Mechanisms for Ethanol Electrooxidation on Pt(111) and Adsorption Bond Strengths Defining an Ideal Catalyst

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Ethanol electrooxidation on the Pt(111) electrode has been studied with computational theory. Using a solvation model and a modified Poisson-Boltzmann theory for electrolyte polarization, standard reversible potentials for forming 17 reaction intermediates in solution were calculated with density functional theory. Reversible potentials for adsorbed intermediates were then determined by inputting calculated adsorption energies into a linear Gibbs energy relationship. A path to CO2 was found where surface potentials were low and close to the calculated 0.004 V reversible potential for the 12 electron oxidation of ethanol. An exception was the 0.49 V potential for forming the OH(ads) from H2O(1), this being required for oxidation of CO(ads) and RH(ads) intermediates. The surface potentials show that acetyl, OCCH3(ads) forms at small positive potentials and decomposes to CH(ads), CH3(ads), and CO(ads), which poison the surface at these potentials. Energy losses due to non-electron transfer reaction steps are small and cause a small shift in the reversible potential for the 12 electron oxidation. Values for adsorption bond strengths over a perfect catalyst were determined. It is concluded that on an ideal catalyst most intermediates will adsorb more weakly and OH more strongly than on Pt(111).

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Unlike a fossil fuel, ethanol is renewable and can be produced from biomass. Compared to methanol, ethanol is less toxic. The specific energy density of ethanol is high (8.0 kWh/kg). It is liquid, which makes it easy to store and transport. These advantages make the direct ethanol fuel cell (DEFC) a promising green energy source. However, commercialization of DEFC is hindered by the slow insufficient electrooxidation reaction of ethanol on platinum. Platinum is active as the anode electrocatalyst in hydrogen fuel cells but is much less active for ethanol oxidation. Theoretical understanding of the failures of platinum will establish the specific steps during the electrooxidation which present the challenges. As shown in this paper, some of these challenges can be overcome by using electrocatalysts where reaction intermediates have specific adsorption energies to the active site. Designing materials with these properties is the goal for electrocatalyst development.

The complete electrochemical oxidation reaction which takes place at the anode surface produces twelve electrons, twelve protons, and carbon dioxide:

\[ \text{HOCH}_2\text{CH}_3(aq) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{CO}_2(g) + 12\text{H}^+(aq) + 12e^- \quad [1] \]

The reversible potential, \( U^0 \), is 0.090 V in aqueous solution under standard conditions, as calculated from standard thermodynamic data. However, cyclic voltammetry studies reported in 2002 by Iwasita indicated that under the conditions 1 mol L\(^{-1}\) \( \text{HOCH}_2\text{CH}_3 \) + 0.1 mol L\(^{-1}\) \( \text{HClO}_4 \), 50 mV s\(^{-1}\) and 298 K, ethanol oxidation does not occur on well-defined Pt(111) electrodes at potentials below about 0.4 V on the reversible hydrogen electrode (RHE) scale. Reference 2 is of a review nature and contains references to earlier pioneering work of the Iwasita group. Similar results were seen in 2004 by the Lamy group in polarization curves for ethanol oxidation over carbon-supported platinum electrodes under the conditions 1 mol L\(^{-1}\) \( \text{HOCH}_2\text{CH}_3 \) + 0.1 mol L\(^{-1}\) \( \text{HClO}_4 \), 5 mV s\(^{-1}\) and 293 K. Very recent experiments by Cantane and Gonzalez for electrodes containing black platinum supported on gold show an onset potential for ethanol oxidation between 0.4 V and 0.5 V under the conditions 1 mol L\(^{-1}\) \( \text{HOCH}_2\text{CH}_3 \) + 0.1 mol L\(^{-1}\) \( \text{HClO}_4 \), 100 mV s\(^{-1}\) and 298 K. Thus, the overpotential for oxidation is about 300 mV-400 mV under typically employed conditions of study.

However, the oxidation is not complete, and several final oxidation products have been observed over platinum electrodes. Iwasita’s on-line differential electrochemical mass spectroscopy (DEMS) measurements identified acetaldehyde, OCHCH3, forming at potentials greater than about 0.3 V and identified CO2 forming at potentials greater than about 0.5 V. Fourier transform infrared (FTIR) spectroscopy provided evidence for the functional groups in acetic acid, HOOCCH3, acetaldehyde, and adsorbed methyl (CH3) or methylene (CH2) fragments. The Lamy group obtained functional group vibrational signatures using subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) and single potential alteration infrared spectroscopy (SPAIRS). They concluded that carbon monoxide (CO) and acetyl (OCCH3) were intermediates, acetaldehyde was an intermediate and final product, and acetic acid, carbon dioxide, and methane were final products.

In addition to the above, there have been numerous other investigations that have given additional insight into the details and complexities of ethanol electrooxidation on platinum and some of them are comparative studies of platinum and platinum alloys,

and a few study temperature dependencies of the electrooxidation and Findings in several of these studies will be discussed later in this paper.

Theoretical analyses and predictions concerning ethanol electrooxidation are limited in number and all of them are applications of ex-situ modeling of structures and energies using density functional theory (DFT) calculations of properties of the surface-vacuum interface. The surface chemistry of ethanol at the vacuum interface on Pt(111) has been examined this way, and the findings provide rough guidance to the electrode surface chemistry at the potential of zero charge (PZC), which is the potential of the uncharged electrode immersed in the electrolyte. However, the PZC can change by hundreds of millivolts between reactants and products and generally is different from the applied potential. This makes it necessary for theoretical studies to add the dimension of electrode potential to the calculations in order to provide definitive predictions. Interactions with solvent water molecules and electrolyte ions must be included for the modeling of the electrochemical interface to be accurate and complete. The purpose of this paper is to give results of our examination of the steps during the electrochemical oxidation of ethanol over the Pt(111) electrode using the theory outlined below. We will first obtain results for each oxidation reaction occurring with simultaneous generation of H+ (aq) + e oxidation product. The results of our study of electrooxidation of ethanol also apply to CO2 reduction to ethanol, acetic acid, acetaldehyde, and adsorbed intermediates.

Self-consistent field density functional theory, SCF-DFT, is used to calculate standard reversible potentials, \( U^0 \), for electron transfer steps between the electrode and reaction intermediates in solution. These potentials are used in the theory for predicting reversible potentials for reactions on the catalyst surface and they are calculated.
because experimental values are not available for most of the electron transfer steps. In this theory, called the linear Gibbs energy relationship, LGER, the electrode surface is viewed as a perturbation to an electron transfer process in solution. The perturbation consists of the difference between the adsorption bond strengths between the electrode surface and the reactants and products of the electron transfer reaction. Although the adsorption energies are calculated at the PZC, the LGER approach has yielded predicted reversible potentials for electron transfer reactions on Pt(111) surfaces in error by less than 0.2 V in most of the cases where experimental data can be found for comparison.25

Knowing the redox potentials for adsorbed intermediates can greatly assist understanding the electrocatalysis. Modifying these potentials to approach the reversible potential for the overall process, for example 0.090 V for the 12 electron oxidation of ethanol, by finding new catalytic materials and possibly new electrolytes is a goal for development of higher efficiency ethanol anodes for use in fuel cells. The electron transfer kinetics are expected to be generally fast at the reversible potentials. This is because past experience in this laboratory, found in reference 25 and references therein, indicates that activation energies for coupled electron plus proton transfer reactions at the reversible potentials on platinum surfaces are approximately 0.1 eV. This low value is compatible with fast reactions at the anode. At potentials higher than the reversible potential, the activation energies will be even less and at lower potentials they will increase.25 For reduction the inverse holds and activation energies increase as the electrode potentials increase.

The overpotential for current flow is around 300 mV to 400 mV, but at these potentials the oxidation current density is much less than would be obtained for the 12 electron oxidation. This is because at 300 mV overpotential the oxidation is only partial, generating two electrons and forming acetaldehyde. At higher overpotentials additional products form, some of which desorb and are not oxidized further, and little full oxidation to CO2 takes place. Therefore, the electrical power obtained is a small fraction of the thermodynamic limit for complete oxidation. A goal for catalysis improvement is to find catalytic materials that hold all intermediates on the electrode surface until CO2 has formed and is able to desorb rapidly.

There can be thermodynamically induced overpotentials caused by exergonic reactions on the electrode surface. These reactions waste Gibbs energy as heat and entropy, as happens at platinum and platinum alloy oxygen cathodes, resulting in effective reversible potentials that are less than the standard one for reduction reactions,25,26 and greater than the standard one for oxidation reactions as shown later in this paper. An ideal catalyst will adsorb the intermediates with appropriate adsorption bond strengths so as to make these reaction energies zero and shift the reversible potential for each electron transfer step to the overall reversible potential. As shown later, an ideal catalyst for ethanol electrooxidation can do both.

**Theoretical Details**

The LGER theory got its start in 1999 for prediction bulk solution reversible potentials and25 was subsequently refined up to the present date for predicting reversible potentials for reactions of adsorbed species.26 This theory uses the standard reversible potentials for reactions in bulk solution and perturbs them with the difference in adsorption Gibbs energies, \( \Delta_{ads} G \), on the electrode surface of products of reduction, the reduced species R, and the reactants that are being oxidized, Ox. The reversible potential for the reaction between adsorbed species, \( U_{surf}^{rev} \), is then

\[
U_{surf}^{rev} = U^0 + \left[ \Delta_{ads} G(\text{Ox}) - \Delta_{ads} G(\text{R}) \right]/nF
\]  

[2]

The \( \Delta_{ads} G \)'s are dependent on the electrode potential, and using values calculated at the PZC instead of at the reversible potential gives reversible potential predictions for surface reactions that have errors usually less than 0.2 V for the aqueous interface when electrolyte and solvation models are used in good quality DFT.25 In the LGER theory, calculated internal energies of adsorption at the vacuum-surface interface, \( \Delta_{ads} E \), with the zero-point vibrational energies not included in \( E \), are substituted for the \( \Delta_{ads} G \), and reversible potential predictions predicted this way also have errors usually less than 0.2 V. This is because changes in the solvation and zero-point vibrational energies upon adsorption have been found to nearly cancel when calculated with accurate theory.25 The conceptual model for this, discussed in refs. 25 and 28, shows how on adsorption approximately equal amounts of weakly-held solvation shells of the reactant and product are replaced by bonds to the surface.

The equation used for \( U_{surf}^{rev} \) predictions in this paper is

\[
U_{surf}^{rev} = U^0 + \left[ \Delta_{ads} G(\text{Ox}) - \Delta_{ads} E(\text{R}) \right]/nF
\]  

[3]

To find the \( U^0 \) values employed in eq. 3, we first calculated Gibbs energies of Ox and R in bulk solution and determined the energy of the electron, that is, the electrode potential \( U^0 \) that satisfied the equilibrium condition:

\[
\text{Ox(aq)} + e^- (U^0) \rightleftharpoons \text{R(aq)}
\]  

[4]

The Gibbs energy balance in eq. 4 at equilibrium yields the equation

\[
U^0 = \left( G^0_{\text{sol}}(\text{R}) - G^0_{\text{sol}}(\text{Ox})/nF \right) - \phi/F
\]  

[5]

In eq. 5, \( F \) is the Faraday constant, \( \phi \) is the thermodynamic work function of the standard hydrogen electrode, calculated to be 4.43 eV,29 and \( G^0_{\text{sol}} \) is the standard Gibbs energy of the molecule in standard pH = 0 aqueous solution. The density functional code Interface was used for determining \( G^0_{\text{sol}}(\text{R}) \) and \( G^0_{\text{sol}}(\text{Ox}) \) for electron transfer reactions in solution and also when the reacting species are adsorbed on the electrocatalyst surface.29,30 The code uses atomic orbitals and atomic pseudopotentials. In Interface, \( G^0_{\text{sol}} \) is calculated as a sum of energy components by using the equation

\[
G^0_{\text{sol}} = E + \Omega_{\text{e,nonel}} + \Omega_{\text{a,nonel}} - TS + H_{\text{el}} - TS_{\text{el}}
\]  

[6]

Here \( E \) is the molecule’s internal energy, \( \Omega_{\text{e,nonel}} \) and \( \Omega_{\text{a,nonel}} \) are the respective Gibbs energies from non-electrostatic solute-solvent and ion-solute interactions with the molecule, determined using dielectric continuum for the solvent and a modified Poisson-Boltzmann equation for the ion distribution, \( T \) is the temperature of the system, \( S \) and \( S_{\text{el}} \) are entropies of the electrons and ions, \( H_{\text{el}} - TS_{\text{el}} \) are the vibrational contributions to the enthalpy and entropy of the molecule. The components of eq. 6 were calculated using the RPBE functional. Details of the computations are in ref. 29 and its follow-up paper.30 The same procedure was also used in refs. 25–28 and others. To reduce computational effort, the Gaussian09 code31 was used to calculate the \( H_{\text{el}} - TS_{\text{el}} \) components.

It might be wondered whether internal energies, \( E(\text{Ox}) \) and \( E(\text{R}) \), could yield useful predictions when substituted for \( G^0_{\text{sol}}(\text{Ox}) \) and \( G^0_{\text{sol}}(\text{R}) \) in eq. 5. The answer is yes in some cases, at least. As shown in ref. 27 for five different reduction reactions involving \( \text{O}_2, \text{H}_2 \text{O}, \text{OH}, \) and \( \text{H}_2 \text{O}_2 \), there is a linear correlation between \( E^0 \) calculated this way and the measured values. The existence of the linear relationship is the result of the small differences of the small hydration energies of the neutral reactant and product molecules. The calculated values are on average 0.43 V less than the experimental values. Other series involving groups of molecules possessing similar solvation energy differences might be expected to show trends too with an offset differing from 0.43 V, but there has not yet been exploration of the idea.

To be safe, it is better to calculate and use \( G^0_{\text{sol}}(\text{R}) \) and \( G^0_{\text{sol}}(\text{Ox}) \), as is done for this paper.

With the predicted values for the \( E^0 \) in hand, we proceeded to calculate \( \Delta_{ads} E(\text{Ox}) \) and \( \Delta_{ads} E(\text{R}) \) for use in eq. 3 to determine values for \( U_{surf}^{rev} \). Calculations of the adsorption internal energies were performed with the two-dimensional periodic boundary condition option of the Interface code. Adsorption internal energies, with vibrational zero point energies omitted, were calculated as follows:

\[
\Delta_{ads} E(\text{Ox}) = E(\text{Ox(ads)}) - E(\text{Surf}) - E(\text{Ox})
\]  

[7]

\[
\Delta_{ads} E(\text{R}) = E(\text{R(ads)}) - E(\text{Surf}) - E(\text{R})
\]  

[8]
In cases of intermediates with two carbon atoms, 1/12 ML coverage was used to minimize interactions among the adsorbates. A three-layer-thick slab was created using a $2\sqrt{3} \times 3$ unit cell with 2-dimensional periodic boundary condition as shown in Figure 1. The unit cell was made of 36 atoms with 12 in the bottom layer frozen in bulk platinum sites and the positions of the remaining 24 were optimized for lowest energy. For intermediates with a single carbon atom, 1/6 ML coverage was used and a $3 \times 2$ unit cell was employed. The previously calculated lattice constant value of 4.03 Å was used. A $3 \times 4 \times 1$ grid of k-points was used for the $2\sqrt{3} \times 3$ unit cell and $3 \times 6 \times 1$ grid was used for $3 \times 2$ unit cell to give a uniform Monkhorst-Pack sampling in the Brillouin-zone.

### Results

**Adsorption internal energies.**—Like methanol and water, ethanol adsorbs by electron lone-pair donation from oxygen to a Pt atom, bonding on the top site with the C-C bond nearly parallel to the surface. The calculated low-coverage, 1/12 ML, adsorption bond strength, shown to be 0.25 eV in Table I, is close to those of low-coverage, 1/6 ML, methanol and water, 0.28 and 0.23 eV, respectively, which we calculated in a study of methanol electrooxidation over Pt(111). Numbers from Table I are rounded to two figures after the decimal when used in the text. There are three possibilities for the dehydrogenation: loss of H from (i) the α-C of the ethyl group, (ii) the hydroxyl group, and (iii) the methyl group; the last was not calculated.

H loss from the α-C in ethanol, (i), gives 1-hydroxyethyl (HO*CHCH3), which bonds to a Pt atom through the α-C with bond strength 2.03 eV. Note that each time the * notation occurs in the formulas, it means the atom following this symbol is bonded to the surface in the variationally optimized structure. The OH and CH3 groups bend away from the surface and the CO bond length is 1.40 Å. By removing the second H from the α-C, 1-hydroxyethylidene (HO*CCCH3) is formed and it remains on the top site. The adsorption strength is increased to 3.23 eV and the CO bond length shortens to 1.31 Å. Loss of H from the OH group now generates acetyl (O*CCH3), which bonds through the α-C, standing upright on a Pt atom with both O and CH3 group pointing away from the surface. The adsorption bond strength is 2.36 eV and now the C-O bond length is shortened to 1.20 Å. Structures for these and other intermediates considered in this study are shown in Figure 2. It is noted that the C-C distances for the adsorbed intermediates are relatively constant, lying in the range 1.31 Å for ethoxy (α-OCH2CH3) to 1.48 Å for ketenyl (O*C*CH).

If the first H loss in ethanol is instead from the hydroxyl group, (ii), ethoxy is formed and it is bonded through oxygen, by 1.43 eV, with a shortened 2.01 Å Pt-O distance, compared to 2.41 Å for ethanol. Loss of H from the α-C of ethoxy gives acetaldehyde (α-O*CHCH3), which has a weak adsorption energy of 0.35 eV. The most stable site for acetaldehyde at 1/12 ML coverage is bridging, with oxygen and carbon bonded to adjacent Pt atoms. The O-C bond is nearly parallel to the surface, and the methyl group is tilted away from it. If it forms, stays on the surface, and loses the remaining α-H, it becomes acetyl. Loss of H from the β-C in acetyl gives ketene (O*C*CH2) with 1.80 eV adsorption bond strength and a short, 1.20 Å, C-O bond length. Loss of a second H from the β-C gives ketenyl (O*C*CH), which is strongly adsorbed by 3.55 eV, and also has short 1.20 Å C-O bond length.

Table I includes 13 additional adsorption energies and C-C and C-O bond lengths. Some of the data are taken from our earlier study of methanol electrooxidation and CO2 reduction. From these data is seen that products of C-C bond breaking are strongly adsorbed, bonding through the carbon atoms with strengths in the order, COCH3 < CH3 < CH. The last is strongly adsorbed with 6.13 eV bond strength. Methane and CO2 are weakly adsorbed at 0.02 and 0.05 eV, respectively.

Other intermediates include strongly adsorbed hydroxymethylene (HO*CH, possibly formed by combining OH(ads) and CH(ads)). Loss of one hydrogen atom from it gives strongly adsorbed hydroxymethylene (HO*CH) or formyl (O*CH), and adsorbed CO is formed when the last H is removed. The strongly adsorbed hydrocarboxyl radical (HOOC), and non-adsorbed acetic acid (HOOCCCH3), are suggested later to be produced by reaction between OH(ads) and respective adsorbed intermediates CO and acetyl. Hydrocarboxyl bonds through the carbon with the hydrogen pointing toward the surface. The adsorption bond strength of acetic acid is negative, meaning that though a local energy minimum was found with the variational structure optimization, the structure is metastable and acetic acid is
predicted to not chemisorb. On the other hand, the acetate radical, (OOCCH3), is strongly bonded by 1.97 eV to the surface through both oxygen atoms, and it stands upright over two adjacent Pt atoms with the methyl group pointing away from the surface. In comparison, the acetate anion (OOCCH3~), is weakly adsorbed by 0.30 eV.

To summarize: all intermediates adsorb strongly to the surface except acetaldehyde, acetic acid, acetate anion, and methane, all of which are observed partial oxidation products. The reactants ethanol and water and the product carbon dioxide also adsorb weakly.

### Predicted standard reversible potentials for reactions in aqueous solution.

We calculated Gibbs energies for 18 electron transfer reactions in bulk aqueous solution phase and obtained standard reversible potentials by using them in eq. 5. The energies for oxidation reactions, \( \Delta G^0_{\text{sol}} = G^0_{\text{sol}}(R) - G^0_{\text{sol}}(\text{Ox}) \) with 4.43 eV subtracted from them, are given under the heading \( \Delta G^0_{\text{sol}}/\text{eV} \) in Table II. The predicted \( U^0 \) values are in the second columns of Table II and their signs are necessarily the same as those calculated for \( \Delta G^0_{\text{sol}} \). The reaction Gibbs energies would have the opposite sign had the reactions been written for reductions. There is a wide range of calculated standard reversible potentials for the redox reactions considered, ranging from −3.00 V to 2.44 V.

### Predicted reversible potentials for oxidations of adsorbed molecules.

The LGER equation of eq. 3 was used to predict reversible potentials for oxidation reactions of adsorbed molecules from the calculated standard reversible potentials and the calculated internal energies of adsorption for the reactants and products. Because the Pt(111) surface is hydrophobic and the interaction with ethanol should be similar and the CO2 adsorption energy is <0.05 eV, H2O, HOCH2CH3 and CO2 adsorption energies were set to zero. The calculated reaction Gibbs energies for the adsorbed molecules are in the third column of Table II and the predicted reversible potentials are in the fourth column. In the following discussion, numbers taken from Table II will be rounded to two figures after the decimal.

All the predicted reversible potentials for the adsorbed molecules are closer to the overall ethanol oxidation potential than the standard reversible potentials of the solution phase molecules. The reversible potentials are best discussed in view of the reaction network in Figure 3. Here it is seen that there are two initial reaction branches, the left-hand one for OH bond oxidation, with a positive reversible potential of 0.98 V and the right-hand one where H bonded to the \( \alpha \)-C is oxidized, with a reversible potential of ~0.35 V. The latter is more likely to occur near the overall reversible potential of 0.09 V, being negative of it. Both branches lead to OCCH3(ads), for which three possible reactions are shown. There is also a crossover from HOCHCH3(ads) to acetaldehyde, OCH(ads), in the left-hand branch which has predicted reversible potential 0.58 V. This is higher than, but close to, the ~0.35 V potential where acetaldehyde is first observed as the potential of a platinum is increased. Staying with the right-hand branch, HOCHCH3(ads) is oxidized to HOCH2(ads) with a negative reversible potential and this is oxidized to OCCH3(ads) with a slightly positive reversible potential. Acetaldehyde formation by reduction of OCCH3(ads) is prevented in the potential range of interest, near 0.09 V, because the reversible potential is ~0.80 V.

The OCCH3(ads) has three pathways open as shown in Figure 3. The left-hand one combines it with OH(ads) if the electrode potential is >=~0.5 V to form acetic acid in a 0.32 eV exothermic reaction; the central one has it oxidized to OCCH2 with a slightly negative reversible potential; and the right-hand has it undergoing exothermic C-C bond scission with a loss of 1.10 eV to form CO(ads) and CH3(ads). The CO(ads) is oxidized to CO2 at potentials where OH(ads) is present and CH3(ads) is reduced to methane with a slightly negative reversible potential. We did not explore methyl oxidation.

The left-hand branch, combining OH(ads) with the OCCH3(ads), forms acetic acid, which, because of the negative adsorption bond strength in Table I, does not bond to the surface. The reaction energy is calculated for this reaction is 0.32 eV, which is small enough for reaction to take place. The solvated acetic acid molecule is calculated to be oxidized with reversible potential ~0.08 V to adsorbed acetate radical. It is also calculated to become ionized to acetate anion and H+(aq) with a 0.32 eV energy increase.

Continuing down the central path, OCCH2(ads) is oxidized with a small positive reversible potential to OCCH(ads), and OCCH3(ads) dissociates with 1.17 eV energy loss to CH(ads) + CO(ads). If the potential is high enough for it to form, the CO(ads) combines with...
Table II. Calculated Gibbs reaction energies, $\Delta G^\circ_{\text{sol}}$ and $\Delta G_{\text{surf}}$, and calculated reversible potentials, $U^\circ$ and, $U^\text{rev}_{\text{surf}}$ according to the LGER theory surface. $\Delta G^\circ_{\text{sol}}$ stands for $\Delta_{\text{sol}}G^\circ \cdot \varphi$ and $\Delta G_{\text{surf}}$ stands for $\Delta_{\text{surf}}G^\circ / \varphi$, where $\varphi = 4.43 \text{ eV}$.

| Reaction                     | $\Delta G^\circ_{\text{sol}} / \text{eV}$ | $U^\circ / \text{V}$ | $\Delta G_{\text{surf}} / \text{eV}$ | $U^\text{rev}_{\text{surf}} / \text{V}$ |
|------------------------------|------------------------------------------|----------------------|--------------------------------------|---------------------------------------|
| HOCH$_2$CH$_3$(aq) $\rightarrow$ HOCH$_2$CH$_3$ + H$^+$ (aq) + e$^-$ | 1.677 | 1.677 | -0.353 | -0.353 |
| HOCH$_3$CH$_2$OH (aq) $\rightarrow$ HOCH$_3$CH$_2$OH + H$^+$ (aq) + e$^-$ | 0.928 | 0.928 | -0.274 | -0.274 |
| HOCH$_3$ + H$^+$ (aq) + e$^-$ | -0.817 | -0.817 | 0.057 | 0.057 |
| OCCH$_3$ + H$^+$ (aq) + e$^-$ | -0.605 | -0.605 | -0.044 | -0.044 |
| OCCH$_3$ + H$^+$ (aq) + e$^-$ | 1.893 | 1.893 | 0.139 | 0.139 |
| OCCH$_3$ $\rightarrow$ CO + CH$_4$ | 3.048 | - | -1.167 | - |
| CO + OH $\rightarrow$ HOOC | -1.076 | - | 0.195 | - |
| HOCO $\rightarrow$ CO$_2$ + H$^+$ (aq) + e$^-$ | -2.093 | -2.093 | 0.227 | 0.227 |
| CH + OH $\rightarrow$ HOCH | -4.874 | - | 0.098 | - |
| HOCH $\rightarrow$ OCH$^+$ + H$^+$ (aq) + e$^-$ | -0.843 | -0.843 | -0.130 | -0.130 |
| OCH $\rightarrow$ CO + H$^+$ (aq) + e$^-$ | -1.449 | -1.449 | -0.697 | -0.697 |
| HOCH $\rightarrow$ HOC + H$^+$ (aq) + e$^-$ | 0.662 | 0.662 | -0.575 | -0.575 |
| HOC $\rightarrow$ CO$^+$ (aq) + e$^-$ | -2.955 | -2.955 | -0.252 | -0.252 |
| H$_2$O $\rightarrow$ OH$^+$ (aq) + e$^-$ | 2.445 | 2.445 | 0.494 | 0.494 |
| HOCH$_2$CH$_3$ $\rightarrow$ OCH$_2$CH$_3$ + H$^+$ (aq) + e$^-$ | 2.159 | 2.159 | 0.981 | 0.981 |
| OCH$_2$CH$_3$ $\rightarrow$ OCHCH$_3$ + H$^+$ (aq) + e$^-$ | -1.581 | -1.581 | -0.501 | -0.501 |
| OCH$_2$CH$_3$ $\rightarrow$ OCCH$_3$ + H$^+$ (aq) + e$^-$ | 1.210 | 1.210 | -0.797 | -0.797 |
| OCCH$_3$ $\rightarrow$ CO + CH$_3$ | 0.235 | - | -1.098 | - |
| CH$_3$ + H$^+$ (aq) + e$^-$ $\rightarrow$ CH$_4$ | -1.981 | 1.981 | -0.070 | -0.070 |
| OCCH$_3$ + OH $\rightarrow$ HOOCCH$_3$ | -3.986 | - | 0.323 | - |
| HOOCCH$_3$ $\rightarrow$ OOCCH$_3$ + H$^+$ (aq) + e$^-$ | 1.889 | 1.889 | -0.084 | -0.084 |
| HOOCCCH$_3$ $\rightarrow$ OOCCH$_3$ + H$^+$ (aq) + e$^-$ | 0.323 | - | - | - |
| OOCCH$_3$ $\rightarrow$ OOCCH$_3$ + e$^-$ | 1.565 | 1.565 | -0.103 | -0.103 |

$\Delta G_{\text{ads}}$ is replaced by $\Delta_{\text{ads}}G$ in LGER theory.

**Figure 3.** Pathways calculated for ethanol electrooxidation to CO$_2$ showing side reactions generating methane and acetate. Reversible potentials (V) and reaction energies (eV) are from Table II.

**Figure 4.** Calculated reversible potentials for ethanol electrooxidation by the path discussed in the text. The values for bulk solution along the top scale are connected by lines to the values for the species adsorbed on the Pt(111) surface.

OH(ads) and the HOCO(ads) product is oxidized to carbon dioxide. The CH(ads) combines with OH(ads) to form HOCH(ads), which is oxidized by removal of H to form CO(ads) which is oxidized to carbon dioxide.

The path with favorable potentials that leads exclusively to carbon dioxide follows the right-hand path to OCCH$_3$ and goes through the OCCH$_3$(ads) intermediate. All calculated reversible potentials along this path are less than the 0.49 V reversible potential calculated for oxidation of H$_2$O(ads) to form the OH(ads) intermediate. The branch to acetic acid is allowed by the 0.32 eV activation energy calculated for combining OCCH$_3$(ads) with OH(ads).
closer to 0.004 V, which is the calculated 12 electron reversible potential. On an ideal catalyst all of the reversible potentials would be shifted to 0.004 V. The water oxidation potential is higher than all the others both in solution and on the surface, showing how the generation of the OH(ads) oxidant may be the cause of the observed overpotential. Results given below support the conclusion that it is the cause.

Adsortion bond strengths on the ideal catalyst for electro oxidation of the intermediates.— It is possible to determine a unique set of optimal adsorption energies for the intermediates as was accomplished in ref. 33 for methanol electrooxidation. We have done this using the calculated value of 0.004 V as the reference potential, obtained by summing energies for the steps along the favored path outlined in the previous paragraph, which is the only path leading entirely to CO2 product, and dividing by 12. The procedure is given next.

Consider the path from HOCCH3(aq) through OCH(ads) to CO2(g). Including H2O(ads) and H(ads), there are 14 different adsorbed molecules along this path, which means there are 14 different adsorption bond strengths to be determined. It is also necessary to have the CC bond scission energy in OCCH(ads) be equal to zero to prevent energy loss as well as the OC bond formation energy in HOOC to minimize the activation energy for its formation. These constraints reduce the number of adsorption bond strengths to be determined to 12. In oxidation steps, 12 electrons are transferred. Three of these oxidation steps are the same because they involve forming OH(ads) from H2O(ads). This means there are 10 electron transfer potentials to be set to 0.004 V and there are 12 adsorption bond strengths to determine. It is not possible to find them all uniquely. Two of the adsorption bond strengths involve the adsorption of ethanol and water molecules. If these are given arbitrary values, that leaves 10 adsorption bond strength constraints and 10 reversible potentials to be fit to 0.004 V. This will also predict a value for the adsorption energy of CO2(g). Thus, the adsorption energies of two of the species could take any value, and the value for the third will be dependent on their values when all the reversible potentials are 0.004 V. We overcome this difficulty by making a reasonable approximation. Using the fact that the adsorption energies of ethanol, water and carbon dioxide are small, we set them to zero, which in fact they would be on an ideal catalyst, and then calculated the adsorption energies for an ideal catalyst that are presented in Table I. Were a catalyst discovered which presented these adsorption energies, all bulk reversible potentials would be focused on 0.004 V.

The differences between the ideal adsorption bond strengths and the calculated values on Pt(111) are in the last column of Table I. There it may be seen that intermediates that bond through C adsorb on Pt(111) too strongly by several tenths of an electron volt, with the exception hydroxymethylene, which bonds slightly too weakly. Carbon monoxide in particular adsorbs with a bond that is too strong by 0.91 eV. The hydroxyl radical adsors with a bond that is 0.50 eV too weak and water adsors about 0.23 eV too strongly, which is why forming the OH(ads) takes place at high potential and, since it is the oxidant for CO(ads) and all oxidation steps leading to CO2 are < 0.20 V, this is why CO(ads) is not removed at low overpotential.

On platinum, the calculated energies and reversible potentials allow for forming acetic acid and methane are at potentials ~ < 0.06 V, which matches the experimental observations. However, when methane is generated, CO(ads) is generated simultaneously and it will build up and block the surface at potentials < ~ 0.2 V. It is noted that one could similarly determine the ideal adsorption bond strengths for forming acetic acid or methane + CO2 through the HOCH2CH3(aq) to OCCH3(ads) route shown in Figure 3. However, these are not desired products and the power generated during their formation is small.

The above is all in good accord with the potential-dependent observations of the Iwasita,2 and Lamay4 groups, and with Cantane and Gonzalez.4 Under-potential-deposited (upd) H(ads) and coadsorbed could also be a reaction-blocking adsorbate up to around 0.1 V, as has been suggested by Behm and coworkers.9 There is a large literature on upd H(ads) on platinum surfaces. A recent theoretical study using calculated Gibbs energies was able to accurately reproduce the cyclic voltammogram for Pt(111) in acid and found that at 0.1 V the H(ads) coverage was ~ 1/4 ML.34 Reference 34 may be consulted for entries into the experimental and theoretical literature concerning upd H(ads) on various Pt surfaces.

Temperature-dependent properties and CC bond activation.— The activated breaking of the CC bond in various adsorbed intermediates has been a focus of theoretical and experimental attention. Probably the best estimates of the activation energies are from the phenomenological theoretical modeling of Vesselli et al. who predict activation energies of 0.26 eV for CC cleavage in OCCH adsorbed on Pt(111) and 0.22 eV for CC cleavage in adsorbed OCCH3.21 The group of Herrero and Feliu have been particularly engaged in exploring the CC bond scission on stepped and alloyed Pt surfaces.12-14

Effective activation energies have been measured recently by several groups using Arrhenius plots.5,7,26 From DEMS measurements for acid solutions at low temperatures, Cremers, Stimming and coworkers determined effective activation energies for oxidation of 0.1 M ethanol over carbon-supported platinum in the 30–60 °C range.5 For the overall reaction they obtained 31 kJmol−1 and for the CO2 component the result was 53 kJmol−1. Efficiency was at a maximum at 0.6 V and decreased as a function of ethanol concentration. They noted that, once formed, acetic acid did not react further but acetaldehyde did. They deduced that under fuel cell conditions ethanol to CO2 current efficiency is 75% and acetaldehyde to CO2 current efficiency is 86%. We calculate reversible potentials for acetaldehyde and acetic acid oxidation of ~ 0.053 V and 0.31 V, respectively. These values agree with both being oxidized at 0.6 V, the potential used by the Stimming group in the study of temperature dependence of ethanol oxidation. Acetaldehyde is hydrophobic, as is the platinum surface,30 which explains how it can approach the surface for adsorption and further oxidation. Acetic acid, being hydrophilic, is relatively stable in the bulk electrolyte solution and is retarded from approaching the surface for further oxidation.

Behm and coworkers made a DEMS study of ethanol oxidation over carbon-supported platinum at higher temperatures, 23–100 °C and at 3 bar overpressure.7 Using 0.1 M ethanol at 0.58 V, they found the overall activation energy to be 41 kJmol−1 and the CO2 activation energy 67 kJmol−1. They attributed the observed increase in CO2 efficiency at lower ethanol concentrations to transport effects. They pointed out that “catalysts with an improved activity for CC bond breaking are not beneficial for the ethanol oxidation reaction, unless they are also more active for oxidation of adsorbed COads and CH2ads species.”5

At intermediate temperatures, meaning in the range 235–260 °C, Otomo and coworkers, using a proton-conducting solid electrolyte and analyzing collected gaseous reaction products with a gas chromatograph, found CC bond scission to be > 90%.16 The onset potential for ethanol oxidation was seen at just over 100 mV (RHE) per a Pt/c catalyst at 250 °C and this at potential H2 was the dominant oxidation product. At about 150 mV CO2 became the dominant product and its concentration increased for potential increases to 600 mV, while the H2 contribution decreased to a small value. The amounts of CO and OCHCH3 formed were very small over this range of potentials while some CH2 was seen and its amount decreased slowly as the potential increased to 600 mV. The apparent activation energy depended on the applied potential, beginning at about 90 kJmol−1 at 160 mV and dropping to about 60 kJmol−1 as the potential increased to 250 mV, and remaining constant for potentials up to 450 mV. This activation energy lies between 53 and 67 kJmol−1 values for the low temperature studies mentioned above, and this led Otomo and coworkers to conclude that at high potentials the rate determining step is the same at intermediate and low temperatures.

Behm and coworkers in their recent attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIRS) study of ethanol electrooxidation over a platinum film in a flow cell, obtained additional evidence for the removal of COads and CH2ads being rate
limiting. For 0.5 M H$_2$SO$_4$ with 0.1 M ethanol running at ambient, they observed OCCH$_3$ in the 0.3–0.6 V potential range with a maximum at 0.4 V.\textsuperscript{15} It was concluded that under steady-state conditions CO(ads) and CH$_2$(ads) formed from OCCH$_3$ decomposition, and nearly blocked the surface at 0.3 V. This means the activation energy for CC bond scission in OCCH$_3$ is low enough to allow reaction at room temperature, leaving the removal of CO(ads) and/or CH$_2$(ads) as slow steps at these potentials. Both of these surface blockers require reaction with OH(ads), which begins to form at a higher potential of \(~0.5\) V.

The measured effective activation energies in several studies discussed above are over double the theoretical estimates of Vesselli et al. for CC bond scission. However, we note that Wierckowski and coworkers\textsuperscript{22} tabulated calculated values for CC bond scission activation energies for various OCH$_2$CH$_3$ species on Pt(111) and the lowest was 0.92 eV, too high for CC bond scission under fuel cell operating conditions. Importantly, in their density functional study, Wang and Liu also found high CC bond scission activation energies on Pt(111) but they calculated 0.53 eV for the CC activation energy on the (100) surface.\textsuperscript{22} This is still high, but possibly the density functional theory predicted CC bond scission activation would be small enough for certain sites to account for the measurements. The above-quoted conclusion of Behm and coworkers is possible because of the CC bond scission activation is small.

**Temperature-dependency of reaction mechanisms and products.**—

In interpreting their measurements at 235–260 °C, Otomo et al. proposed two reaction routes: route 1, which led to H$_2$, CH$_4$, and CO$_2$ and route 2, which led to CO exclusively. Thermal decomposition and the water-gas shift reaction were postulated to be occurring for route 1 and the measured current density at the lower potentials was attributed to the electrooxidation of H$_2$. At higher potentials the current efficiency of route 1 decreased from 80% to 20% while the current efficiency for route 2 increased from 20% to 80%. All generated current was attributed to oxidation of H(ads), forming H$^+$aq and H$_2$O, forming H$^+$aq and OH(ads). Decomposition of the intermediates on the surface at 250 °C was ascribed to thermal reactions.

Activation energies for C-H bond breakings during the proposed decomposition steps may have values consistent with the proposal of Otomo et al. Vesselli et al. estimated a barrier of 0.52 eV for breaking an $\alpha$-CH bond in ethanol on Pt(111), and activation energies for subsequent H removal steps to OCCH$_2$(ads) were even lower.\textsuperscript{18} Using density functional theory, Wang and Liu calculated barriers of 0.98, 0.46, and 0.40 eV barriers for removing, respectively, $\beta$-CH, $\alpha$-CH, and OH bonds on Pt(111).\textsuperscript{22} The agreement with Vesselli for the $\alpha$-CH bond is good. The hydrophilicity of the OH end of ethanol is expected to keep the OH moiety in the double layer and away from surface Pt atoms to prevent OH scission and the formation of adsorbed ethoxy. We cannot be sure of the accuracy of density functional theory for determining CC and CH bond activation energies, but such thermal decomposition steps cannot presently be discarded in favor of direct proton transfer into solution with simultaneous electron transfer into the electrode, but as the accuracies of the computational theories improves the issue will be eventually resolved. It is noted that the low water to ethanol molar ratio of 3:20 used by Otomo et al may favor ethanol decomposition to H$_2$, CO and CH$_3$. The oxidation mechanism in low temperature fuel cells may be affected by the much higher water to ethanol ratio.

**Effective reversible potential for the ethanol anode.**—

Any steps with negative reaction energies contribute to free energy loss. Assuming initial reactants, ethanol and water and the carbon dioxide product are not adsorbed, it is found that the sum of all reaction energies for the path from HOCH$_2$CH$_3$ to CO$_2$ is $\sim0.358$ eV, corresponding to a standard reversible potential of $\sim0.03$ V. This is close to 0.0 V and close to 0.004 V calculated for the solution phase reaction, but not quite the same because of treating bond CC and CO bond strengths in adsorbed intermediates differently, as internal energies, from their treatment in the aqeous phase, as Gibbs energies. Along this path only the C-C bond scission is exergonic by 1.167 eV, and this corresponds to energy lost and not available for doing electrical work by the electrons generated and so the 12 electron reaction free energy for ethanol oxidation is reduced by this amount. Dividing this by 12/e and adding the result to $\sim0.3$ V gives an effective reversible potential of 0.07 V. The shift stills leaves the calculated standard reversible potential, $U_{\text{eff}}$, near to 0.0 V and also near to the experimental value of 0.004 V. The calculated $U_{\text{eff}}$ is below the potential where upd H(ads) and adsorbed intermediates are removed, and so it does not affect the observed overpotential.

**Reaction intermediates.**— Partial oxidation is well characterized, and the observation of acetyl formation at 0.3 V by Behm and coworkers\textsuperscript{13} is consistent with the negative or slightly positive reversible potentials for getting there by the right-hand path in Figure 3. The CC bond scissions generate the observed CO(ads) and CH$_2$(ads) species\textsuperscript{15} by either the vertical or the right-hand path down from acetyl in Figure 3, the first leading to CH(ads) + CO(ads) and the second to CH$_3$(ads) + CO(ads). The removal of CO(ads) and CH(ads) requires OH(ads) to react with them, forming HOCO(ads) and HOCH(ads), which are then oxidized. We have not explored CH$_3$(ads) oxidation.

In the intermediate temperature study, methane was seen to form from 0.1 V to 0.6 V and this could be due to H(ads) formed by CH bond scission and water oxidation. Acetyl can react with OH(ads) over a small activation barrier to form acetic acid as shown in Figure 3. The formation of acetaldehyde that is observed to take place at 0.3 V and higher potentials,\textsuperscript{2} is in fair agreement with the 0.58 V crossover step in Figure 3, a mechanism not considered by Behm and coworkers in ref. 13 who thought an oxygen source was needed for forming acetaldehyde.

Using the data calculated here, we are unable to calculate the overall reaction activation energies and the CO$_2$ activation energies and their potential ethanol concentration dependencies shown in refs. 6, 7, and 16. The values are rather high, being $\sim0.4$ eV for the former and $\sim0.7$ eV for the latter in ref. 7 for example. In ref 7 Behm et al. discuss earlier effective activation energy determinations from other labs, noting that they were smaller, and that they are affected by the complexity of having many individual reactions and mass transport effects. Although activation barriers for electron + proton transfer oxidations and reductions involving oxygen-containing species have been found in model calculations to be small, $\sim0.1$ eV, at the reversible potentials,\textsuperscript{25} values for electron and proton transfer to and from carbon species have not been calculated and it is not known if they are so small, though it is difficult to think of reasons for their not being so. How they would compare with CH bond scission activation energies on the surface is unknown, though theory from other labs, as discussed above, suggests some of them may be $\sim0.5$ eV, which means that they might be capable of dominating the overall reaction activation energies. More complete theories and more complete double layer models should resolve this in the future.

**Conclusions**

A path to CO$_2$ has been identified where the calculated surface potentials are close to the calculated 0.004 V reversible potential for the 12 electron oxidation of ethanol. Many of the oxidation steps have potentials less than 0.004 V, meaning the oxidation reactions are spontaneous. The one exception being the 0.49 V potential for forming the OH(ads) from H$_2$O(l). Adsorbed hydroxyl radicals are required for oxidation of CO(ads) and CH(ads) intermediates. Using the total Gibbs energy loss for C-C bond dissociation on the platinum electrode surface, an effective reversible potential of 0.07 V for the 12 electron oxidation of ethanol is assigned, too close to 0.07 V to account for the observed overpotential, which leaves OH(ads) formation is the probable cause of the overpotential. The surface potentials show that acetyl, OCCH$_2$(ads), forms at small positive potentials and decomposes to CH$_2$(ads), CH$_3$(ads), and CO(ads), which poison the surface at these potentials. Agreement with conclusions of recent spectroscopic studies from the literature is excellent. It is shown how
the ideal catalyst will have all Gibbs energies for CH bond oxidations and CH bond dissociations equal at potentials close to 0.0 V and 0.0 eV, and with the constraints that ethanol and water reactants and the CO₂ product have adsorption bond strengths of zero, these values were determined. From them, it is evident that on an ideal catalyst most intermediates will adsorb more weakly and OH more strongly than on Pt(111). Understanding the measured activation energies remains an important problem for theory to accomplish. The question whether the RH(ads) dissociation reactions for which ∆Uₜₜₜ is most negative have activation energies low enough to compete with direct oxidation will be answered in future studies.

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