Final Progress Report

Project title: Bimetallic and Trimetallic Nanoparticles for Fuel Cell
Electrocatalysis

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Project Summary: Theoretical, high level ab initio investigations on representative clusters as well as on extended systems are conducted to determine the electronic, geometric, and thermodynamic factors that determine catalytic and electrocatalytic behavior, focusing in the reduction of oxygen in acid medium. The study of adsorption and reaction processes generates the information needed for force field development to be used in the analysis of nanocatalyst particles, their support, and their environment through large-scale molecular dynamics simulations, which include collective effects at the nanosecond time scale. Ab initio molecular dynamics simulations are used to explore reaction mechanisms, and this technique along with transition state theory calculations allows us to obtain the information needed about activation energies and estimates of the rate constants. Dynamic Monte Carlo simulations combine the results of the first three sets of studies yielding kinetics information within a time scale in the range of seconds and length scales of the order of hundreds of nanometers, including nanocatalyst/support/environment.

Progress Report: During this year, research efforts focused on the following areas:

- ***Design of bimetallic catalysts for oxygen electroreduction (OER)***
 - We have reported a complete analysis of the four-electron OER mechanism on Pt catalysts, including structural and dynamic details.[6, 8, 11] Our studies are based on adsorption of molecular oxygen in the presence of a hydrated proton $[\text{H}_3\text{O}(\text{H}_2\text{O})_3]^+$ and follow the evolution of the chemistry of chemisorption, electron and proton transfer and identification of intermediate and product species. Our ab initio results were used in a coarse-grained Dynamic Monte Carlo simulation of the electrochemical cell yielding the evolution of the overall reaction as a function of cell potential. These studies clearly show the rate determining steps and the influence of the most important variables on the OER on Pt electrocatalysts. [3, 4]
 - Analysis of each individual reduction step on bimetallic clusters: adsorption and dissociation of intermediates: H_2O_2 , OOH , OH , H_2O , and transition states for OOH dissociation.[2, 5, 10] We have reported detailed information about adsorption and dissociation of OOH , the product of the first reduction step, and H_2O_2 , another key intermediate species. We also discussed the role of metals other than Pt on the adsorption of the intermediate species and on the overall reaction.
 - Thermodynamic guidelines for the design of bimetallic catalysts: Based on the above analyses we are now able to present a summary of thermodynamic guidelines for the design of bimetallic catalysts for O_2 reduction.[1] Basically, our idea focuses on the effect of foreign elements alloyed with Pt on the ΔG of reaction for each of the four intermediate steps. Moreover, we have found that a simple two-dimensional diagram could be obtained by the characterization of the sign of ΔG for the first step vs. ΔG for the sum of the other three steps. This simple diagram clearly indicates that Pt is the best OER catalyst, but also reveals which elements are the best to be alloyed with Pt for the enhancement of the overall reaction.[1]

- **Mass transfer studies:** Analyses of the catalyst/hydrated polymer interface—studies of water structure and dynamics and diffusion of hydrated proton—examination of the polymer conformation over the catalyst. We observed the formation of ionic clusters where water nucleates at the membrane hydrophilic sites on the catalyst surface. These ionic clusters are either totally disconnected, partially connected, or forming a continuum phase, depending on the ratio water/S sites in the polymer. When this ratio is ~ 25 , the clusters have an approximate diameter of 1 to 1.5 nm, and they are connected by multiple water bridges, favoring proton transport, whereas molecular oxygen transport is expected to take place through the hydrophobic regions.[9]
- **Physical state and dynamics of supported bimetallic nanocatalysts:** We reported a novel method[7] to characterize the surface composition of bimetallic nanocatalysts. The method is based on the analysis of the phonon spectra of the nanoparticles which permits the identification of the type of atoms adsorbed at the surface and in the core sites. Although we discovered the method through the analysis of MD simulation results, we showed that it can be implemented experimentally measuring partial phonon spectra in nanoparticles.

Unexpended funds: We plan to spend all the funds by the end of this period, 07/31/05.

List of publications during the current year:

1. Y. Wang and P. B. Balbuena, "Design of oxygen reduction bimetallic catalysts: Ab-initio derived thermodynamic guidelines," *J. Phys. Chem. B*, 109, 18902-18906, (2005).
2. P. B. Balbuena, S. R. Calvo, E. J. Lamas, and J. M. Seminario, "Adsorption and dissociation of hydrogen peroxide on Pt-based bimetallic clusters alloyed with Cr, Co, and Ni," submitted.
3. S. R. Calvo, Y. Wang, and P. B. Balbuena, "Dynamic Monte Carlo Simulations of the Oxygen ElectroReduction Reaction on a Pt(111) Surface," in preparation.
4. S. Calvo, D. S. Mainardi, A. P. J. Jansen, J. J. Lukkien, and P. B. Balbuena, "Test of a Mechanism for O₂ Electroreduction on Pt(111) via Dynamic Monte Carlo Simulations." In "*Power Sources Modeling*", R. G. Jungst, J. W. Weidner, B. W. Liaw, and K. Nechev, Eds., Pennington, NJ, in press, 2005.
5. J. M. Seminario, L. A. Agapito, L. Yan, and P. B. Balbuena, "Density Functional Theory Study of Adsorption of OOH on Pt-Based Bimetallic Clusters Alloyed with Cr, Co, and Ni," *Chem. Phys. Lett.*, 410, 275-281, (2005).
6. Y. Wang and P. B. Balbuena, "Potential Energy Surface Profile of the Oxygen Reduction Reaction on a Pt Cluster: Adsorption and Decomposition of OOH and H₂O₂," *J. Chem. Theory and Comp.*, 1, 935-946, (2005).
7. S. R. Calvo and P. B. Balbuena, "Molecular dynamics studies of phonon spectra in mono- and bimetallic nanoclusters," *Surf. Sci.*, 581, 213-224, (2005).
8. Y. Wang and P. B. Balbuena, "Ab initio Molecular Dynamics Simulations of the Oxygen Reduction Reaction on a Pt(111) Surface in the Presence of Hydrated Hydronium (H₃O)⁺(H₂O)₂: Direct or Series Pathway?," *J. Phys. Chem.*, 109, 14896-14907, (2005).

9. P. B. Balbuena, E. J. Lamas, and Y. Wang "Molecular modeling studies of polymer electrolytes for power sources," *Electrochimica Acta*, in press, 2005.
10. P. B. Balbuena, D. Altomare, N. Vadlamani, S. Bingi, L. A. Agapito, and J. M. Seminario, "Adsorption of O, OH, and H₂O on Pt-based bimetallic clusters alloyed with Co, Cr, and Ni," *J. Phys. Chem. A*, 108, 6378, (2004).
11. Y. Wang and P. B. Balbuena, "Roles of proton and electric field in the electroreduction of O₂ on Pt(111) surfaces: Results of an ab initio molecular dynamics study," *J. Phys. Chem. B*, 108, 4376-4384, (2004).

Invited book chapter:

P. B. Balbuena, Y. Wang, E. J. Lamas, S. Calvo, L. A. Agapito, and J. M. Seminario, "Reactivity of bimetallic nanoclusters toward the oxygen dissociation in acid medium," invited chapter for the book on Materials and Device Modeling in PEM fuel cells, edited by Stephen J. Paddison, publisher Springer Verlag, submitted, July 05.

Reactivity of bimetallic nanoclusters toward the oxygen reduction in acid medium

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Abstract

Bimetallic catalysts are extensively sought as alternatives to the use of platinum in low-temperature fuel cell electrodes, particularly for the cathode, where the kinetically-slow oxygen electroreduction takes place. One of the first questions that arise in trying to search for alternative catalysts relates to the understanding of the mechanism of the oxygen four-electron reduction on Pt, the best catalyst currently known, and how the mechanism would be altered (if at all) by the presence of other catalyst active sites. We discuss the nature of O₂ adsorption, and of the various intermediates, such as OOH, OH, O, H₂O₂, and H₂O in the presence of hydrated protons (acid medium) on Pt and Pt-alloy catalysts, on the basis of density functional theory on small clusters and extended surfaces, and Car-Parrinello molecular dynamics simulations. We conclude with an overview of the current status and future perspectives for the design of new efficient and less expensive fuel cell catalysts.

1. Introduction

The oxygen reduction reaction (ORR) on Pt and Pt-alloys, the slowest of the two electrode reactions of low temperature fuel cells, has been studied for a long time in an effort to fully understand its mechanism and therefore being able of developing improved catalyst materials which may significantly contribute to enhance the overall fuel cell efficiency.^{1,2}

The standard potential for the four-electron reduction of oxygen in acid medium is 1.23 V with respect to the standard hydrogen electrode. However, a negative overpotential -for the ORR- of about 0.3 to 0.5 V is needed to start the reaction on a Pt electrode, Pt being the best catalyst known so far for this reaction.³ This overpotential is usually attributed both to kinetic and mass transport limitations at the cathode electrode. Nanoscale proton-exchange membrane (PEM) electrocatalysts have been used since the 60's,¹ however they are in most cases the result of lucky trial and error experimentation and there is no assurance that they correspond to the optimal materials.² There are advantages and challenges due to the nature of the nanometer-scale regime for the electrocatalytic system; nanocatalysts not only provide enhanced reaction rates with respect to those obtained from catalysis on extended surfaces,⁴⁻⁹ but most importantly, they may be suitable for alternative reaction paths that are available only because of the electronic characteristics at nano-dimensions. Besides, the feature size of nano-scale systems allows a theory-guided and a controlled atomic manipulation that should enable the fabrication of nanosystems with very precise characteristics.

alternative catalytic materials.^{24,26-39}

Oxygen (air) is reduced at the cathode catalytic surface. It is generally accepted that the first electron transfer is the rate determining step (*rds*) in a four-electron oxygen reduction mechanism in acid medium, yielding water as the final product,^{3,13,28,39,40} but some disagreement still exists with respect to the reaction mechanism. The overall reduction reaction is:

However, some authors propose a *direct* pathway where four electrons are sequentially added, others suggest a *series* of two electron reductions with the production of H_2O_2 as an intermediate, and finally a *parallel* (direct and series) mechanism is also suggested based both on experimental and theoretical evidences.³

A second controversy exists with respect to the mechanism of the first step. One view is developed on the basis of the early proposition by Damjanovic et al,⁴⁰⁻⁴² that proton and electron are simultaneously transferred to a weakly adsorbed molecule in the *rds*: $(O_2)_{\text{adsorbed}} + H_3O^+ + e^- \xrightarrow{\text{catalyst}} (OOH)_{\text{adsorbed}} + H_2O$. A second view, advocated by Yeager,⁴³⁻⁴⁵ suggested that the most likely mechanism of the direct four-electron oxygen reduction on Pt involves dissociative chemisorption of the O_2 molecule on a Pt surface probably accompanied by electron transfer, $O_2 + e^- \xrightarrow{\text{catalyst}} (O_2^-)_{\text{adsorbed}}$. They also concluded that the dissociative adsorption of O_2 is the *rds* and that the proton transfer follows rather than being involved in the *rds*.⁴³

Several reports indicate that Pt-based alloys are at least as good as pure Pt, and in many cases the alloyed material shows a better performance for the oxygen electroreduction (OER).^{26,27,33,46-48} Experimental data on the catalytic activity of bimetallic surfaces regarding the OER is controversial. It is clear that certain bimetallic catalysts (Pt-Cr, Pt-Fe, Pt-Co, Pt-Ni) yield a slightly enhanced oxygen reduction current, but the reported degree of enhancement differs among researchers.²

Theoretical and experimental studies have investigated the reasons for such enhancement,^{24,26,27,31-33,46,49} whose magnitude is not yet significant enough to induce a huge step forward in fuel cell technology, which requires reducing four times the current amount of Pt used, maintaining maximum power density and fuel cell efficiency.²

Thus, a strong motivation exists to find alternative catalysts with at least a four-fold increase in their activity. But characterization of the experimental catalysts is far from being complete,

mainly because of uncertainties about the structure of the nanoparticles (usually in the range of 2-5 nm, but sometimes with a much wider size distribution) and about the overall atomic distribution of the two components, since those aspects are extremely dependent on the nanoparticle fabrication method.⁵⁰⁻⁵⁵ Recent studies attributed the catalytic activity enhancement to the effect induced by the amorphous structure of the nanoparticle.⁴⁷ This is certainly a good point since particles in such size range have melting points much lower than their bulk counterparts,⁵⁶⁻⁵⁸ and both morphology changes and solid-solid structural transitions which can take place at relatively low temperatures, are extremely dependent on the overall composition and on the nature of the substrate.^{56,57,59-62} Such variable morphology characteristic of nanostructures may play an important role in the output of the catalytic process, and should be accounted in the analysis of catalytic activity. Others attribute the activity enhancement to differences between Pt and Pt-alloys in relation to their ability to form an oxide layer, which is found to be dependent on the ratio water/acid, i.e., in the water activity.⁴⁸

Some aspects of the current catalysts –in many cases not properly accounted when discussing catalytic activity- include the facts that under the PEM fuel cell conditions of temperature (~353 K) and pressure (1-2 atm), and under the effect of the surrounding medium (hydrated polymer), nanocatalysts are not necessarily in their lowest energy geometries, and their structures can adopt local minima configurations, including amorphous structures.⁶³⁻⁶⁵ The substrate can also significantly alter the conformation and chemistry of the active sites.⁶⁶⁻⁶⁸

The problem we would like to address is schematically shown in Figure 1: A catalytic interface (inset) is surrounded by a proton-carrier hydrated membrane; the reactants, intermediates, and products diffuse in and out to reach or leave the catalyst surface, and the substrate is the electronic conductor material which may also influence the reactive system given the nanoscale of the actual catalysts. When a new material is proposed and tested theoretically or experimentally, it is of paramount importance to understand the reaction and mass transfer mechanisms; for complex systems, such as that in Figure 1, the theoretical approach that we illustrate in this chapter becomes essential to aid and complement the design of costly experimental synthesis and testing efforts.

The structure of our chapter is as follows: we first discuss the oxygen reduction mechanism on Pt(111) surfaces based on our recently reported Car-Parrinello molecular dynamics simulations,^{21,69} making emphasis on the effects of degree of proton solvation, proximity proton-molecular oxygen, and surface charge on the first step of the reaction, in relation to the catalyst/hydrated membrane interfacial structure that might be expected in the actual membrane electrode assembly of low-temperature fuel cells. In this context we also analyze the effect that alloy catalyst ensembles may have on the first reduction step based on our own density functional theory (DFT) calculations and others theoretical and experimental results. Second, we discuss the subsequent electron reduction steps, emphasizing the differences between the adsorption of intermediates such as O, OH, and water, the production, adsorption, and dissociation of hydrogen peroxide, on Pt and Pt-alloy surfaces and clusters. Finally, we discuss the current status and perspectives for the design of more efficient and less costly fuel cell electrocatalysts.

2. Oxygen reduction mechanism in acid medium on Pt and Pt-alloys

As recently reviewed by Gasteiger et al.², a variety of experimental techniques have been applied to investigate the origins of the enhancement on the catalytic activity of some Pt alloys with respect to ORR currents in acid medium. Experimental studies suggested that the enhanced

activity originates in the inhibition of OH formation in alloy surfaces where the second element (such as Ni or Co) is easily oxidized.⁴⁶ On the theoretical side, Norskov et al.³⁹ introduced a relatively simple approach to investigate the potential energy surface for the ORR on Pt and on other metal surfaces, based on DFT calculations of the adsorbed energies of OH and O on those surfaces. They found a volcano-type description that correlates ORR activity with oxygen binding energy concluding that Pt and Pd would be the metals producing the smallest overpotentials. Experimental studies^{27,28,34,46,70} had suggested that Pt-skin surfaces consisting of a monolayer of Pt deposited over an alloy of Pt with Ni, Co, Cr, or Fe yielded various degrees of catalytic enhancements depending on the electrolyte, catalyst preparation, and temperature. The same idea has been tested theoretically^{24,49} where the strain effect caused by the lattice mismatch has been analyzed. In the same spirit of Norskov et al, Xu et al²⁴ introduced correlations between transition state energies and final energies for O₂ dissociation, suggesting that reasons for the enhanced activity of the Pt-Co skin surfaces may include a lower affinity of Pt-skin by atomic oxygen, and the presence of a few Co atoms that would easily dissociate O₂ and bind O more strongly. In agreement with these findings, Kitchin et al⁴⁹ have suggested that conservation of the d-band filling causes a d-band broadening and lowering of the average energy as a result of the interactions of Pt with the subsurface atoms, inducing weaker dissociative energies of adsorbates such as H₂ and O₂ on these surfaces. Moreover, DFT calculations⁷¹ have also shown that both strain and the presence of adsorbates⁷² are at least partially responsible for the displacement of the d-band center inducing changes in reactivity. Some of these concepts have been also proved by recent experiments from Adzic's group⁷³ that correlate ORR currents with DFT calculated oxygen binding energies and also with the energy corresponding to the alloy d-band center suggesting that most of the Pt-skin surfaces should have an intermediate value of such energy, providing a compromise between the ability to dissociate O₂ and that to avoid poisoning of the surface with oxygenated intermediates or products. Regarding the ORR mechanism, experimental evidence suggests that the mechanism remains unaltered when Pt is alloyed with other transition metals such as Co, Ni, Cr, Fe.^{46,48,74}

Finally, the most important concerns regarding alloys as substitutes for Pt in fuel cell electrodes include the potential leach and contamination of the electrolyte membrane with cations coming from the dissolution of the base-metal, therefore the design of new catalysts requires not only optimizing the catalytic activity but also analyzing the stability of the Pt and non-Pt elements under proton exchange fuel cell conditions.

2.1 The first reduction step

As outlined in the Introduction, a couple of suggested pathways have been proposed for the first electron transfer step: (a) dissociative chemisorption of O₂ (rds) probably accompanied by e-transfer and followed by proton transfer; (b) simultaneous proton and electron transfer to a weakly adsorbed O₂ molecule. We have recently shown through CPMD^{21,69} and DFT⁷⁵ results that both pathways may take place under different conditions of the interfacial structure; i.e. proton transfer may be involved in the first reduction step depending on the relative location of the O₂ molecule with respect to the surface and to the proton, on the degree of proton hydration, and on the surface charge which is dependent on the electrode potential.

Moreover, it was shown that proton transfer may precede or follow the first electron transfer, but in most cases the final product of the first step is an adsorbed HOO*.

These points are illustrated in a series of snapshots from CPMD simulations. The initial configurations are displayed by Schemes 1 and 2. First we analyze the effect of the distance d_{OH} between the oxygen molecule and the closest H of a hydronium ion solvated by two water molecules (Scheme 1) for various values of the distance d_{OS} between the oxygen molecule and the surface.

Figure 2. Snapshots from CPMD simulations⁶⁹ of the first ORR reduction step on Pt (111) for initial distances $d_{OH} = 2.2 \text{ \AA}$ and $d_{OS} = 3 \text{ \AA}$, at a low degree of proton solvation (see Scheme 1). Left: at 0.11 ps, Center: at 0.36 ps, Right: at 0.46 ps. The sequence illustrates that when O_2 is sufficiently close to a weakly solvated proton, proton transfer precedes chemisorption.

At the shortest initial d_{OH} distance ($2.2 \text{ \AA}$), Figure 2 (left) a hydrated proton -still H-bonded by the water molecules- gradually migrates towards O_2 . The O_2 molecule, initially located parallel to the surface (Scheme 1), rotates from the symmetric bridge site to a canted top-bridge site as found in previous work;^{76,77} and is partially polarized by the surface, that in this case carries a negative charge due to the addition of one electron to the unit cell to counterbalance the positive charge, as discussed in a later section.^{19,20,75} At this point there is no clear chemisorption of O_2 , which is still far from the surface. After 0.25 ps, the next image (Figure 2, center) shows the formation of an end-on chemisorbed species $*OOH$; analysis of the CPMD trajectory⁶⁹ shows that the O-O distance elongates whereas the distance from the OH group to the surface (HO-S) becomes shorter, as a consequence of the increasing interaction between the OH group and the

surface, while the electronic energy remains approximately constant. At 0.46 ps, (Figure 2, right) the chemisorbed $^*\text{OOH}$ is decomposed into adsorbed O and OH, after a lifetime of approximately 0.15 ps. DFT studies on small Pt_n clusters ($n = 3, 4, 6$, and 10) carried out to investigate the adsorption and dissociation of $^*\text{OOH}$,⁷⁵ confirmed the existence of an end-on adsorbed $^*\text{OOH}$ state which can be decomposed with an activation barrier of ~ 0.25 eV for the case of Pt_3 .

The effect of increasing the initial OH distance between O_2 and the hydrated proton (still under low solvation, Scheme 1) tested by CPMD simulations⁶⁹ shows that these conditions may revert the sequence of events for the first reduction: as illustrated by Figure 3, O_2 chemisorption takes place first (Figure 3, left), followed by proton transfer and formation of $^*\text{OOH}$ (Figure 3, center), and $^*\text{OOH}$ decomposition (Figure 3, right).

Figure 3. Snapshots from CPMD simulations⁶⁹ of the ORR first reduction step on Pt (111) for initial distances $d_{\text{OH}} = 3$ Å and $d_{\text{OS}} = 3$ Å, at a low degree of proton solvation (see Scheme 1). Left: at 0.22 ps, Center: at 0.38 ps, Right: at 0.87 ps. The sequence illustrates that longer separation between the O_2 molecule and the solvated proton causes chemisorption to take place first, followed by OOH formation, chemisorption, and dissociation on the surface.

The initial step (Figure 3, left) is characterized by a strong chemisorption, accompanied by O-O bond elongation to ~ 1.5 Å, and a drastic decrease of the electronic Kohn-Sham energy. However, the chemisorbed O_2 is not dissociated and instead a proton transfer takes place, forming adsorbed $^*\text{OOH}$, suggesting that the O_2 dissociation has a higher barrier than the $^*\text{OOH}$ formation under these conditions of low proton solvation. At 0.87 ps (Figure 3, right) finally $^*\text{OOH}$ decomposes, with the resulting adsorbed O^* adsorbed on top site, instead of being at the most favorable hollow site location. We speculated that H-bonding to neighbor water molecules may be responsible for this type of adsorption.⁶⁹

Figure 4. Snapshots from CPMD simulations⁶⁹ of the ORR first reduction step on Pt(111) for initial distances $d_{\text{OH}} = 2.5$ Å and $d_{\text{OS}} = 3$ Å, at an intermediate degree of proton solvation: $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_3$ (Scheme 2 shows the initial configuration). Left: at 0.12 ps, Center: at 0.19 and 0.22 ps, Right: at 0.30 ps. The net effect of higher proton solvation is the delay of proton transfer; thus chemisorption takes place first, followed by OOH formation, chemisorption, and dissociation on the surface. Proton transfer from hydronium to a water molecule is also detected (third image from the left).

Second, we examined the effect of solvation on the barriers for proton transfer. As found in previous work,²⁰ CPMD simulations revealed that using an intermediate degree of solvation, such as $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_3$, O_2 chemisorption precedes proton transfer even if the distance between the O_2 and the closest H atom is initially relatively low (Scheme 2). Figure 4 illustrates the sequence of events: O_2 chemisorption takes place first (Figure 4 left), followed by proton transfer from the closest water molecule (Figure 4, center), and proton transfer from the hydronium ion to water, and finally $^*\text{OOH}$ dissociation. Thus, the net effect of higher solvation is the delay of proton transfer.

In order to assess further solvation effects, new CPMD simulations were carried out using a high degree of proton solvation which includes a first and a second shell of water molecules surrounding the hydronium ion: $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_3(\text{H}_2\text{O})_6$. Snapshots of the dynamic sequence are depicted in Figure 5.

Figure 5. Snapshots from CPMD simulations of the ORR first reduction step on Pt(111) for initial distances $d_{\text{OH}} = 2.5 \text{ \AA}$ and $d_{\text{OS}} = 3 \text{ \AA}$, at a high degree of proton solvation: $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_3(\text{H}_2\text{O})_6$. First row: Initial configuration (left), at 0.7 ps (center), and at 0.8 ps (right). Second row: At 1.1, 1.2, 1.6, and 2 ps. Chemisorption takes place followed by O_2 decomposition, whereas OOH formation was not observed during 5 ps.

In the initial configuration, the O_2 molecule is located at about $3 \text{ \AA}$ from the surface, with the closest H atoms located at $1.76 \text{ \AA}$ (Figure 5, top left). During the initial 0.7 ps, proton transfer is observed from the hydronium ion to one of the water molecules (Figure 5, top center), whereas the O_2 molecule approaches the surface, and locates over a bridge position (Figure 5, top right). Note also the rotation of the water molecule close to one of the oxygen atom, favoring H-bond formation, while the O-O bond is elongated from an initial value of $1.21 \text{ \AA}$, to $1.43 \text{ \AA}$ in Figure 5, top right. In the next images (Figure 5, bottom) the dissociation of O_2 is observed, the O-O bond length is 2.6, 3.12, 4.62, and $6.36 \text{ \AA}$ respectively in the four bottom images of Figure 5. The adsorbed oxygen atoms are located on top-bridge-top (at 0.7 and 0.8 ps, top center and right)

locations, diffusing to top and hollow upon dissociation at 1.1 ps (bottom left), the O adsorbed in hollow site diffuses to bridge site at 1.2 ps (bottom center) and then both adsorbed O diffuse to two-fold bridge sites at 1.6 and 2 ps (bottom right). Although the closest water molecules become very close to the adsorbed O atoms (Figure 5, bottom right), formation of adsorbed OH was not observed in the total duration of the CPMD simulation, 5 ps. Thus, the strong solvation effect causes O₂ chemisorption to take place first, followed by O₂ dissociation, but proton transfer is much delayed.

Figure 6. Effect of adsorbed O₂ on the density of states of a Pt surface calculated by a DFT/Green function method,³² as a function of the O-O distance. For all curves, the center of the O-O bond is located at 2.10 Å from the center of the Pt-Pt bond. The Pt-Pt (2.47 Å) and the Pt-O bond distances are kept constant, whereas the O-O bond length is varied progressively from the gas phase O-O bond length, 1.2 Å, to 5 Å.

To analyze the possible influence of alloys on the dissociative pathway –where O₂ is dissociated previous to protonation- we discuss the results of a combined density functional theory and Green function approach to determine electron transfer through an interface that was applied to investigate the effect of alloying on O₂ dissociation.³² Such procedure yields the variation of the density of states of the complex adsorbate/adsorbent, as illustrated by Figure 6 for O₂ adsorbed on a bridge site as a function of the O-O distance. The dissociation limit – density of states (DOS) curves located at the front of the graph in Figure 6- is represented by the atomic orbitals of the oxygen

atoms (indicated by an arrow in Figure 6), each is doubly degenerated since there are two atoms; on the other hand, when the O-O distances become close to the value of the O-O bond length (1.2 Å) the DOS shows that the single peak of O is substituted by two peaks corresponding to the molecular orbitals of the oxygen molecule, usually one above and one below the Fermi level of Pt (-5.93 eV). The splitting of the single peak becomes clear as the O-O distance decreases, forming the O-O bond (Figure 6). We found that this feature, the separation between peaks corresponding to the frontier crystal orbitals, is

an indication of the ability of the system towards oxygen dissociation,³² the closest the two peaks the greater the tendency of the system to split into two adsorbed oxygen atoms. Figure 7 illustrates the effect of the adsorbate on the DOS as a function of adsorption geometry and nature of the neighbor atoms for bimetallic Pt-based systems alloyed with Co.

The density of states in Figure 7 were calculated based on DFT optimizations of O₂ adsorbed on Co₂Pt (a and c) and Pt₂Co (b and d); the density matrix information from such calculations is fed to an integrated DFT-Green function procedure⁷⁸ where the system is defined as the cluster embedded in a Pt bulk matrix, yielding the effect of the adsorbate on the density of electronic states of bulk Pt.

Figure 7. DOS of O₂ adsorbed on bridge Co-Co (a), Pt-Co (b and c) and Pt-Pt (d) sites of a Pt(111) surface, calculated on the basis of Co₂Pt (a and c) and Pt₂Co (b and d) clusters embedded in a Pt matrix. The separation between the peaks of the occupied (left of Fermi level) and unoccupied (right of Fermi level) is an indication of the degree of O₂ dissociation.

Figures 7 (a) and (c) correspond to a Co₂Pt cluster located on the surface of Pt bulk, but O₂ is adsorbed on bridge Co-Co in (a) and on the Pt-Co bridge in (c). In Figures 7 (b) and (d) the system is a Pt₂Co cluster located on the surface of Pt bulk, O₂ is adsorbed on Pt-Co bridge site in (b) whereas is adsorbed on bridge Pt-Pt in (d). The O-O distances are 1.49, 1.45, 1.40, and 1.38 Å in (a) to (d), and their corresponding O₂ binding energies are -2.93, -1.50, -1.44, and -0.62 eV respectively. Adsorption on the Co-Co bridge (Figure 7, a) appears the most favorable to O₂ dissociation, note also the proximity of the band of occupied states to the Fermi level of the metal, and to the peak of lowest unoccupied states. The advantage of the present procedure compared to the “extended periodic systems” is that the method allows active sites to be treated with larger basis sets using the best theoretical methods available for these systems. Experimental results suggested that Ni, Co, and Cr would become oxidized and act as “sacrificial sites” where other species may adsorb, leaving the Pt sites available for O₂ dissociation.^{29,30} Although this may be the case for Ni, we showed that alternative mechanisms are possible, especially for Co and Cr, which act as active sites for O₂ dissociation. Using this theoretical screening technique, we found that XXPt (X = Co and Cr) are the best active sites to promote O₂ dissociation. On the other hand, ensembles involving Ni atoms produce similar degrees of O₂ dissociation as those of pure Pt.

2.2 The catalyst/hydrated membrane interface

The next question is which of the above discussed scenarios is most likely to be found at the catalyst/hydrated membrane interface. It is generally accepted that the proton conductivity of the membrane depends on the characteristics of ionic clusters formed surrounding the polymer hydrophilic sites, both within the bulk

polymeric structure and at the interface with the catalyst.⁷⁹ The ionic clusters located at the membrane/catalyst interface are the ones that close the circuit of this electrochemical system. That is, these ionic clusters act as bridges through which protons and other hydrophilic reactants and products may pass from the membrane to the catalyst surface and vice versa during fuel cell operation. To get some insights into the possible formation of ionic clusters, we have analyzed the conformation of a hydrated model nafion membrane over Pt nanoparticles deposited on a carbon substrate via classical MD simulations⁸⁰ at various degrees of hydration.

Usually a λ parameter is defined as the number of water molecules per sulfonic site to characterize the degree of membrane hydration. Our MD simulations were carried out at various values of λ to analyze the possible water structure in such environment.⁸⁰ As shown by Figure 8, at low water contents ($\lambda = 5$), small water clusters are nucleated near the sulfonic hydrophilic sites, which are barely connected with each other. Thus, at these conditions, proton transfer could be severely limited because of the poor contact between water clusters. At a much higher water concentration ($\lambda = 45$, not shown), water forms a continuous phase⁸⁰ occupying almost all accessible sites on the surface; thus oxygen diffusion will be reduced because of the low O_2 solubility in water. When λ is 24 (Figure 8), a value close to the amount found experimentally in fully hydrated PEM membranes,⁷⁹ the interface is defined by a semicontinuum water film where water clustering can be identified. According to the classical MD simulation results,⁸⁰ these clusters have diameters of 1 to 1.5 nm and are interconnected by multiple water bridges. The average water density in this phase is estimated to be about 0.682 g/cm^3 , much lower than that of the bulk water phase at 353 K, as a consequence of the reduced water density present in the cluster bridging areas.

Figure 8. MD simulations of water distribution near platinum nanoclusters on a graphite substrate surrounded by nafion at different λ (water:S ratio) values. Nafion atoms other than the sulfonic (SO_3^-) groups are not shown in order to clearly illustrate the water clusters. At $\lambda = 24$ the clusters are interconnected. S atoms are yellow, O atoms are red, and H atoms are white.

Trying to reproduce events at the electrochemical interface, it is essential to elucidate the effects of the potential difference between the two electrodes. The existence of a charged electrochemical double layer is generally recognized and it is included in several microscopic⁸¹ and macroscopic models.⁸² In our CPMD simulations,⁶⁹ such effect was incorporated either by adding one electron to the cell (in all cases shown in Figures 2 to 5) or through a background

charge.⁸³ In the first case, the average charge on the Pt surface is initially negative (Figure 9) and becomes increasingly positive as charge is transferred to the adsorbates, as indicated by the time evolution of the net charge of the OOH group. Comparing the net charges in the slab and those on the first surface layer shown in Figure 9, it is seen that most of the negative charge is carried by the first layer, whereas no significant changes are observed on the charge carried by the Pt atom initially close and then bonded to an adsorbed O atom.

Figure 9. Time evolution of the net charge (in e) of the Pt slab, Pt first surface layer, OOH group, and Pt atom bonded to an adsorbed O atom. The results were obtained from CPMD trajectories⁶⁹ corresponding to Scheme 1 and Figure 2.

Using the second approach of counterbalancing the positive charge of the hydronium ion by a negative background charge, the net charge on the Pt surface is initially positive and becomes even more positive after electron transfer to the adsorbates.⁶⁹ CPMD simulations done at $d_{\text{HO}} = 2.2$ and $2.5 \text{ \AA}$ (Scheme 1) using this alternative approach yielded an opposite sequence for the first reduction step to that shown in Figure 2, i.e., O_2 chemisorption takes place first, the proton is repelled and oxygen is attracted by the more positive surface, suggesting that there is competition between the positively charged surface and the proton for the high electronic density available in O_2 . A less positive surface charge as shown in Figure 9 causes less attraction between O_2 and the surface, and a proton reacts with O_2 previous to chemisorption (Figure 2). Thus, changes in the electrode potential will be manifested as different distribution of surface charges which would also alter the sequence of events. The first step equations can be summarized as:

Or

Except in the highly solvated case shown in Figure 5, the final product of the first reduction step is the formation of adsorbed *OOH .

A related question is how the presence of a foreign element on the surface or in subsurface layers may affect the first reduction step. According to Norskov et al.,³⁹ the origin of the overpotential is independent of the details of the first step, and the strength of the interactions with intermediates such as OH and O determine a volcano type dependence for both the “associative” mechanism (forming *OOH) and the dissociative mechanism. Panchenko et al.²⁵ emphasized the structure-sensitive character of this reaction, in particular in relation to nanocatalysts where crystallographic facets other than (111) may be present. Thus, they made a careful evaluation of the adsorption of relevant ORR intermediates and products, such as O, OH, OOH, H_2O_2 and H_2O on small clusters and surfaces representing the Pt (111), (110), and (100) surfaces.

A comparison of OOH adsorption on elements different than Pt obtained from DFT calculations of OOH adsorbed on Pt-based alloy 3-atom clusters,⁸⁴ revealed a stronger *OOH adsorption to foreign elements (such as Ni, Co, Cr) compared to Pt, with characteristics that depend on the specific adsorption site, cluster composition, and nature of the foreign element. As shown by Figure 10, the end-on adsorption on top is preferred in Pt_3 clusters, and similar configurations but with stronger binding energies are found when one of the Pt atoms is substituted by a Cr, Co or Ni (not shown). Ensembles containing two foreign atoms can stably adsorb OOH in bridge configuration with two (Figure 10, top center) or one (Figure 10, top right) of the oxygen atoms connected to the two metal atoms. Cr has the strongest ability to bind OOH and some Cr-containing ensembles are able to dissociate *OOH without barrier.⁸⁴

Figure 10. DFT optimized geometries of OOH adsorption to selected mono and bimetallic clusters.⁸⁴

Therefore the presence of Cr, Co, and Ni would strongly bind OOH, but not always favoring *OOH dissociation and the continuation of the reduction process.

2.3 The subsequent reduction steps

2.3.1 *The second electron transfer.* Two alternative pathways may follow the formation of adsorbed *OOH, as described by the equations:⁶⁹

and

Equation (6) represents the formation of the one-end adsorbed HOO*H generated via reduction of HOO*, i.e., the *series* pathway, which may be followed by equation (7) because of the high instability of the adsorbed HOO*H. Electrochemical experiments done on Pt and Pt-alloy surfaces⁴⁶ indicated that the amount of H₂O₂ found at potentials below 0.8V (with respect to the standard hydrogen electrode) depends on the strength and nature of the acid medium, surface composition, and temperature. Similar experiments carried out on nanoparticles (3 to 4 nm) deposited on carbon substrates³⁰ showed that alloys with compositions Pt₃X (X = Ni and Co) yield no significant differences with respect to the production of H₂O₂, in all cases considered negligible. However, higher contents of Ni (~50%) make the catalysts unstable and large amounts of H₂O₂ are detected. Earlier work by Arvia et al^{85,86} found that the (100) facets would favor the *series* reduction pathway. Similar studies were reported recently by Mukerjee's group,⁴⁸ pointing again to the complexity of the nanoparticle environment.

DFT studies of the adsorption and dissociation of H₂O₂ on Pt_n clusters (n = 3, 4, 6, and 10),⁷⁵ showed the existence of a one-fold weakly adsorbed state, with binding energies ranging from -0.67 eV (on Pt₃) to -0.36 eV on Pt₁₀.⁷⁵ Similar weak adsorbed states were identified on bimetallic clusters, whereas spontaneous H₂O₂ decomposition has been observed in all cases where H₂O₂ is located on a bridge position both on Pt and Pt-alloy clusters and surfaces (Figure 11).^{31,75}

Equation (5) is the alternative 2nd electron transfer path, where HOO* is not reduced but dissociates first forming adsorbed O* and HO*, which is followed by reaction (8) whereby an electron and proton are transferred to HO*, probably the preferred site because of the highest negative charge carried by the oxygen atom of HO* as compared to that of O*.⁶⁹ The adsorbed water formed by reaction (6) is observed to be unstable, rotating from its initial position and becoming parallel to the surface, where it forms H-bond with the adsorbed oxygen atom, transfers a proton, and the end product are two adsorbed *OH radicals.

Table 1 provides a comparison of the various binding energy strengths of the relevant oxygenated compounds on mono and bimetallic clusters, which may be used to evaluate the relative affinities. The range of energies shown under each of the bimetallic clusters refers to adsorption on the various corresponding bridge or top sites. For example, adsorption on Pt₂Ni can occur on bridge Pt-Pt or Pt-Ni, on top Pt or Ni, or in the hollow site. On average, the strongest affinities are found on the PtX₂ compounds, where the X element becomes easily oxidized. Ni and Co show similar behavior and Cr has the strongest affinities for the oxygenated compounds, and in many cases is able to spontaneously dissociate peroxide compounds such as OOH or H₂O₂. In the presence of the alloy elements, Pt binds less strongly to the oxygenated compounds. Thus, this is in agreement with the cooperative effect where one of the elements

acts to bind specific intermediates, whereas the Pt sites are used to dissociate O₂ suggested on the basis of other theoretical and experimental results.

Figure 11. DFT calculated adsorption of H₂O₂ on bimetallic clusters (top) showing one-end weak adsorption on Ni,

and on a Pt-skin (Pt₃Co) surface (bottom, right). Spontaneous dissociation into two adsorbed OH is observed both in small clusters (top, center and right), and surfaces (bottom left).³¹

Table 1. DFT calculated binding energies (BE) of oxygenated reactants and intermediates of the ORR to Pt₃ and Pt-based alloy clusters

	-BE (eV)						
	Pt ₃	Pt ₂ Ni	PtNi ₂	Pt ₂ Co	PtCo ₂	Pt ₂ Cr	PtCr ₂
O ₂ ³²	1.08	0.92-1.55	1.28-2.14	0.62-1.5	1.44-2.93	0.38-1.58	1.25-3.09
O ⁸⁷	3.24	3.23-3.36	3.60-3.99	3.03-3.87	1.88-3.90	4.09	4.15-4.98
OH ⁸⁷	2.10-2.92	3.07-3.13	2.74-3.88	2.94-3.56	2.88-4.32	2.90-3.58	3.32-4.89
H ₂ O ⁸⁷	1.02	1.25	0.12-0.97	0.86-1.06	0.69-0.97	0.81-1.02	0.39-1.05
OOH ⁸⁴	0.86-1.72	1.48-1.84	1.49-2.65	1.70-2.20	1.65-2.92	1.69-2.40	1.43-4.90
H ₂ O ₂ ³¹	0.75-0.88	0.75-1.06	0.58-0.93	0.84-1.09	0.62-0.81	0.71	0.31

Based only on energetics, Table 1 suggests that adsorption of two *OH radicals (as in equations (7) and (9)), is more favorable than the alternative products of the second step, *O and *H₂O (equation (8)) and HOO* H (equation (6) not only for Pt but for Pt alloys.

2.3.2. The third and fourth electron transfers. The last two steps consist of successive formation of water molecules by electron and proton transfer to the adsorbed OH species, given by equations (10) and (11).

Figure 12. Snapshots from CPMD simulations of the ORR third (left and center) and fourth (right) reduction steps on Pt(111) for initial distances $d_{\text{OH}} = 2.5 \text{ \AA}$ and $d_{\text{OS}} = 3 \text{ \AA}$, at an intermediate degree of proton solvation: $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_3$ (Scheme 2 shows the initial configuration). Water is formed by proton transfer to one of the adsorbed OH (left), and the proton becomes shared by the two *OH (center). A fourth proton and electron transfer yields two weakly adsorbed water molecules, usually forming H-bond if adsorbed in neighbor locations.

Here the effect of the applied field, as well as a realistic representation of the surrounding environment should be crucial as it will determine the specific orientations of water on the surface, influencing adsorption or desorption of water or H_2O_2 , as observed experimentally.⁴⁶

3. Summary and conclusions

Recent experiments by Bard et al.³⁸ reported ORR polarization curves measured for catalysts designed on the basis of an alloy model where one of the metal elements had the function of dissociating O_2 and the other metal would easily reduce adsorbed atomic oxygen. Carbon-supported bi- and trimetallic catalysts were prepared with such selection rule and it was concluded that for the metals examined (Ag, Au, and Pd), adding 10 to 20 % of Co showed a good catalytic activity that however was inferior to that of Pt electrocatalysts. Better degree of success was achieved with non-Pt catalysts reported by Savadogo et al.³⁷ and the Pt-skin catalysts by Adzic et al.⁷³ In most of these catalytic designs it is encouraging that first principles calculations are at the point of contributing useful insights into developing new understanding of the reaction mechanisms,^{17,69,88} helping in the interpretation of experimentally found enhanced activities,^{36,49,71,73} and even providing a theory-based guidelines.^{39,72,89}

We would like to emphasize however that ab initio electrochemistry is still in its infancy. Besides the complexity of the problem of assessing the true interfacial structure including hydrated nafion, O_2 and catalyst actual nanostructure, surface segregation effects, there are other challenges such as the need of a proper description of the applied potential. We expect that advances in theory, computational implementation, and faster computers will help us to achieve less expensive and more efficient fuel cell catalysts in the near future.

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