# Oxygen Electroreduction on $Fe^{II}$ and $Fe^{III}$ Coordinated to $N_4$ Chelates. Reversible Potentials for the Intermediate Steps from Quantum Theory

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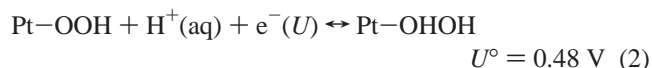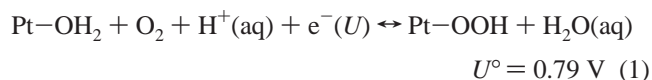*Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106*

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On the basis of spin-unrestricted hybrid gradient-corrected Becke, Lee, Yang, and Parr B3LYP density functional calculations and the reaction site models $Fe(NH_2)_2(NH_3)_2$ for $Fe^{II}$, and $Fe(NH_2)_2(NH_3)_2OH$ for $Fe^{III}$, $Fe^{II}$ is predicted to be the active site for the four-electron reduction of oxygen by heat-treated iron macrocycles. It is favored over $Fe^{III}$ in the first step of the mechanism because of a site blocking effect: $H_2O$ bonds strongly to the $Fe^{III}$ site, blocking it against $O_2$ adsorption, and it does not bond strongly to $Fe^{II}$. The stronger bonding of the product of the first reduction step, OOH, to $Fe^{II}$ compared to $Fe^{III}$ also helps by contributing to a more positive reversible potential for its formation over $Fe^{II}$. Subsequent reduction steps have high reversible potentials over both centers, paralleling an earlier study of oxygen reduction over a single Pt site. However, the important difference compared to Pt is the hydrogen-bonding interaction between (OHOH) bonded to $Fe^{II}$ and a nitrogen lone-pair orbital in the $N_4$ chelate. This is in addition to the O lone-pair donation bond to the $Fe^{II}$ center and is proposed to prevent hydrogen peroxide from leaving as a two-electron reduction product, as it was predicted to do over a single Pt site, and provides a path for reduction to water.
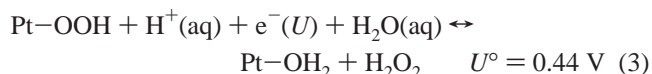
## Introduction

**Two- and Four-Electron Reduction of $O_2$ on Platinum Electrodes: Mechanistic Concepts.** Knowing reversible potentials for forming intermediates on surfaces of electrocatalysts is important to the understanding of electrocatalyzed reactions and improving their efficiency. Discovering the mechanistic details of oxygen reduction on surfaces of electrocatalysts has proved to be a difficult task. Recently, a quantum-theoretical approach to predicting activation energies and reversible potentials for forming surface intermediates during the course of electrocatalytic reactions was developed and applied to $O_2$ reduction on 1- and 2-fold adsorption sites of platinum electrodes.[1,2]

According to ab initio MP2 calculations used to model the reduction in acid electrolyte, when $O_2$ bonded to a 1-fold site in an end-on configuration, the two-electron reduction to hydrogen peroxide was the predicted outcome, a consequence of $H_2O_2$ bonding weakly to the site and desorbing after forming.[1] Based on results in ref 1, with a correction to the first equation, this reaction has two reduction steps, with the indicated calculated reversible potentials, $U°$:

$$Pt-OH_2 + O_2 + H^+(aq) + e^-(U) \leftrightarrow Pt-OOH + H_2O(aq)$$
$$U° = 0.79 \text{ V} \quad (1)$$

$$Pt-OOH + H^+(aq) + e^-(U) \leftrightarrow Pt-OHOH$$
$$U° = 0.48 \text{ V} \quad (2)$$

Taking into account the displacement of $H_2O_2$ by $H_2O$, $U°$ is decreased slightly:

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$$Pt-OOH + H^+(aq) + e^-(U) + H_2O(aq) \leftrightarrow$$
$$Pt-OH_2 + H_2O_2 \quad U° = 0.44 \text{ V} \quad (3)$$

The predicted standard reversible potential for the two-electron reduction of $O_2$ to hydrogen peroxide is 0.61 V (the measured standard value is 0.695 V). At all potentials the first step was calculated to have the higher, rate-limiting, activation energy.

Adsorption of $O_2$ to a 2-fold site was predicted to be side-on, according to spin-unrestricted hybrid gradient-corrected Becke, Lee, Yang, and Parr B3LYP functional calculations.[2] In this case the OOH(ads) intermediate was predicted to dissociated before $H_2O_2$ was formed. According to the calculations, the O(ads) and OH(ads) dissociation products will be readily reduced. The first reaction for this four-electron reduction was

$$Pt(OH_2)-$$

$$Pt(OH_2) + O_2 + H^+(aq) + e^-(U) \leftrightarrow Pt_2OOH + 2H_2O(aq)$$
$$U° = 0.97 \text{ V} \quad (4)$$
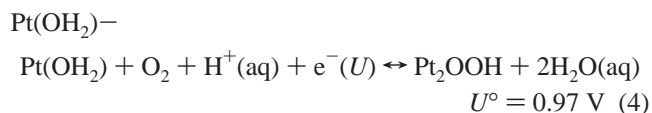
This has a predicted 0.21 V contribution to the overpotential for the four-electron reduction of $O_2$ to water relative to the predicted standard reversible potential of 1.18 V (the measured standard value is 1.23 V). The $Pt_2OOH$ was calculated to dissociate to $Pt(O)-Pt(OH)$ with a small activation energy barrier, $E_a = 0.06$ eV. Reduction of OH(ads) was studied on the more stable site, that is, the 1-fold site:

$$Pt-OH + H^+(aq) + e^-(U) \leftrightarrow Pt-OH_2$$
$$U° = 0.57 \text{ V [MP2]}$$
$$0.61 \text{ V [B3LYP]} \quad (5)$$
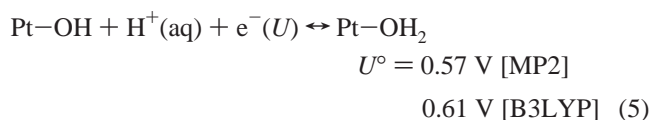
The low reversible potential for OH(ads) reduction means it can block the active sites, remaining stable above ∼0.6 V, and causing an overpotential because the electrode must be at a

potential <0.6 V for it to be reduced to $H_2O$. It also means that $H_2O(ads)$ can be oxidized at potentials greater than ~0.6 V and form $OH(ads)$, which bonds strongly to the site and poisons it by blocking $O_2$. The $O(ads)$ that forms from the dissociation of $OOH(ads)$ is reduced at a high potential:

$$Pt-O + H^+(aq) + e^-(U) \leftrightarrow Pt-OH$$
$$U° = 1.32 \text{ V [MP2]}$$
$$0.97 \text{ V [B3LYP]} \quad (6)$$
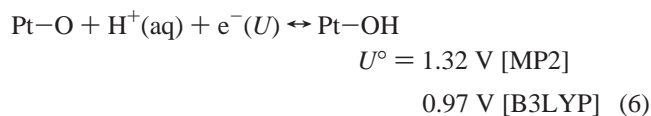
As will be discussed below, the reversible potentials that are predicted in our work are dependent on the bond strengths. This means that changes in reversible potentials can, to a good approximation, be simply related to changes in adsorption bond strengths on the electrode surfaces that might be caused by modifying the structure or composition of an electrode surface.

**Reduction on Supported Transition Metal Macrocycles.** A number of supported transition metal macrocycles have been studied for $O_2$ electroreduction and some show activity toward two-electron reduction and others are active for four-electron reduction. The supports used, graphitized carbon, have low $O_2$ reducing capability. Further information is available in reviews.[3,4] Iron phthalocyanine, FePc, is a four-electron reducer of $O_2$ in acid and base solution. The cobalt macrocycle CoPc reduces $O_2$ to $H_2O_2$ above 0.3 V and reduces $H_2O_2$ to water below this potential but a direct four-electron reduction is not observed. Modification of CoPc or cobalt porphyrin can promote four-electron reduction over two-electron reduction.[5,6] Certain metalated cofacial diporphyrins have been found to be four-electron $O_2$ reduction catalysts. The $O_2$ molecule is believed to bridge the two metal atoms and the systems are active when graphite supported, provided it is on the edge of the graphite planes.[7] It was shown recently that a single iron porphyrin on graphite catalyzes the four-electron reduction of $O_2$.[8] Despite continuing work in the field, the understanding of the mechanisms for $O_2$ reduction on these materials is incomplete and still presents challenges. Certain properties are fairly well established. The metal atoms are oxidized by two electrons when bonded to the multidentate porphyrin or phthalocyanine ligands, which themselves bear a compensating −2 electronic charge. The initial adsorption of $O_2$ is believed to further oxidize the metal center:[9−11]

$$M^{II} + O_2 \rightarrow M^{III}-O_2^- \quad (7)$$
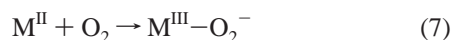
It is believed that if the II oxidation state could be stabilized at higher potential the onset potential for $O_2$ reduction would increase. A semiempirical molecular orbital analysis has discussed $Fe^{II}$ Mulliken charges in various macrocycles and rationalized $O_2$ reduction activity in terms of these charges.[12] A full understanding will address details of the mechanistic steps, their reversible potentials, and the mechanisms and activation energies for proton and electron transfer.

**Reduction on Transition Metal Macrocycles That Have Undergone Pyrolysis.** The pyrolyzed systems, supported on graphite, have shown interesting activities, approaching that of platinum,[13] and even surpassing it in methanol-containing electrolytes.[14] Heating the transition metal macrocycle to <1000 °C gives relatively stable, active systems. The active sites are not well understood. It has been proposed that $O_2$ might be reduced over N in a low oxidation state and attached to the support.[15] However, it has been demonstrated that to form an active catalyst both iron and nitrogen must be present during the pyrolysis.[16] Carbon- and nitrogen-containing compounds and

transition metal salts can also be used as precursors.[17,18] It has been proposed that low temperature (500−700 °C) pyrolysis yields a catalytic $FeN_4/C$ bonded to the carbon support and higher temperature pyrolysis (>800 °C) yields a more active $FeN_2/C$ bonded to the support, though the two N species are only part of the coordination and the remaining parts of the coordination are still unknown.[18] Consistent with this is other work indicating that only part of the $FeN_4/C$ participated in $O_2$ reduction; this study also proposed that Fe(II) is the $O_2$ adsorption site.[19] The four-electron reduction was found at high potentials on pyrolyzed iron porphyrin and at lower potentials two-electron reduction to hydrogen peroxide predominated.[20] Peroxide was shown to decompose the four-electron active $FeN_2/C$ sites by removing iron.[21]

**Theoretical Studies of $N_4−M$ Systems.** The bonding of $O_2$ to iron porphyrin was modeled by Goddard 27 years ago using self-consistent calculations by coordinating four $NH_2$ ligands to an iron atom[22] and by Hoffmann 23 years ago with nonself-consistent extended Hückel calculations.[23] The self-consistent calculations apparently put the iron atom in the IV oxidation state and in the extended Hückel calculations the model was $Fe(NH_2)_4{}^{2−}$ with the iron atom in the II oxidation state. These works and most subsequent ones have dealt primarily with structure and state characterizations and not with oxygen reduction mechanisms. For example, density functional theory has been applied to characterize the end-on bonding of $O_2$ to $Fe^{II}$ in iron porphyrin.[24] The proton and electron-transfer steps leading to either two- or four-electron reduction have not yet been studied with quantum theory.

**In This Paper Quantum Theory Is Used To Study $O_2$ Reduction on $Fe^{II}$ and $Fe^{III}$ Centers.** The steps of two- and four-electron reduction in acid electrolyte shown in reactions 1−6 are applied to the iron centers. The $Fe^{II}$ is coordinated to two $NH_2$ ligands and two $NH_3$ ligands placed diagonally from one another in a square, making it an approximate model for Fe in the center of a porphyrin. The actual porphyrin site has all four Fe−N bonds essentially identical. However, structures of pyrolyzed metallic porphyrins, phthalocyanines, and other compound mixtures as mentioned above have not yet been determined. If a result of heat treatment is the breaking off of some of the conjugated ring systems, then the active $Fe^{II}$ site might well have different types of coordinated nitrogen groups similar to this model. The model is a generic one for nitrogen-coordinated $Fe^{II}$. However, both the Fe macrocylces and the heat-treated systems have been shown to carry out the four-electron reduction of $O_2$, and so the $N_4−M$ model is a worthwhile starting point.

The theme of this study is the dependence of the electrochemistry on the oxidation state of the metal site. To create the $Fe^{III}$ site, a hydroxyl group is added to the Fe, making it five-coordinate in a square pyramid. Some of the questions addressed in this study are based on issues that are problems for platinum electrodes; namely, does $H_2O$ become oxidized at a potential far negative of the four-electron $O_2$ reduction potential on these systems as it does for platinum?[1,2] The $OH(ads)$ that forms by $H_2O$ oxidation on platinum electrodes contributes to the ~400 mV overpotential on working oxygen cathode half-cells in fuel cells. Does $O_2$ bond strongly enough to the active reduction site to displace $H_2O$ that forms when the M−OH intermediate is reduced as in reaction 5 above? For platinum our past theoretical work says it does.[1,2] Will reactions 1 and 2, which have too low reversible potentials on the 1-fold Pt site, also have low potentials on the Fe sites, and if not, will the Fe−(OHOH) bond be strong enough to hold the $H_2O_2$ for the next
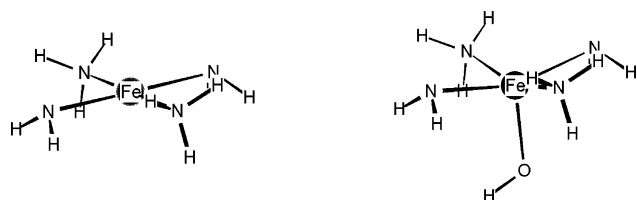
Oxygen Electroreduction on Fe$^{II}$ and Fe$^{III}$

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**Figure 1.** Fe$^{II}$ site modeled by Fe(NH$_2$)$_2$(NH$_3$)$_2$ on the left and Fe$^{III}$ site modeled by Fe(NH$_2$)$_2$(NH$_3$)$_2$OH on the right.

reduction step rather than releasing it? As will be developed below, both Fe$^{II}$ and Fe$^{III}$ both coordinate H$_2$O$_2$ strongly and both seem to have the desired properties of high reversible potentials for the last three reduction steps. However, only Fe$^{II}$ has a sufficiently weak Fe$-$OH$_2$ bond for H$_2$O displacement by O$_2$ to be allowed and a high reversible potential for the first reduction step, which, according to our model, mean that it, and not Fe$^{III}$, is capable of the four-electron reduction of O$_2$.

**Theoretical Approach**

**Method for Calculating Reversible Potentials from Reaction Energies**. It has been found recently that for several solution phase reactions involving oxidation and reduction of H$_x$O$_y$ molecules in acid[25,26] and base[26] the formula for reversible potential, $U°$,

$$U° = -E_r/nF - 4.6 \text{ V} + c \quad (8)$$

where $E_r$ is the reaction energy in units of electronvolts (eV), $n$ is the number of electrons transferred, $F$ is the Faraday constant, 4.6 V comes from the 4.6 eV thermodynamic work function of the standard hydrogen electrode, and $c$ is a constant that provides a fit to measured data and predictive capability for elecrocatalysis.[1,2] Equation 8, which is used for the predictions in this paper, is in the form of the familiar formula

$$U° = -\Delta G°/nF \quad (9)$$

where the change in Gibbs energy, $\Delta G$, is given as

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad (10)$$

It is evident that c stands for the $P\Delta V - T\Delta S$ contributions to $\Delta G°$.

The value of $c$ depends on the reaction model chosen. The hydronium ion, H$^+$(aq), is modeled as H$_3$O$^+$(H$_2$O)$_3$, and Born$-$Oppenheimer equilibrium energies and structures are calculated using spin-unrestricted hybrid gradient-corrected Becke, Lee, Yang, and Parr B3LYP density functional theory from Gaussian 94 with the 6-31G** basis set for light atoms.[27] As in past work, zero-point energies are neglected because the number of O$-$H bonds is conserved so that the net change for each reaction is small.[1,25] All reactants and products are isolated molecules, and the constant $c$ was determined to give a good linear fit to five acid solution phase reactions of the type studied here, for which experimental $U°$ are known.[26] The value of the $c$ constant in this case is 0.49 V.[26] This is the approach used in this paper.

In the present study the four N atoms were fixed at the corners of a square with 4.0 Å long edges and the Fe was allowed to relax up and down from the center of the square as OH and all the other ligands were bonded to it and their structures were fully optimized. The B3LYP approach was used as described above, and an effective core potential and LANL2DZ basis set
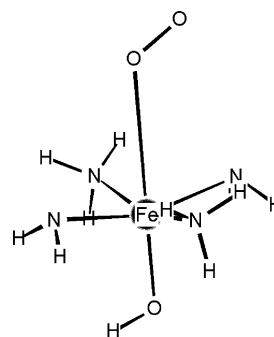


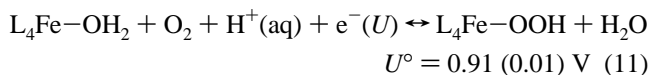**Figure 2.** Structure of O$_2$ bonded to Fe$^{III}$.

was used for the iron atom. Figure 1 shows the Fe$^{II}$ and Fe$^{III}$ reaction centers.

**Results and Discussion**

**H$_2$O Bonding to Fe$^{II}$ and Fe$^{III}$.** In all of the following an Fe$^{III}$ result will appear in parentheses and a result for Fe that is not in parentheses will be for the II oxidation state. In these calculations Fe$^{II}$ favored the triplet state and Fe$^{III}$ favored the quartet state. A water molecule would, according to the calculations, form relatively strong hydrogen-bonding interactions to the lone pairs of the NH$_2$ ligands. In a somewhat strained bridging structure across the Fe site, to form hydrogen bonds to each NH$_2$, the stabilities were 0.47 (0.53) eV for Fe$^{II}$ (Fe$^{III}$). These are comparable to the heat of vaporization of water; that is, they are comparable to the hydrogen-bonding energy of water molecules in water. A water molecule formed a slightly stronger single hydrogen bond to a single N lone pair, 0.58 (0.56) eV. Consequently, it is concluded that if lone-pair orbitals are available on N atoms coordinated to Fe in the pyrolyzed catalysts, they may have H$_2$O molecules blocking them so that a H$_2$O molecule will be able to approach the Fe atom and bond to it by lone-pair donation through its oxygen atom. This was studied by constraining the Fe$-$O bond to remain on the N$_4$ 4-fold axis and otherwise optimizing its structure. The Fe$-$OH$_2$ bond strengths were 0.10 (0.53) eV, the effect of a stronger donation bond to the Fe in the higher oxidation state being present.

**O$_2$ Bonding to Fe$^{II}$ and Fe$^{III}$ and Displacing H$_2$O.** The O$_2$ molecule bonded to the Fe sites end-on and tilted with strengths of 0.12 (0.06) eV, as may be seen for the Fe$^{III}$ case in Figure 2. The favored states are quintet (doublet). This means that O$_2$ is capable of displacing H$_2$O from Fe$^{II}$ but not from Fe$^{III}$. In what follows below, reversible potentials for the O$_2$ reduction steps over Fe$^{III}$ will be presented despite this.

**$-$OO Reduction to $-$OOH.** The optimized Fe$-$OOH states are quartet (triplet), and the Fe$-$OOH bond strengths are 1.04 (0.57) eV. Fe$-$OOH has a trans structure like hydrogen peroxide. The predicted results are

$$L_4\text{Fe}-\text{OH}_2 + \text{O}_2 + \text{H}^+(\text{aq}) + \text{e}^-(U) \leftrightarrow L_4\text{Fe}-\text{OOH} + \text{H}_2\text{O}$$
$$U° = 0.91 \ (0.01) \text{ V} \quad (11)$$

The 0.90 V lower potential for Fe$^{III}$ is caused by the 0.43 eV stronger Fe$-$OH$_2$ bond on the left side of eq 11 and the 0.47 eV weaker Fe$-$OOH bond on the right side.

**$-$OOH Reduction to $-$(OHOH).** The product H$_2$O$_2$ takes a trans structure with O on one end forming a weak lone-pair donation bond to the iron and the OH on the other end forming a hydrogen bond to a lone pair on one of the NH$_2$ ligands, as shown in Figure 3 for the Fe$^{II}$ and Fe$^{III}$ centers. The Fe$-$(OHOH) bond strengths are 0.51 (0.90) eV. The Fe$-$(OHOH)
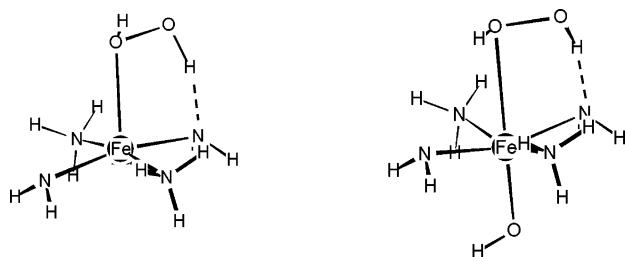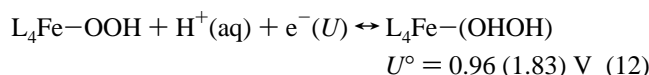
**Figure 3.** Structure of $H_2O_2$ bonded to $Fe^{II}$ and $Fe^{III}$.

states are quintet (quartet). The reversible potentials are favorable for the reaction

$$L_4Fe-OOH + H^+(aq) + e^-(U) \leftrightarrow L_4Fe-(OHOH)$$
$$U° = 0.96\ (1.83)\ V\ (12)$$

The 0.87 V higher reversible potential for $Fe^{III}$ is due to the 0.40 V stronger bonding of $H_2O_2$ and the 0.47 eV weaker bonding of OOH to $Fe^{III}$. Energy needed to displace a water molecule blocking the nitrogen site would change both potentials in reaction 12 but probably not by much because the N−H hydrogen bond will be replaced by an O−H one when the water molecule leaves the site.

**−OOH Reduction to −O + $H_2O$.** An alternative reaction would reduce the OH end of Fe−OOH. The Fe−O states are calculated to be triplet (quartet). The Fe−O bond strengths are predicted to be 1.69 (2.02) eV. The calculated reversible potentials are unfavorable for $Fe^{II}$ and favorable for $Fe^{III}$:

$$L_4Fe-OOH + H^+(aq) + e^-(U) \leftrightarrow L_4Fe-O + H_2O$$
$$U° = 0.44\ (1.24)\ V\ (13)$$
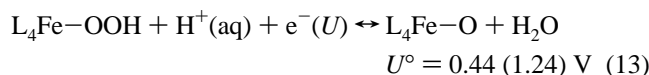
The 0.80 V higher reversible potential for $Fe^{III}$ is a consequence of the 0.47 eV weaker bonding of OOH and the 0.33 eV stronger bonding of O to $Fe^{III}$.

**−O Reduction to −OH.** The product of this reaction is the well-known surface-blocking poison on Pt oxygen reduction cathodes. The Fe−OH bond strengths are calculated to be 2.37 (2.00) eV and the states are quartet (triplet). The structure for $Fe^{II}$ is in Figure 1, and Figure 4 shows the structure for $Fe^{III}$. The reaction proceeds at high potential on both Fe centers:

$$L_4Fe-O + H^+(aq) + e^-(U) \leftrightarrow L_4Fe-OH$$
$$U° = 2.96\ (2.26)\ V\ (14)$$
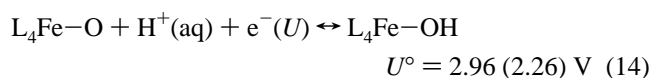
The 0.70 V lower reversible potential for $Fe^{III}$ is caused by the 0.33 eV stronger bonding of O and 0.37 eV weaker bonding of OH to $Fe^{III}$. These high reversible potentials indicate that $L_4$-Fe−O, with Fe in the IV oxidation state, is easily reduced to $L_4$Fe−OH in the potential range for $O_2$ reduction, which is ≤1.23 V.

**−(OHOH) Reduction to −OH + $H_2O$.** Favorably high reversible potentials are calculated for this reaction for both iron oxidation states:

$$L_4Fe-(OHOH) + H^+(aq) + e^-(U) \leftrightarrow L_4Fe-OH + H_2O$$
$$U° = 2.43\ (1.67)\ V\ (15)$$
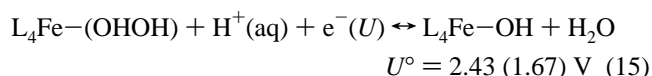
The 0.76 V smaller reversible potential for $Fe^{III}$ is the result of the 0.39 eV stronger bonding of $H_2O_2$ and 0.37 eV weaker bonding of OH to $Fe^{III}$.

**−OH Reduction to −$OH_2$.** A high potential for this step is thought to be the key for improvement of conventional Pt electrodes because OH(ads) forms from water oxidation begin-
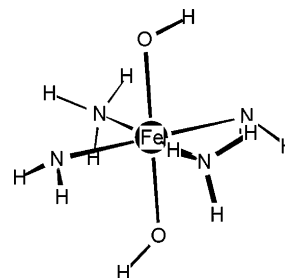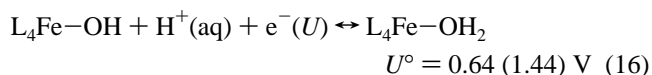


**Figure 4.** Structure of OH bonded to $Fe^{III}$.

ning at ∼0.6 V and progressively blocks surface sites that are needed for catalyzed $O_2$ reduction as the potential is increased.[28,29] For the present system results are

$$L_4Fe-OH + H^+(aq) + e^-(U) \leftrightarrow L_4Fe-OH_2$$
$$U° = 0.64\ (1.44)\ V\ (16)$$

The 0.80 V higher reversible potential for $Fe^{III}$ follows from the 0.37 eV weaker bonding of OH and 0.43 eV stronger bonding of $H_2O$ to $Fe^{III}$. The reversible potential on $Fe^{II}$ is about the same as calculated for Pt[1], which suggests that Fe−OH formation from water oxidation or from oxygen reduction is responsible for the observed overpotential on pyrolyzed iron macrocycles in the same way as it is for platinum electrodes.

**Further Comparison with Platinum Electrodes.** Activation energies and their electrode potential dependencies have been calculated for the steps in the two- and four-electron reduction of oxygen on 1- and 2-fold platinum sites.[1,2] In both cases the rate-limiting (highest activation energy in the overpotential range of interest) step was the first one, generating 1-fold Pt−OOH or bridging $Pt_2$−OOH. Later steps had lower activation energies, and over the 1-fold Pt site they were the same steps as treated above for $Fe^{II}$ and $Fe^{III}$, except for reaction 13, the reduction of Fe−OOH to Fe−O + $H_2O$. Though not reported in ref 2, we have calculated activation energies for the reduction of Pt− OOH to Pt−O + $H_2O$ and found them higher than for the first step. The activation energies for the steps in oxygen reduction over $Fe^{II}$ and $Fe^{III}$ sites, being determined by bond strengths and the electron affinities of the reaction centers,[1,2] might be anticipated to behave similarly to those on Pt, though a computational study has not yet been made. If so, then the first reduction step will be responsible for the observed effective activation energy, just as it is generally believed to be on Pt.[2,30,31]

**Conclusions**

$Fe^{II}$ is predicted to be the active site for the four-electron reduction of oxygen by iron in the $L_4$Fe systems employed in the calculations, and it may be suggested that the same should be expected for heat-treated iron macrocycles. Indeed, the $Fe^{II}$ iron phthalocyanine is known to be a four-electron reducer,[3,4] as are pyrolyzed iron macrocycles, wherein the active sites have been proposed to be $Fe^{II}$.[19,20] In the present calculations $Fe^{II}$ is favored over $Fe^{III}$ in the first step of the mechanism essentially because, although $H_2O$ bonds strongly to the $Fe^{III}$ site, blocking it against $O_2$ adsorption, it does not bond strongly to $Fe^{II}$. The stronger bonding of the product of the first reduction step, −OOH, to $Fe^{II}$ compared to $Fe^{III}$ results in the significantly more positive reversible potential calculated for its formation over $Fe^{II}$. Subsequent reduction steps have high reversible potentials over both centers, paralleling the earlier study of oxygen reduction over a single Pt site. However, the important difference compared to Pt is the hydrogen-bonding interaction between −(OHOH) bonded to $Fe^{II}$ and a nitrogen lone-pair orbital in

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the N$_4$ chelate. This prevents hydrogen peroxide from leaving as a two-electron reduction product, as it was predicted to do over single a Pt site, and provides a path for reduction to water. Finally, our low predicted reversible potential value for L$_4$Fe–O formation from L$_4$Fe–OOH reduction on Fe(II) argues against the mechanism proposed in ref 20 for the four-electron reduction, but our results provide an alternative interpretation that is consistent with observations. We find that adsorbed hydrogen peroxide is the favored intermediate formed from L$_4$Fe–OOH over Fe(II) in the 0.44–0.96 V range. This can be released into solution only at potentials less than the reversible potential for H$_2$O$_2$(aq) formation, which has the standard value 0.695 V. At potentials higher than the reversible potential for H$_2$O$_2$(aq) formation in the particular system under consideration (for given O$_2$ pressure, pH, and so on) the H$_2$O$_2$(ads) intermediate can only be reduced to L$_4$Fe–OH. At lower potentials, potential-dependent kinetics determine the product distribution, and according to ref 20, at low potentials less and less hydrogen peroxide is released, which suggests that the potential dependence of the activation energy for reaction 15 is paramount.

These conclusions are in the spirit of using the simplest physical model that seems to come close to predicting reversible potentials and activation energies for electron–proton transfer reactions involving mono and dioxygen species bonded to metal sites. For each of the reactions the hydrogen-bonded water network surrounding the metal site and ion positions will affect the energies, as will the structure assumed for the active site itself. These effects can eventually be added as a perturbation to the findings in this paper.

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