) (blue squares), as in Fig. 1 but with the energies referred to the adsorption energy of O_2 on the surface with two water molecules present.

In contrast to most recent DFT studies, we have elected to plot the results in terms of the directly calculated DFT energies of the systems as the O-O bond is stretched, with the numbers of atoms necessarily remaining constant. The approach is essentially that which would be used in a purely chemical reaction in a closed system, so that, as the reaction proceeds, a reverse driving force builds up. The way this occurs in the present approach is that the effective electrochemical potential U becomes more positive during the reaction, which would cause the rate of a reduction reaction such as the ORR to slow down.

U can be thought of as a linear function of the Fermi energy E_F, which can be plotted versus the reaction coordinate (Figure 6). In order to produce a reaction profile in which U is constant, it will be necessary to perform calculations on a series of similar systems in which the initial E_F is varied and then curve-fit the energy surface, i.e., the energy vs. E_F vs. reaction coordinate.

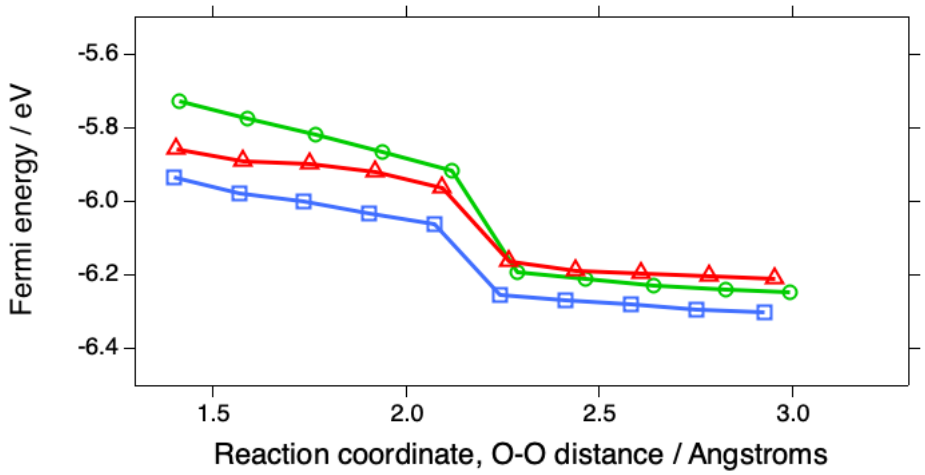

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Figure 6. Variation of E_F during the first stages of the ORR involving O_2 adsorbed in the bridging configuration at (100) steps on Pt(533) (green circles), at (110) steps on Pt(553) (red triangles), and on Pt(111) (blue squares).

3. Discussion

The present work attempts to shed light on the reasons for the increased ORR rate in acid electrolytes on stepped Pt surfaces with increasing step density, based on the simplest possible assumption, which is that the O_2 adsorbs more strongly at the steps than on the terraces. This point is crucial, because, on Pt(111), water adsorption is similar in strength to that of O_2, and, on certain alloys, O_2 adsorption can be significantly weaker than that of water. Therefore, steps are necessary in order to ensure that O_2 can be captured effectively from the electrolyte. It has been proposed by various groups that the effect of the step is to modulate the water structure close to the catalyst surface and thus stabilize or destabilize intermediates in the ORR. However, this model does not take into account the competition between O_2 and water for adsorption sites on the (111) terrace.

4. Materials and Methods

DFT calculations were carried out with the use of the DMol^3 program (BIOVIA, Dassault Systemes, v. 2023) with periodic boundary conditions for Pt(533), Pt(553) and Pt(111). The first steps in the ORR have been modeled starting with one O_2 molecule and two H_2O molecules.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/doi/s1, DFT calculation methodology.

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Data Availability Statement: The authors will supply necessary data upon request.

Conflicts of Interest: The author declares no conflicts of interest.

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