Theories for Predicting Reversible Potentials of Reactions on Electrode Surfaces 
from Internal and Gibbs Energies: Applications to ORR

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When I arrived at Case in January of 1979, Ernie Yeager introduced me to the oxygen cathode reaction, which was then, as now, the kinetic bottleneck for hydrogen fuel cells. Armed with a slow semiempirical quantum theory that lacked charge self-consistency, I soon found that even the dissociative adsorption of O₂ on platinum surfaces could not be calculated accurately. My semiempirical band shift technique was good only for estimating electrode potential dependencies of vibrational frequencies and some dissociation processes involving adsorbed molecules. By the late 1990’s, charge self-consistent calculations were at last feasible in my lab and I began using them to develop ways to calculate reversible potentials and potential dependencies of electron transfer reactions for adsorbed molecules. Sadly, Ernie passed away about the time I began making progress in understanding the oxygen reduction reaction. Here, emphasizing O₂ reduction, is an overview of these quantum electrochemistry developments at Case.

Introduction

Ernest Yeager was a brilliant spokesman for electrochemistry. His interest was infectious and his command of the topic covered everything between the horizon of the early days and the nebulous horizon of the future. Ernie knew what was important to the progress of electrochemistry and, through his ability to recognize, develop, and direct the best of their talents, he was able to guide anyone who took an interest in it to contribute toward advancing the field. He acknowledged that new perspectives were needed and he was pleased that physicists and surface scientists began taking an interest in electrochemistry. In fact, he said that, given the growing interest of the physicists, electrochemistry was becoming a science at last.

Many students and visitors passed through Ernie’s lab and went on to hold prominent positions at universities, companies, and government laboratories in the US and abroad. However, one did not have to be his student to learn from him. He organized interdisciplinary research proposals, such as the one that kicked off the Office of Naval Research Selected Research Opportunities (SRO) program. The theme of this project was the passive film and the focus was determining its structures, dynamic properties, and stabilities of passive films on ferrous metals. It brought together Case faculty from Chemistry, Physics, Chemical Engineering, and Metallurgy and Materials Science Departments. I was fortunate and grateful, as a beginning faculty member, to be a part of the research program. It made me fully aware of the excitement, educational value, and pleasure of interdisciplinary research; I have continued interactions on various topics with the engineering departments to the present time. Even if one were not a student or a
collaborator with Ernie on a research project, one could still learn from him by attending university and departmental seminars. At the end of most seminars he attended, Ernie would raise points or ask questions in his clear and resonant voice that all present in the audience could appreciate for the clarification, understanding, and insight they sparked.

The work presented in the following overview owes much to Ernie Yeager. Although early on we jointly published only one study, Ernie provided the necessary momentum and sufficiently cleared away mental undergrowth that my subsequent theoretical work in electrochemistry was natural, if not inevitable. Three theories are introduced in the following: (i) a semiempirical band shift approach to model effects of changing electrode potential, (ii) a linear Gibbs energy relationship (LGGER) for predicting reversible potentials for forming intermediates adsorbed to electrode surfaces, and (iii) a fully self-consistent theory, including surface charging and electrolyte ions in the double layer region, for determining reversible potentials at the electrochemical interface. The last is implemented in a two-dimensional density functional atomic orbital band theory code Interface 1.0. Brief mention will be made of a fourth theory, a resonant electron tunneling approach using a local reaction center model for calculating transition state structures and activation energies for (generally coupled) electron-proton transfer reactions.

Valence Band Shift Model for Predicting Effects Electrode Potential Changes on Properties of Adsorbed Molecules

So far as I know, the first time the effect on adsorption properties of shifting the valence band of a metal surface model was calculated was in 1981 (1). The semiempirical atom superposition and electron delocalization molecular orbital (ASED-MO) theory was used. This semiempirical method is one I developed and it combined an attractive extended-Hückel-like molecular orbital delocalization energy representing chemical bond formation with a repulsive energy component representing the coming together of rigid atoms. This theory allowed the prediction of molecular structures, which extended Hückel generally could not provide accurately. It was introduced in 1975 (2) and reviewed in 1994 (3) as its usefulness wound down due to faster computers allowing more accurate ab initio predictions of structures and reaction mechanisms. Currently Google finds 6,370 hits for this theory, for which I made available the computer program free to those who asked for it, so it had a good run in its time.

Input parameters for the ASED-MO theory included Slater valence orbital exponents and valence state ionization potentials (VSIP). Adjustments in these parameters were made so that the calculations would give accurate bond lengths, atomic charges, dissociation energies for diatomic fragments before calculations on larger or polyatomic systems commenced. Once set up, the shift in the electronic density of states in a surface, whether for a cluster model of a metal surface or for solid, by means of band calculations, shifted on the energy scale by amounts nearly proportional to a shift in metal atom VSIP’s. In other words, the surface Fermi level and electrode potential could be changed by an amount linear in the applied VSIP changes, up or cathodic when the VSIP were decreased or down or anodic when the VSIP were increased.
In terms of molecular orbital theory, bonding between adsorbates and surfaces was then, and still today, understood in terms of sigma and pi orbital donations to the surface and surface donations to the molecules’ sigma (σ) and pi (π) antibonding orbitals. The donation and back-donation interactions both generally contributed to forming the bond between the adsorbed molecule and the surface and weakening bonds within the adsorbed molecule. These elementary MO bonding concepts go back to their introductions by Dewar (4) and Chatt and Duncanson (5) who were thinking about ligand bonding in transition metal coordination complexes. Blyholder applied these ideas to describe adsorbate-surface bonding (6). Figure 1 illustrates the associated energy level shifts.

![Figure 1](image-url)

Figure 1. The heavy dashed lines show dominant σ donation interaction from molecules like CN⁻ to a metal surface and metal back-donation to the molecular π* orbitals.

It is, from the point of view the previous two paragraphs, not a surprise that when a sigma donor and pi acceptor molecule such as the cyanide ion, CN⁻, bonds to a silver electrode surface the, C-N vibrational frequency, \( \omega \), decreases as the surface Fermi level moves to higher energy due to surface charging that decreases the electrode potential. When Kötz and Yeager told me about their Raman measurement of the vibrational frequency dependence on potential \( d\omega/dU \) where \( \omega \) is frequency and \( U \) is potential, for cyanide on a silver electrode, I was certain that the ASED-MO theory could, with band shifts, be used to calculate the observed trends in C-N and Ag-C frequencies. So we joined forces and published a joint experimental and theoretical study on the topic (7). Linear regions in the C-N and Ag-C force constants vs. electrode potential were found for a planar Ag cluster surface model and compared with results of the Raman measurements. The respective experimental and theoretical rates of C-N frequency decrease were 26 cm⁻¹V⁻¹ and 32 cm⁻¹V⁻¹; for the Ag-C bond experimental and theoretical rates were 27 cm⁻¹V⁻¹ and 20 cm⁻¹V⁻¹. The predicted C-N frequencies were accurate, ~3% less than the experimental values, which means the non-self-consistent ASED-MO standard parameters were good for the study. The calculated Ag-C frequencies were ~87% higher than the experimental values, which suggests the ASED-MO description of the Ag-C bond strength was lacking. It was concluded that the changes in adsorbate-surface bonding due to simply moving the Fermi level, which corresponds to changing the electrode potential, allows quite accurate predictions of the changes in these vibrational frequencies. This is despite the omission of surface charging and double-layer...
polarization, which have not been taken until recently taken into account, and their effects will be discussed later in this article.

The ASED-MO band shift theory was applied to the dehydrogenation reactions of \( \text{H}_2\text{O(ads)} \) and \( \text{OH(ads)} \) on an iron (100) surface (8). In these cases the O-H \( \sigma \) and \( \sigma^* \) orbitals respectively donated to or accepted electron charge from the surface by means of their overlap with the metal valence d band orbitals, with the metal valence s and p orbitals mixed in. Calculated activation energies decreased and the adsorbed dissociation products became more stable as the Fe band was moved up in energy, corresponding to decreased electrode potential. These changes correlated with the increased involvement with the empty O-H \( \sigma^* \) orbitals in the bonding with the surface metal atoms. It is not yet known if this has been experimentally verified for an iron electrode in acid or base. For the Pt(111) there is almost certainly proton transfer to \( \text{H}_2\text{O(l)} \) molecules in acid (9) or \( \text{OH}^-(\text{aq}) \) in base (10), while an electron transfers simultaneously to the electrode.

The metal electrode valence band shift technique was applied to the iron dissolution reaction under the auspices of the above-mentioned Navy SRO grant that Yeager spearheaded. Using a cluster model of the Fe(110) surface, this study showed that as the potential was increased less and less energy was needed to remove an iron atom with OH bonded to it from the surface than one without OH (11). The removed species was assumed to be \( \text{(FeOH)}^+ \), and calculations showed it to be stable in the solvated form \( \text{FeOH(H}_2\text{O)}^+_5 \). This was assumed to deprotonate and precipitate \( \text{Fe(OH)}_2 \), a component of the passive film. This process would be interesting to study again using the modern self-consistent method described later in this article.

The metal valence band shift technique continued to be used in my lab. Others were interested in explaining the potential dependencies of vibrational signals of adsorbed molecules, especially CO, which became a test case for other models. Holloway and Norskøv introduced a model wherein the metal valence band was fixed and an electric field assumed to depend linearly on applied potential was used to shift the CO \( \pi^* \) orbital energy levels. The rate of frequency change as a function of potential calculated this way was 2.5 times greater than the measured rate (12). Lambert devised a parameterized model based on the formula

\[
d\omega/dU = (d\omega/dE)(dE/dU)
\]

where \( E \) is the electric field, and \( d\omega/dE \) is called the Stark tuning rate, specifying how the shift in the frequency due to the Stark effect changes with changes in the electric field (13). By making plausible assumptions about the differential capacitance and dielectric constant, Lambert estimated \( d\omega/dE \). To estimate \( dE/dU \), he used the IR absorption spectrum and electroreflectance data for CO on Ni(110) in ultrahigh vacuum. Using these two estimated factors in Equation [1] led to the value \( 30 \pm 11 \text{ cm}^{-2}/\text{V} \) for \( d\omega/dU \). Experimental values were \( \sim 30 \text{ cm}^{-2}/\text{V} \) for a Pt electrode (14), \( 48 \text{ cm}^{-2}/\text{V} \) for Pd 1-fold sites, and \( 63 \text{ cm}^{-2}/\text{V} \) for Pd bridge sites (15). If one accepts the parameterization for \( dE/dU \), there are clearly structure and bonding effects influencing the Stark tuning rate. On the other hand, why should one set of parameters work for surfaces of different metals? This is a topic that bears reexamination using the self-consistent method in the code Interface 1.0 that is introduced later in this article. Bagus et al. introduced the idea of bathing metal clusters with adsorbed CO in a uniform electric field and was able to
calculate, using ab initio quantum theory, for Cu trends in frequency vs. assumed electric field (16). By this time the name “Stark tuning rate” for this potential-dependent effect was firmly entrenched and there were many studies, theoretical and experimental, using the presumed and actually unknown electric field rather than the Fermi level shift effect on bonding and structure in their interpretations. A more detailed discussion along with our band shift results for CO adsorbed on the one-fold, two-fold, and three-fold sites on Pt(111) was published (17). In this study we were able to account for the stable adsorption site changing from one-fold to bridging as the Pt(111) electrode potential is decreased, a predicted result that was later observed. The bridge site becomes favored because as the band moves up, as in Figure 1, the mixing of the C-O π* orbitals with the filled metal surface orbitals becomes more important and this mixing is stronger when CO bonds to the bridge site.

Results of ASED-MO calculations with the metal valence band shift explained why, at the vacuum interface, CO adsorbs on three-fold sites of Pd(111) and on two-fold sites of Pd(100) (18). On Pt(111) one-fold adsorption is observed, while on Pt(100) a mixture of one- and two-fold coordinations are observed at the vacuum interface. The question was asked by Michel Van Hove during my visit to Berkeley in 1985. The difference was traced, as anticipated, to the VSIP parameters. The d orbital ionization energy in a Pd atom is about 1.0 eV less than in a Pt atom. The calculations showed for the (111) surfaces that shifting the Pt band up 1.0 eV led to CO adsorption at the Pd sites and shifting the Pd band down 1.0 eV led to CO adsorption at the Pt sites. The band shift theory also correctly dealt with the (100) surfaces. It was concluded that the band position determines the stable binding sites for CO on the (111) and (100) surfaces of Pt and Pd.

I published a review of the above-mentioned work from this lab and other labs in 1990 (19). It included details about the perturbation theory interpretation of the diagrams in Figure 1, along with many pertinent references. This paper gives my perspective on potential dependencies of vibrational and electronic spectra and structures of adsorbed molecules on electrodes and outlines the conceptual models of the time. Around this time I heard a prominent theoretical physicist exclaim at a national meeting that if he had a big enough computer he could calculate anything. In my lab at Case it would be another ten years until computer power rose to the point that ab initio calculations were possible. And even with today’s superb computational power, devising conceptual models is no less important than in the days of approximate semiempirical and small basis set ab initio calculations. The following models are my contributions to the predictive and conceptual development of electrocatalysis.

**Linear Gibbs Energy Relationship for Predicting Reversible Potentials**

The linear Gibbs energy relationship, or LGER, is a conceptual model that is useful for predicting reversible potentials for electron transfer reactions taking place in molecules adsorbed on the electrode. It also applies when either the reactant or product molecule remains in solution and is not adsorbed. Let a standard reduction reaction be written as

\[ R(aq) + H^+(aq) + e^-'(U^0) \rightleftharpoons P(aq) \]  \[ \text{[2]} \]
where R is the reactant, $U^o$ is the standard reduction potential, and P is the product. Then with R and P adsorbed we have

$$R(\text{ads}) + H^+(\text{aq}) + e^- (U^{\text{rev}}) \rightleftharpoons P(\text{ads})$$  \[3\]

The LGER relationship comes from the exact equation

$$U_{\text{rev}}(\text{ads}) = U^o(\text{aq}) + \frac{[\Delta_{\text{ads}}G(P) - \Delta_{\text{ads}}G(R)]}{e}$$  \[4\]

with internal energies of adsorption, $\Delta_{\text{ads}}E$, substituted for Gibbs energies of adsorption, $\Delta_{\text{ads}}G$:

$$U_{\text{rev}}(\text{ads}) = U^o(\text{aq}) + \frac{[\Delta_{\text{ads}}E(P) - \Delta_{\text{ads}}E(R)]}{e}$$  \[5\]

Equation [5] was motivated by our work that discovered a linear relationship between gas phase reaction energies and the standard reversible potentials for the reactions O$_2$ reduction to H$_2$O$_2$ or H$_2$O, H$_2$O$_2$ reduction to OH + H$_2$O or 2H$_2$O, and OH reduction to H$_2$O (20).

The success of equation [5] depends on:

(i) the solvation energies of R and P being small and nearly canceling;
(ii) zero-point vibration energies being nearly the same for R and P and nearly canceling;
(iii) changes in R and P adsorption bond strengths due to surface charging being small;
(iv) other thermal corrections to R and P energies being small;
(v) $H^+(\text{aq})$ not interacting significantly with the surface of the electrode.

The conceptual picture for Equation [5] is in Figure 2: the part of the relatively weakly-bonded solvation sphere around OH(aq) and H$_2$O(aq) is replaced by strong adsorption bonds to the electrode surface atoms.

![Figure 2. Replacement of part of the solvation shells, represented by circles, by adsorption bonds to the surface.](image-url)
To understand why the $H^+(aq)$ energy does not appear in equations [4] and [5], the standard hydrogen electrode workfunction, $\varphi$, is used to generate the Gibbs energy equality for solution:

$$G(R_{aq}) + G(H^+_{aq}) - \varphi - e U^o = G(P_{aq})$$

[6]

For reactions transferring a single electron, the Gibbs energy equality for the adsorbed species is

$$G(R_{aq}) + \Delta_{ads} G(R) + G(H^+_{aq}) - \varphi - e U_{rev}^{surf} = G(P_{aq}) + \Delta_{ads} G(P)$$

[7]

From the difference of Equations [6] and [7], the following is found:

$$U_{rev}^{ads} = U^o + [\Delta_{ads} G(P) - \Delta_{ads} G(R)]/e$$

[8]

Substituting internal energies for Gibbs energies yields Equation [5].

**LGER Predictions for H$_2$O(ads) Oxidation to OH(ads)**

Equation [5] was the basis for my contribution to a 2001 proposal to the Department of Energy headed up by United Technology Fuel Cells and including experimental electrocatalysis and polymer groups at several other universities. We proposed to apply it to understand the Pt skin effect on H$_2$O(ads) electro oxidation to OH(ads) on Pt alloys. At the time, OH(ads) was viewed as a surface poison on oxygen cathodes in fuel cells because it formed from the oxidation of water at potentials around 0.6 V and higher. It must not be forgotten that OH(ads) is also an intermediate in the four-electron reduction of O$_2$. The goals of electrocatalyst development today are with a view toward pushing the OH(ads) reduction potential positive, closer to the reversible potential for the overall four-electron process, the standard value being 1.229 V, and increasing long-term electrode stability.

Yeager had proposed pathways to O$_2$ reduction when coordinated to transition metal cation sites in coordination complexes, wherein the first two proton transfers took place before any electrons transferred (21). If the O$_2$ molecule bonded side-on to a one- or two-cation site, two coordinated OH were believed to form by transfer of 2 $H^+$ in acid, with the cations undergoing oxidation by 2 $e^-$. Subsequent reduction by 4 $e^-$ and the addition of 2 $H^+$ yielded two H$_2$O. If the O$_2$ bonded end-on to a cation site, coordinated OO$^-$ (superoxide) was believed to form, with the oxidation state of the cation increased by 1. In this case two pathways were proposed: four-electron reduction to 2H$_2$O or two-electron reduction to H$_2$O$_2$, hydrogen peroxide. The standard reversible potential for H$_2$O$_2$ is 0.695 V, and forming it is to be avoided in fuel cell. Thus, Yeager postulated a relationship between the structure of coordinated O$_2$ and the reduction product, and it seemed to correlate with observations for cobalt porphyrins and cofacial cobalt porphyrins. These coordination structures became models for thinking about reduction products over metal electrocatalyst surfaces as well. For example, at the onset potential of the under-potential-deposited (upd) hydrogen potential region, ~ 0.3 V on Pt(111) electrodes, total current begins to decrease and H$_2$O$_2$ begins to form. These results are attributed to blocking surfaces site by upd H, with the result that end-on but not side-on
O₂ adsorption is possible. Unfortunately, due to his passing in 2002, Yeager was not aware of the following LGER studies, which surely would have pleased him.

The contribution to the UTC Fuel Cells project began by using the Vienna ab initio Simulation Package (VASP) density functional slab-band method to calculate H₂O and OH adsorption energies on Pt(111) and on a monolayer skin on Pt₃Cr. These energies were used in the following LGER-based formula to predict the shifts in onset potentials for oxidation H₂O(ads) (23):

\[
\Delta U^{rev} = U^{rev}(\text{alloy}) - U^{rev}(\text{Pt}) = \left[ E_{\text{ads}}(\text{OH/Pt}) - E_{\text{ads}}(\text{OH/alloy}) - E_{\text{ads}}(\text{H₂O/Pt}) + E_{\text{ads}}(\text{H₂O/alloy}) \right] / e
\]

The calculated increase in reversible potential on the Pt skin was 0.11 V, compared to measured values from the literature in the 0.04-0.06 V range. Similar results were obtained for OH(ads) formation on the Pt skin on Pt₃Co (24) and reduced potentials were found for the Cr atoms in Pt₃Cr surfaces without Pt skins, consistent with the low potential onset of anodic dissolution of the more electropositive metal (25). The Pt skin effect was calculated using higher concentrations of Co in the alloy and the potential shift for OH(ads) formation was predicted to increase up to 0.27 V, in the case of Co₃Pt, but for the Pt skin on pure Co there was no further increase (26). These results implied that nanoparticles consisting of electropositive transition metal cores with Pt skins would be effective oxygen reduction catalysts that would also conserve platinum.

LGER Predictions for Steps in Two- and Four-Electron O₂ Reduction

The LGER theory has been used to relate mechanism to overpotential for several oxygen reduction electrocatalysts. In these studies, either cluster models and the hybrid density functional theory in the Gaussian software package or density functional slab-band models and the VASP software were used to model the active sites and calculate adsorption bond strengths, and in some cases both models were employed.

Two-Electron Reduction on Graphene and Nitrided Graphene. A joint experimental study was made with the Popov group (27). The first step in H₂O₂ generation on graphite was calculated, using LGER, to be OOH(ads) formation on an edge CH at 0.31 V reversible potential, which matched the observed onset potential for untreated graphite according to disc and ring currents. This end-on bonded intermediate is reminiscent of Yeager’s end-on O₂ reduction intermediate. The calculated reversible potential for reducing the OOH(ads) to H₂O₂ was 1.10 V. Nitrogen-treated graphene was modeled with one substitutional N atom in the middle of a graphene cluster. The N atom introduced an unpaired electron into the cluster which was localized predominantly on the neighboring C atoms in the sheet. The OOH(ads) was calculated to form on one of these atoms with a reversible potential 0.84 V, and the reversible potential for its reduction to H₂O₂ was predicted to be 0.54 V, which agreed with the observed onset potential for two-electron reduction over nitrided graphite.

Graphene with pyridinic edge substitutional N has also been studied using LGER (28). The motivation was to see if adjacent edge N could provide a site for the four-electron reduction of O₂; claims had been made in the literature that nitride graphite was active for
the four-electron reduction in the absence of transition metals. We found the stable edge in the potential range of interest consisted in N-O and N-H, a site with an unpaired electron and the bridging C provided an adsorption site for generating H_2O_2 with reversible potential 0.66 V, which was a little larger than in the previously mentioned study. No evidence was found for four-electron reduction at potentials greater than the H_2O_2 equilibrium potential of 0.695 V. We concluded that transition metals must be present for four-electron reduction to occur. In a previous study we found a mechanism for the four-electron reduction over Co^{II} coordinated to the two pyridinic edge N atoms (29). In it, H_2O_2 formed with a oxygen lone-pair donation bond to the Co^{II} that was strong enough to hold it for the next reduction step, forming OH(ads) and releasing H_2O. We suggested that, due to the weakness of the Co^{II} coordination, this active site was susceptible to anodic dissolution.

Four-Electron Reduction Studies. Several other studies where O_2 is reduced to water have been made. An interesting one was the modeling of a copper laccase enzyme known to reduce O_2 with very little overpotential. Its active site contains three Cu^{I} centers that are able to move to significant extent. We found O_2 reacted with H_2O to form \( \mu \)-bridged OH and OOH (30). It is noted that this was not a mechanism in Yeager’s list. Using LGER, four reduction steps were calculated to have reversible potentials not much less than the reversible potential for the overall four-electron reduction. It was concluded that the ideal four-electron electrocatalyst will have adsorption bond strengths for each intermediate that are just right for the reversible potentials for each step to equal that for the overall process.

A slab-band study density functional was made of O_2 reduction over cobalt sulfide (31). First, a stable partially oxidized surface model was found and then three interesting features were predicted: (i) O_2 adsorbed dissociatively, with significant heat loss calculated to be 1.13 eV, (ii) bonding of O and OH to both Co and S sites was predicted (iii), and the lowest reduction reversible potential was similar to that for platinum. This was followed by a combined experimental and theoretical study with the Popov group of cobalt selenide using the same surface structure model as for the sulfide (32). Results were similar but 1.38 eV heat was predicted to be liberated in the O_2 adsorption step. The lowest predicted reversible potential, 0.61 V, matched the observed low onset potential for reduction which was in the range 0.5 V to 0.6 V for this poor electrocatalyst. In these cases, the mode of O_2 adsorption and dissociation and reduction to 2OH(ads) was in partial accord with one of Yeager’s suggested pathways.

The LGER theory is clearly useful for screening potential electrocatalysts. We noticed in the literature that selenium nanotubes have a very broad double-layer potential range (33). Calculations suggest it is a suitable candidate for testing as an oxygen cathode electrocatalyst (33).

**Interface 1.0. A Comprehensive Program for Theoretical Treatment of the Electrochemical Interface**

This theory brings together the key theoretical components in one place (34, 35). Molecular structures and bond strengths at the electrochemical interface are accurately calculated using a two-dimensional density functional theory employing atomic orbitals
and pseudo potentials. Two-dimensional density functional theory allows electrochemical potential, which, within a constant, equals the Fermi level, to be calculated directly without further modeling. Atomic orbitals are a necessary basis in a two-dimensional theory since plane waves cannot be used. The interface is immersed in a dielectric continuum and electrolyte ions are allowed to respond to surface charging and their distribution is calculated using a modified Poisson-Boltzmann theory. A position-dependent function for the relative permittivity connects the atom electron densities with the bulk solution permittivity. Electron charge is added to or subtracted from the translational unit cell to change the Fermi level and electrode potential. The Gibbs energy for the whole system is calculated self-consistently. Calculated vibrational spectra are used to find zero-point vibrational energies and partition functions that are used in standard thermodynamic formulas to evaluate contributions to the Gibbs energies. The regions of the electrochemical interface model are in Figure 3.

Figure 3. The model used in the Interface 1.0 code includes a metal slab with dielectric or vacuum on one side and the electrochemical interface under investigation on the other. This cross-sectional view shows two translational unit cells and part of a third. There is a smooth change in permittivity between atom and bulk solution values in the region indicated by arrows. The 1.0 M electrolyte +1 and -1 ions form distributions in response to surface atom charging according to a modified Poisson-Boltzmann theory as suggested by the waves.
The full Gibbs energy change for a reduction reaction, including potential dependence, is given by

$$\Delta G(U) = \{G_{\text{Red}}(U) - G_{\text{Ox}}(U)\} + n(\phi + FU) \tag{10}$$

When the potential is changed and equilibrium is achieved $\Delta G(U)$ is zero and

$$U^o = \{G_{\text{ox}}(U^o) - G_{\text{red}}(U^o)\}/nF - \phi/F \tag{11}$$

This theory was initially applied to calculating reversible potentials for 34 bulk solution electron transfer reactions, for which the mean absolute error is less than 0.2 V (34). This was followed by calculating reversible potentials for probable steps in the four-electron reduction of O$_2$ on Pt(111) where it was shown that strong hydrogen-bonding between reaction intermediates and at least neighboring water molecule must be included for accurate reversible potential predictions (34). We concluded that the dielectric continuum model does not fully describe the solvation associated with strong hydrogen-bonding to negatively charged OH(ads), but the model is satisfactory for producing solvation energies for molecules of low charge.

The interface code has been applied to calculating the OH(ads) and H$_2$O(ads) coverage dependencies of the reversible potentials for OH(ads) reduction on Pt(111) (36). Increments of 1/6 ML were used up to a total coverage of 2/3 ML. It was found that the values clustered around 0.65 V, which is in the potential range observed experimentally, but when the H$_2$O(ads) and OH(ads) coverage was such that upon reduction of 1/6 ML OH(ads) the number of hydrogen-bonds to OH(ads) did not change, the reversible potentials increased to around 1.2 V. This is a physically inaccessible potential because oxidation of OH(ads) to O(ads) commences at about 0.8 V (37, 38). We also found that the calculated potential of zero charge (pzc) was sensitive to the surface structure (36). The average value for different H$_2$O coverage models was around 0.4 V, but at higher potentials, where OH(ads) was present, the pzc was generally higher because the surface was in an oxidized state.

Recently we used several coverage models to calculate reversible potentials for the first reduction step, O$_2$(ads) going to OOH(ads) and found the potentials to be around 0.4 V (39). Thinking in terms of the LGER, this value is low relative to 1.229 V because OOH adsorption bond strength is too weak by about 0.8 eV on Pt(111). However, the Interface 1.0 calculation of the reversible potential for the four-electron reduction is not exact, and yields 1.01 V for the reversible potential instead of 1.229 V (34). Based on this calculated value, the OOH adsorption bond strength is too weak by about 0.6 eV. Let us suppose it were 0.6 eV stronger. Now consider dissociation of OOH(ads) to O(ads) + OH(ads), which was calculated to be exergonic by about 1.2 eV when OH was on the surface. This becomes 0.6 eV exergonic if the OOH adsorption is 0.6 eV stronger. Now, if the calculated adsorption bond strengths of O and OH were respectively 0.35 and 0.25 eV less, the reversible potentials for both O(ads) reduction to OH(ads) and OH(ads) reduction to H$_2$O(ads) would increase to about 0.9 V, for an overpotential for the four-electron reduction of 0.1 V. Small contributions to the reversible potentials will come from the displacement of H$_2$O(ads) by O$_2$(aq) at the start, but again the point is made that
the proper balance of adsorption bond strengths of the intermediates is the desire of catalyst development.

Even if each electron transfer step takes place at exactly the reversible potential for the overall many electron process, kinetic limitations are expected because there will be activation energies for the electron transfers. It is now necessary to digress into the topic of electron transfer activation energies and dependencies on electrode potential.

**Local Reaction Center Model for Resonant Electron Transfer**

A computational approach for calculating activation energies for electron transfer reactions was devised over ten years ago (20). Our conceptual methodology may be foreseen in the works of Gurney in 1931 (40) and Butler in 1936 (41). The idea is that, for a reduction reaction, if the electrode is set at a given potential $U(V)$, electron transfer to the species to be reduced will take place by resonant electron tunneling if the electron affinity, $EA$, of the reduction center is given by

$$EA = (\phi - U/V)\text{eV}$$  \[12\]

The electron affinity varies with the structure of the reaction center and a constrained variation program is presently used to find the lowest energy structures with the requisite $EA$ (9), though in the early studies such as Reference (20) this was done by trial and error variation of a limited number of structure variables.

Figure 4 shows the Pt$_2$OO···H··OH$_2$(OH$_2$)$_2$ local reaction center model used to calculate activation energies for forming OOH(ads) by reduction of adsorbed oxygen. The counter charge to the hydronium ion is assumed to be a point charge representing a Madelung sum of ion charges in solution and is added to the Hamiltonian. Initially, the local reaction center structure is optimized with the hydronium ion hydrogen-bonded to the molecule to be reduced, as shown in Figure 4. The optimized structure is called the reduction precursor, and its $EA$ corresponds to what we term, using Equation [12], the reduction precursor potential, $U_{rp}$; for it the activation energy is zero. For the reaction

![Figure 4. Local reaction center model undergoing reduction and its relationship to surrounding surface and bulk atoms, shown by dashed circles.](image-url)
shown in Figure 4, the precursor potential has been called a “critical potential” and was experimentally estimated to be about 0.2 V to 0.4 V (42, 43). For electrode potentials $> U_{rp}$ there will be an increasing activation energy for electron transfer and on a metal surface at potentials $< U_{rp}$ the activation energy remains zero on a metal electrode but can be $> 0$ V on a semiconductor electrode. Additional discussion of this nomenclature has been published (44). The stretching of the O-H$^+$ bond in the hydronium ion along with other structure changes cause the center’s $EA$ to increase to match a chosen electrode potential $U > U_{rp}$, but the structure changes raise the energy of the local reaction center, and this gives the activation energy, $E_a(U)$, its electrode potential dependence in this theory. The $E_a(U)$ curves for both oxidation and reduction cross at a point taken to approximate the reversible potential for the reaction. Many studies have predicted the activation energies at the reversible potentials for the coordinated electron + proton transfer reactions to be about 0.2 eV and less at the reversible potentials. The $E_a(U)$ curves will shift on the potential scale in response to under- or over- estimated adsorption bond strengths that may result from using a small number of electrode surface atoms, which narrows the surface band. The curves are also sensitive to the Madelung charge approximation. However, they are robust in shape when shifted on the potential scale by changes in the Madelung potential and can be adjusted to accommodate a known precursor potential or a known reversible potential (45).

In a joint experimental and theoretical study with the Mukerjee and Markovic groups we found that over the range of 0.7 V to 0.85 V the measured effective activation energy for the four-electron reduction increased from 0.20 eV to 0.29 eV on platinum (46). The theoretical predictions for OOH(ads) formation were from 0.1 eV to 0.2 eV in this potential range. When the 0.4 V reversible potential is taken into account and the reversible potential in terms of reduction and oxidation activation energies (47) is shifted accordingly, the predicted values of $E_a(U)$ range from 0.3 eV to 0.4 eV over this potential range, higher by 0.1 eV. From this, it seems that the effective $E_a(U)$ for the four-electron reduction could be dominated by the OOH(ads) forming step.

There are several reasons for discarding an alternative pathway wherein O$_2$(ads) dissociates before OOH(ads) can form:
(i) Cluster calculations produced an activation energy of 0.74 eV for dissociation of O$_2$(ads) on a platinum di-σ bridging site, and for OOH(ads) dissociation the barrier was only 0.06 eV (49).
(ii) Density functional slab-band calculations with the VASP software showed that O$_2$ adsorbed stably in molecular form on Pt(111), while OOH(ads) dissociated spontaneously over the triangular fcc site and therefore will be able to dissociate once it forms (50).
(iii) The measured potential-dependent effective activation energies for the four-electron reduction and the calculated activation for O$_2$(ads) reduction to OOH(ads) are in satisfactory agreement.

**Grand Summary for O$_2$ Reduction on Pt(111)**

Data based on the reversible potentials discussed above, the activation energies for O$_2$ reduction to OOH(ads) (47), O(ads) reduction to OH(ads) (48), and OH(ads) reduction to H$_2$O(ads) (45), are summarized in Table I. It is noted that the activation energies for O$_2$...
TABLE I. Summary of the reactions and data predicted for oxygen reduction to water on Pt(111).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( U_{\text{rev}} ) or ( \Delta G )</th>
<th>( E_a(U_{\text{rev}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2(\text{ads}) + \text{H}^+(\text{aq}) + e^- \rightarrow \text{OOH}(\text{ads}) )</td>
<td>( U_{\text{rev}} \approx 0.4 \text{ V} )</td>
<td>( E_a \approx 0.15 \text{ eV} )</td>
</tr>
<tr>
<td>( \text{OOH}(\text{ads}) \rightarrow \text{O}(\text{ads}) + \text{OH}(\text{ads}) )</td>
<td>( \Delta G \approx -1.2 \text{ eV} )</td>
<td>( )</td>
</tr>
<tr>
<td>( \text{O}(\text{ads}) + \text{H}^+(\text{aq}) + e^- \rightarrow \text{OH}(\text{ads}) )</td>
<td>( U_{\text{rev}} \approx 0.8 \text{ V} )</td>
<td>( E_a \approx 0.2 \text{ eV} )</td>
</tr>
<tr>
<td>( \text{OH}(\text{ads}) + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}(\text{ads}) )</td>
<td>( U_{\text{rev}} \approx 0.6 \text{ V} )</td>
<td>( E_a \approx 0.05 \text{ eV} )</td>
</tr>
</tbody>
</table>

Figure 5. Reversible potentials and potential-dependent activation energies for the electron transfer steps during oxygen reduction to water over Pt(111) as determined using Gibbs energies from Interface 1.0 calculations and LGER calculations. The potential scale is SHE.

The data in Table I are graphed in Figure 5 and, to establish the trends, activation energies at higher potentials are added for each reduction. It is shown that as the potential is increased from the 0.4 V upd H(ads) onset potential, the activation energy for
OOH(ads) formation from O₂(ads) seems to dominate the Arrhenius factor through the double-layer potential range, 0.4 V to 0.65 V and beyond. Below 0.4 V site blocking by upd H(ads) is the cause of the increase in H₂O₂ production as the potential is decreased. Above 0.65 V as the potential is increased the activation energy for OOH(ads) formation increases and, at the same time, the surface becomes increasingly blocked by OH(ads) as it approaches its maximum coverage of 1/3 ML at 0.8 V. Beyond 0.8 V, O(ads) becomes stable and since it resides in three-fold sites on Pt(111) the surface is quickly passivated against O₂ reduction as the potential is increased further.

From the above, it is evident that to reduce the overpotential for the four-electron reduction all three of the curves in Figure 5 must be pushed to the right. As discussed above, copper laccase has this property and so do many of the platinum alloy catalysts being developed today. For the future the quest will continue to find new active electrocatalysts and achieving stability will become increasingly recognized as necessary.

Concluding Comments

In this review, four useful conceptual frameworks and theories that may be applied to understanding and predicting the elements of electrocatalytic processes have been presented. A summary of the current understanding of oxygen reduction based on using these theories has been made. Clearly these theories can find many applications to electrochemical processes. I acknowledge the inspiration and motivation that Ernest Yeager gave me which led to these results.

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