Ethanol Electro-oxidation on Palladium Revisited Using Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) and Density Functional Theory (DFT): Why Is It Difficult To Break the C−C Bond?

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ABSTRACT: Insights into the ethanol electro-oxidation reaction mechanism on palladium in alkaline media are presented combining polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and density functional theory (DFT) calculations. The synergy between PM-IRRAS and DFT calculations helps to explain why the C−C bond is not broken during ethanol electro-oxidation, and the reaction stops at acetate. Coupling chronoamperometry (CA) with in situ PM-IRRAS enables us to simultaneously identify ethanol electro-oxidation products on the catalyst surface and in the bulk solution. We show that, at lower potential, it is possible to break the C−C bond on Pd/C in alkaline media to form CO2. However, the selectivity is poor, because of competition with the formation of acetate and other side products, which gets worse at higher potentials. DFT computations complete the picture using the computational hydrogen electrode approach. The computations highlight the pivotal role of the CH3CO intermediate that can either undergo a C−C bond scission yielding CO and then CO2 or that can be oxidized toward CH3COO−. The latter is a dead end in the reaction scheme toward CO2 production, since it cannot be easily oxidized nor broken into C1 fragments. However, CH3CO is not the most favored intermediate formed from ethanol electro-oxidation on Pd, hence limiting the production of CO2.

KEYWORDS: ethanol electro-oxidation, palladium, spectroelectrochemistry, direct ethanol fuel cells, DFT, computational hydrogen electrode

1. INTRODUCTION

Fuel cells represent a promising technology for clean power generation, because they convert chemical energy (fuel) into electrical energy with high efficiency and little to no emission of pollutants.1–4 Direct ethanol fuel cells (DEFCs) have several advantages, compared to the most studied hydrogen and methanol fuel cells. First and foremost, ethanol is a nontoxic liquid, which reduces the investment of handling facilities because the current infrastructure for gasoline can be largely used.5,6 Second, ethanol can be conveniently produced from biomass; hence, it is carbon neutral, which mitigates increasing atmospheric CO2. Last but not least, if completely oxidized to CO2, ethanol has a higher energy density than methanol, since it can deliver 12 electrons per molecule, following the anodic reaction described in eq 1.5

\[
\text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- \rightarrow 2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^-
\]

\[E^\circ = +0.19 \text{V/RHE}\] (1)

In a DEFC, eq 1 is counterbalanced at the cathode by the oxygen reduction reaction, generating a theoretical cell voltage of 1.14 V. However, in practice ethanol is known to be partially oxidized to acetic acid (acetate in alkaline media), giving a maximum of 4 electrons, as shown in eq 2:

\[
\text{C}_2\text{H}_5\text{OH} + 5\text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} + 4\text{e}^-
\]

\[E^\circ = -0.20 \text{V/RHE}\] (2)
The almost-exclusive oxidation to acetic acid overshadows the attractiveness of DEFC considerably, as the energy density is divided by 3. The standard potential of acetic acid formation indicates that a reaction path including acetic acid leads to inevitable potential losses of ~0.4 V (the difference between ideal potential for CO₂ and acetic acid “production”).

The development of alkaline fuel cells has mainly been hampered by the lack of stable and efficient anion exchange membranes. However, this challenge has been well-tackled in recent years, allowing the development of alkaline fuel cells (AFCs), which are of particular technological interest, because of their simple designs and ability to operate at low temperatures (25–100 °C). Under alkaline conditions, the kinetics of both the cathodic oxygen reduction and the anodic ethanol oxidation is facilitated. Furthermore, the expensive Pt catalyst can be replaced by the lower-cost and more-active ethanol oxidation mechanism is complex and controversial, there is a general consensus on Pt-based catalysts as a starting point. Although the detailed understanding of ethanol electro-oxidation mechanism is complex and controversial, there is a general consensus on Pt-based catalysts under acidic conditions that the reaction exhibits the so-called “dual pathway mechanism” or “consecutive-parallel mechanism”. According to this dual path reaction scheme, two major pathways are in competition. In the C₂ pathway, the C−C bond does not break and ethanol is oxidized successively to acetaldehyde and then to acetic acid (acetate under alkaline conditions). In the C₁ pathway, the C−C bond is broken, thus generating C₁ fragments. These fragments are oxidized into CO and eventually CO₂. When shifting to alkaline conditions, very few studies provide detailed molecular information.

Christensen et al. have shown in several studies that the interfacial pH drops at higher potentials due to the OH⁻ consumption that is not completely counterbalanced by the OH⁻ diffusion from the bulk to the interfacial region. This phenomenon leads to a transition from alkaline to effectively acidic conditions. The transition potential varies with the diffusion rate of OH⁻, i.e., working temperature, flow rate, and so on. They report that, during the electro-oxidation reaction, ethanol is converted to acetate in alkaline pH while above the transition potential, i.e., under pseudo-acidic conditions, it yields acetic acid and trace amounts of CO₂ as a result of the slow C=C bond splitting. This is in agreement with the results from online mass spectrometry, evidencing CO₂ production over Pt and Pd in 0.01 M NaOH, where the formation of acetic acid is almost absent.

On Pd-based electrocatalysts, ethanol oxidation reactivity differs compared to Pt, which is illustrated most clearly under acidic conditions, where Pt yields mainly acetic acid and even some CO₂, while Pd is completely inactive. Under alkaline conditions, Pd is more active and it is generally proposed that ethanol is dehydrogenated into adsorbed acetyl (CH₃CO) (sometimes erroneously called ethoxy), which is further oxidized to acetate by hydroxide (OH⁻) species. This mechanism has received further credence using in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) measurements. Yang et al. reported that ethanol oxidation starts with the α-C−H bond scission, yielding adsorbed CH₃CO as a pivotal intermediate, which may be further oxidized to acetate or, given enough time, would fragment into C₂ adsorbed intermediates (they observed adsorbed CO). These observations can be rationalized by recalling that the oxidation of acetyl to acetate is an electrochemical step, and therefore favored by oxidative potentials, while the C−C bond cleavage is expected to be only weakly affected by the potential, assuming that this process is not coupled with an electrochemical step such as the C−OH bond formation.

To complement the experimental insights, modeling studies are also being reported. However, the complexity of the Pd/alkaline electrochemical interface not only challenges experiments but also the atomistic modeling of the underlying mechanism. The main ingredients are the electrolyte and its pH, both influencing the reactivity directly (state of the electrode surface) and indirectly (modifying the environment). The electrochemical potential and the inclusion of well-established equilibria, such as the reactivity of acetaldehyde (e.g., enol and aldol formation) or of CO, which can be hydrated to yield formic acid, adds to the complexity of the reaction network. It is currently impossible to consider all these aspects on a consistent level in one exhaustive study. Furthermore, the size of the “straightforward” reaction network for ethanol oxidation already includes 128 potential C₂ and 21 C₁ intermediates.

The influence of coadsorbed species and of explicit water molecules has intrigued several groups. In particular, Neurock and co-workers have modeled ethanol oxidation by O₂ under alkaline conditions by including the aqueous media explicitly and adsorbed hydroxyl on the Pd surface. They have shown that most of the C−H and O−H scissions of the ethanol oxidation network toward acetic acid/acetate have lower barriers when assisted by coadsorbed hydroxyl on Pd((111)), compared with the bare metal. According to their results, acetaldehyde is a first intermediate toward acetic acid. Then, two possibilities exist: (i) the geminal diol, which can be formed by hydration of the acetaldehyde in solution, leads straightforwardly to acetic acid, and (ii) acetaldehyde is either oxidized by the direct formation of a C−OH bond, or the α-C−H bond is broken, leading to acetyl CH₃CO. In a more recent study, Hu and co-workers revisited this mechanism in the electrochemical context, but without accounting for the electrochemical potential. Their conclusions are consistent with the ones of Neurock regarding the oxidation by oxygen using a more advanced description of the structure of the water solvent. It should be noted that, under electrochemical conditions, surface OH is also formed under acidic conditions, provided the electrochemical potential is sufficiently positive. As a consequence, these simulations can be applied under both alkaline and acidic conditions.

In order to complement these studies, one should include the effect of the electrochemical potential. The electrochemical potential can be included at various levels of sophistication. The most important effects are due to a change in thermodynamics when electrons and protons are exchanged. This effect can be easily obtained as a posteriori correction to ab initio energies (typically periodic DFT), as originally proposed by Norskov, known as the computational hydrogen electrode. This approach has been used successfully for MeOH oxidation on a range of metals and includes the thermodynamic driving force of the (H⁺, OH⁻) recombination into H₂O. Several groups have also proposed strategies to include the influence of the potential in the electronic structure.
Although more accurate, these approaches are also computationally more costly, since they require the inclusion of the electrolyte to mimic the capacitance of the interface adequately, either with a continuum model \(^{42}\) or a Poisson–Boltzmann theory \(^{40,43}\), or an explicit, but static description. \(^{44}\) These approaches have been used for the study of small reaction path networks, such as the electrooxidation of formic acid, \(^{45}\) in combination with continuum models for the solvent or methanol and CO oxidation at a Pt catalyst. \(^{46,47}\)

The objective of this work is to provide insights as to why the C–C bond is not broken during ethanol electro-oxidation and to propose a detailed mechanistic schematic, which can be applied in understanding experimental observations. Ethanol oxidation potentials were determined by cyclic voltammetry (CV). Chronoamperometry (CA), coupled with in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), was used to identify the oxidation products both on the catalyst surface and in the bulk solution. Density functional theory (DFT) computations are exploited to explore all possible intermediates including the electrochemical potential using the computational hydrogen electrode at an alkaline pH of 14. This setup allows us to include the thermodynamic effect of the involvement of hydroxide ions in the reaction mechanism without explicitly coadsorbing OH on the catalyst surface. The potential energy profiles of the reactions were used to determine the most likely reaction pathway toward acetate on two different facets: Pd(111) and Pd(100). On the most active facet, a complete study of the C\(_2\) and C\(_1\) intermediates was done on the full range of the 12 electron oxidation (from ethanol to CO\(_2\)) to select the key intermediates for the C–C bond breaking. Besides, for the first time, to the best of our knowledge, we assess the C–C bond breaking from these key intermediates in the context of electro-oxidation. The energy barriers provide general strategies for improving the catalyst toward C–C bond scission.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Synthesis and Characterization of Palladium Nanoparticles. The Pd/C nanoparticles (NPs) were prepared using a polyol method reported in the literature. \(^{38,40}\) In the synthesis, 0.25 g of anhydrous palladium chloride (Fisher) was dissolved in 50 mL of ethylene glycol (EG) (Fisher), and the pH was adjusted to 8 by adding 0.06 M NaOH in EG. The solution was then refluxed at 160 °C for 2 h to form nanoparticles. To the resulting colloids, the appropriate amount of carbon black (Vulcan XC-72 Cabot Corp.) was added to obtain supported catalysts of 20 wt % loading. The mixture was sonicated for 48 h to achieve high dispersion of nanoparticles in carbon. The supported catalyst was thoroughly washed with deionized water (18 Ω cm) to remove EG and salt ions through vacuum filtration and air-dried at 100 °C for 4 h.

The details of physicochemical characterization techniques have been reported in the previous publication. \(^{49}\) In summary, the following techniques were used:

- With regard to high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), a microscope (FEI, Model Titan3 80-300) equipped with a CEOS aberration corrector for the probe forming lens and a monochromatic field-emission gun was used.
- X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source (\(\lambda = 1.54183 \text{ Å}, 40 \text{ kV}, 44 \text{ mA}\)).
- X-ray photoelectron spectroscopy (XPS) measurements were performed in a KRATOS Axis Ultra DLD with a Hybrid lens mode at 140 W and pass energy of 20 eV, using monochromatic Al Kα radiation.

2.2. Spectroelectrochemical Measurements. All experiments were conducted at room temperature in a customized \textit{in situ} cell that is made of Teflon and equipped with a hemicylinder CaF\(_2\) window (RJ Spectroscopy Co.). A glassy carbon (GC) electrode with a geometric surface area of 0.1962 cm\(^2\) was used as the current collector for carbon-supported Pd NPs. All potentials were measured with respect to mercury–mercury oxide (Hg/HgO) (Koslow Scientific) but reported versus the reversible hydrogen electrode (E(EH/E) = E(H/H) + 0.855 vs RHE), unless otherwise stated. A Pt wire served as a counter electrode. A 1 M solution of KOH + C\(_2\)H\(_5\)OH was used as the electrolyte and was continuously purged with nitrogen gas. The catalyst ink was dispersed by dispersing 6 mg of Pd/C powder in 1 mL of deionized water, 200 μL of isopropanol, and 100 μL of Nafion solution. The mixture was sonicated for 10 min to form a homogeneous mixture. The ink solution (10 μL) was deposited onto the GC-electrode surface and air-dried at room temperature for 15 min and used as the working electrode.

The PM-IRRAS measurements were performed using a Bruker Tensor 37 spectrometer equipped with an external Polarization Modulation Accessory (PMA 50 XL), nitrogen-cooled mercury cadmium telluride detector (LN-MCT Narrow PMA50, Infrared Associates, Inc., Stuart, FL), photoelastic modulator (PEM-100 controller with II/ZSSO ZnSe, 50 kHz optical head, Hinds Instruments, Hillsboro, OR), and a demodulator (Synchronous Sampling Demodulator (SSD), GWC Instruments, Madison, WI). The electrode potential was controlled by a BioLogic VSP potentiostat equipped with the EC-Lab software (BioLogic Science Instruments SAS, Claix, France). The cell and PMA-50 XL chamber were thoroughly purged with nitrogen gas to remove background atmospheric CO\(_2\) and water vapor. Although the electrolyte was degassed with N\(_2\) before being introduced into the cell, it was degassed for 30 min once assembled in the optical path, and then the electrode was pushed against the CaF\(_2\) window without stopping the gas flow. The thin cavity obtained was wedged in form but the average thickness was estimated \(^{50}\) to be 10 μm.

Background spectra were collected to track the level of CO\(_2\) in the system. Typically, after 2 h, the reference spectrum was acquired at the open circuit potential (OCP), followed by sample spectra at various ethanol oxidation potentials selected from the cyclic voltammetry (CV) profile. Sample spectra were acquired under chronoamperometry (CA) conditions at 5 min increments, i.e., while holding the potential constant for up to 30 min before stepping to another potential.

The signal was acquired by the co-addition of 256 interferograms (128 forward and 128 backward scans) collected with a resolution of 8 cm\(^{-1}\). With PM-IRRAS, we are able to simultaneously measure the average reflectivity \([R_{\text{ave}} = (R_\parallel + R_\perp)/2]\) and the difference reflectivity \([R_{\Delta} = (R_\parallel - R_\perp)]\) channel with a single detector, because of its double-modulation scheme. \(^{51}\) The parameters \(R_\parallel\) and \(R_\perp\) are the reflectivities for p- and s-polarized light, respectively. Although this property has many advantages, it presents a challenge in processing and interpretation of the data obtained. However, we have recently developed an approach to overcome this challenge which significantly simplifies PM-IRRAS data interpretation. The
Methfessel Brillouin zone integration, together with a second-order species, respectively.

3) unit cell of The Pd surfaces were modeled by a periodic slab with a wave basis set with an energy cutoff employed to describe the core gradient approximation of Perdew, Burke, and Erzenhorf 3 and 4, which corresponds to the surface and bulk-solution g gives more insights of the substrate absorption bands with a very few scans (16–256). The approach also allows direct interpretation of the spectra, and gives more insights of the substrate–film system or the reaction mechanism. The signal is reported as absorbance (A) using eqs. 3 and 4, which corresponds to the surface and bulk-solution species, respectively.

$$A = \log \left( \frac{\text{sample}(R_{ab})}{\text{references}(R_{ab})} \right) \text{ vs cm}^{-1}$$ (3)

$$A = \log \left( \frac{\text{sample}(R_{av})}{\text{references}(R_{av})} \right) \text{ vs cm}^{-1}$$ (4)

With this definition, the positive and negative bands in the spectra correspond to species produced or consumed at the sampling potential, respectively, with respect to the reference spectrum.

2.3. Computational Methods. Density functional theory (DFT) calculations were performed with the Vienna Ab-initio Simulation Package (VASP version 5.3.3).35,52 The generalized gradient approximation of Perdew, Burke, and Erzenhof (PBE)3,5 was used to compute the exchange-correlation energy. The projected augmented wave (PAW) method56,57 was employed to describe the core–electron interaction. A plane-wave basis set with an energy cutoff was set to 400 eV was used. The Pd surfaces were modeled by a periodic slab with a p(3 × 3) unit cell of five Pd layers and a vacuum regions of 10 Å. A 7 × 7 × 1 Monkhorst–Pack k-points mesh was employed for the Brillouin zone integration, together with a second-order Methfessel–Pack smearing method38 with a width of 0.2 eV. Slabs were cut from the optimized Pd bulk unit cell with a lattice constant of a = 3.94 Å, which overestimates the experimental value of 3.89 Å by 1%. In all geometry optimizations, only the top-two Pd monolayers were allowed to relax while the bottom three monolayers were kept fixed. All optimizations were carried out to forces below 0.02 eV/Å.

All energies are referenced to the bare Pd slab, ethanol, water and hydrogen in the gas phase. The latter two serve to introduce oxygen atoms and to account for the coupled proton–electron transfers, respectively. In particular, the reaction energies of electrochemical steps (i.e., steps where the number of protons in the system is changing) are computed according to the computational hydrogen electrode, e.g., the reaction

$$\text{CH}_3\text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{H}^+ + e^-$$ (5)
is computed as

$$E_{\text{red}} = E_{(\text{CH}_3\text{COOH})} - [E_{(\text{CH}_3\text{CO})} + E_{(\text{H}_2\text{O})} + 0.5E_{(\text{H}_2)} + qU]$$ (6)

where q is the elementary charge and U the potential. We have assumed U to be with respect to the pH-insensitive RHE and a pH of 0. Note that at pH 14, we write the same expression for the reaction energy, but formulate the reaction as

$$\text{CH}_3\text{CO} + \text{OH}^- \rightarrow \text{CH}_3\text{COOH} + e^-$$ (7)

Similarly, we can write

$$\text{CH}_3\text{CHO} + \text{OH}^- \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O} + e^-$$ (8)

under alkaline conditions and compute the energy of reaction (E_{\text{red}}) to be

$$E_{\text{red}} = E_{(\text{CH}_3\text{CO})} - [E_{(\text{CH}_3\text{CHO})} + 0.5E_{(\text{H}_2)} + qU]$$ (9)

The transition states (TS) have been located as follows: the state with the broken C–C bond was constructed in analogy to the adsorption mode of the individual fragments. This coadsorbed state was optimized in order to ensure that no significant lateral interactions were introduced. Then, a rough nudged-elastic band (NEB)59 computation with 8 images between the initial and final state was performed, seeded by interpolations between the two states obtained by the Opt’n Path code,60 which uses a combination of internal and Cartesian coordinates. After ~50 cycles of NEB, an improved guess for the transition state was obtained, which was refined by the dimer method61 and verified to be a first-order saddle point by a frequency analysis.

Infrared spectra of surface species were modeled following the same procedure, the intensities being evaluated using density functional perturbation theory.62 Infrared spectra of solution species were computed using the same DFT functional (PBE), combined with a continuum model for the water solvent (PCM)35 with a def2-TZVP basis set using the Gaussian09 version D.01 program.64

Figure 1. (a) CV profile for Pd/C nanoparticles in 1 M (KOH + EtOH) and 1 M (KOH + acetic) at v = 5 mV s⁻¹; (b) CA profile of Pd/C nanoparticles in 1 M (KOH + EtOH) at various potentials, as indicated by the double arrows. The vertical lines and double arrows (colored blue) shows the potentials whose PM-IRRAS spectra are discussed in the text.
3. RESULTS AND DISCUSSION

3.1. Characterization and Electrochemical Performance of Pd/C Nanoparticles. The physical, structural, and chemical characterizations of Pd/C are shown in Figure S1 in the Supporting Information; other details have been published elsewhere.\(^49\) In summary, the supported particle size was determined to be, on average, 4 ± 2 nm. The XRD pattern showed that the nanoparticles retained the face-centered-cubic (fcc) structure of bulk Pd with peaks at 40°, 46°, and 68° 2θ, corresponding to (111), (200), and (220) reflections, respectively.

Cyclic voltammetry (CV) was used to determine ethanol oxidation current/potential profiles for Pd/C nanoparticles. The PM-IRRAS spectra for ethanol electro-oxidation products on Pd/C nanoparticles in 1 M (KOH + EtOH) at (a, b) 0.21 V, (c, d) 0.56 V, (e, f) 0.72, and (g, h) 0.96 V vs RHE. The left panels show oxidation species on the surface and the right panels show oxidation species in the thin cavity/bulk solution. The spectra were processed using eq 3 and the reference spectrum was collected at the open-circuit potential (see the Supporting Information for details). At each potential (row), the y-scale was made the same for easy/direct comparison between surface and bulk species.
under alkaline conditions. Figure 1a shows a representative CV of Pd/C nanoparticles in 1 M (KOH + CH₃CH₂OH) and 1 M (KOH + CH₃COOH) solutions at 5 mV s⁻¹. The slow scanning rate helps to capture the oxidation profile with current densities close to steady-state conditions. For an ethanol profile, during the anodic scan, a positive current starts at 0.39 V and increases gradually to a maximum current density at 0.77 V, and then decreases to zero at 1.00 V. During the cathodic scan, a positive current was obtained starting at 0.76 V, which increases rapidly to a maximum at 0.66 V, and then decreases to zero at 0.39 V. The CV profile for acetic acid did not show any oxidation current densities, which is proof that the resulting acetate (KOH + CH₃COOH) is the dead end product during the ethanol electro-oxidation reaction.

This ethanol electro-oxidation profile (Figure 1a) is typical for alcohols and is generally interpreted as a signature of species blocking the electrocatalyst surface at higher potential that can be removed while scanning back to lower potentials, hence allowing the oxidation of fresh ethanol molecules. To gain insights into the processes that are occurring at different potentials of the CV profile, chronoamperometry coupled with PM-IRRAS were used and the resulting data are discussed in the following section.

### 3.2. Identification of Ethanol Electro-oxidation Products on the Pd/C Surface and in the Bulk Electrolyte Solution

Chronoamperometry measurements were coupled with in situ PM-IRRAS to identify ethanol electro-oxidation products at different potentials. Figure 1b shows the resulting current–time CA response, in which the potential was stepped up from 0.21 V/RHE to 0.96 V/RHE, while collecting spectra at each potential in increments of 5 min, up to 30 min. The spectra collected at 0.21, 0.56, 0.72, and 0.96 V/RHE are shown in Figures 2a–h. As presented above and in the Supporting Information, PM-IRRAS, unlike the regular IRRAS technique, allows us to distinguish between the oxidation species on/near the electrode surface (using the difference absorption intensities of p- and s-polarized reflection) and the oxidation species in the bulk/liquid-phase electrolyte within the thin cavity between the CaF₂ window and the electrode (using the average absorption intensities of p- and s-polarized reflection). Herein, the spectra for the species on the electrode surface and spectra of the sum species in the thin cavity will be referred to as “surface” and “bulk solution” species, respectively.

Prior to the measurement of ethanol electro-oxidation species spectra, it is important to ensure that there is no atmospheric CO₂ and water vapor in the optical path, which would not only decrease the infrared (IR) intensity but also would contribute to observed spectra features. The presence of CO₂ is especially critical, because it is one of the anticipated ethanol oxidation products. This objective was accomplished by purging the electrolyte and the cell chamber (PMA 50) with nitrogen gas and the level of CO₂ in the system was tracked by collecting a series of background PM-IRRAS spectra at open circuit potential (i.e., no applied potential). Figure S7 in the Supporting Information shows the surface background and bulk species spectra collected at various time intervals. The first spectrum (Figure S7, curve (a)) was collected at the beginning of the experiment (i.e., 2.5 h before actual measurements were started). Two other spectra were collected at 30 min (Figure S7, curve (b)) and at 3 min (Figure S7, curve (c)) before the actual measurements were done. In summary, it was determined that, after 2.5 h, there was no significant background contribution to interfere with any spectral features, as confirmed by the straight line of curve (c) in Figure S7. Now, we shift our attention to the spectra features obtained at the various potentials, as shown in Figure 2. The potentials reported were selected from the different regions of the CV profile (Figure 1a) and are meant to shed more insights of the reaction dynamics and/or intermediates/products at those regions.

Figure 2a and 2b shows the PM-IRRAS spectra at 0.21 V/RHE where there is no ethanol electro-oxidation according to CV and CA (Figure 1). At this potential, we see a negative peak centered at ∼2908 cm⁻¹, which is due to breaking of the C–H bond. There are also two positive peaks centered on 2819 and 3668 cm⁻¹, which corresponds to C–H and H₂O vibrations, respectively. These observations tell us that there is some form of reorganization of the electrolyte molecules on the electrode surface. On the other hand, we do not see any significant structural changes features in bulk solution, as shown by the straight line in Figure 2b. This is expected at this low potential.

Figures 2c and 2d show the surface and bulk solution species at 0.56 V/RHE, which is close to the onset potential for ethanol electro-oxidation. The surface species spectra look very noisy, compared with the bulk solution spectra. This phenomenon can be attributed to the dynamic activities that occur on the electrode surface at this potential. Of top interest at this potential is the evidence of the C–C bond cleavage to form CO₂ due to the positive peak at 2353 cm⁻¹. With PM-IRRAS, we were even able to distinguish that the produced CO₂ quickly desorbs/diffuses into the bulk solution, as shown by the intensity of the peak. The conversion of CO₂ into carbonate was not evident (see Figure S2 in the Supporting Information) in this work, probably due to the changing pH conditions within the thin cavity from alkaline conditions to neutral/acidic conditions. One can notice that, while the amount of CO₂ increases clearly with time at lower potential (0.56 V), its accumulation is hampered or overshadowed by other species at higher potential. Although the formation of CO during EOR on Pd in alkaline has been reported, we do not have evidence to

<table>
<thead>
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<th>species</th>
<th>Wavelength (cm⁻¹)</th>
<th>splitting (cm⁻¹)</th>
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<td>1423</td>
<td>1560</td>
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<td>1400</td>
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<tr>
<td>CH₃COO, 2H₂O</td>
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<td>1402</td>
</tr>
<tr>
<td>CH₃COO, 3H₂O</td>
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</tr>
<tr>
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<td>1360</td>
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Table 1. Normal Modes for Acetate in the 1200–1600 cm⁻¹ Region, (i) As Obtained Experimentally (See Figure S3), (ii) As Computed as a Function of the Number of Water Molecules That Solvate the COO⁺ Moiety in Solution, and (iii) As Computed for CH₃COO Adsorbed on a Pd(100) Slab
support that argument in our spectra, even after sub tractively normalized interfacial Fourier transform infrared (SNIFTIR) treatment of our data, as proposed in ref 21. Our data compares well with other similar work in the literature where CO was not observed. Therefore, the formation of CO during C–C bond cleavage may be regarded to be a transient process, because it is directly converted to the observed CO₂.

The presence of positive peaks at 1560 cm⁻¹ (strong), 1423 cm⁻¹ (medium), and 1350 cm⁻¹ (weak) on the surface and bulk solution spectra in Figure 2c−h corresponds to the asymmetric, symmetric, and C–H bending vibrations from the acetate (CH₃COO⁻) produced during ethanol electro-oxidation, in agreement with other literature reports. These peak assignments were confirmed with transmission infrared spectroscopy, as shown in Figure S2 and the DFT simulations as reported in Table 1. The simulated spectra in solution (continuum model) show the same three peaks (1558 cm⁻¹, 1410 cm⁻¹, 1334 cm⁻¹). The strongest peak is also the one at 1558 cm⁻¹ and corresponds to the asymmetric COO⁻ vibrations. The corresponding symmetric mode vibrates at 1334 cm⁻¹ and has the second highest intensity. Finally, the peak at ~1410 cm⁻¹ corresponds to bending modes of the CH₂ group and features only a weak intensity. The relative positioning of the weak C–H bending and strong COO⁻ symmetric stretch are inverted in the DFT computations compared to experiment. This has already been reported in the literature. Depending on the functional, the C–H bending and symmetric COO stretching frequencies are more or less mixed, leading to intensity redistributions between the C–H and COO modes, suggesting that anharmonicity should be taken into account. Because of the very high computational cost of such a treatment, this is, however, beyond the scope of this paper. The COO⁻ symmetric stretch is red-shifted in our computations by ~100 cm⁻¹.

The inclusion of explicit water (see Table 1) mainly affects the COO⁻ stretch vibrations, with the asymmetric and symmetric mode being red- and blue-shifted by 30 and 20 cm⁻¹, respectively. This improves the mode splitting from 224 cm⁻¹ to 171 cm⁻¹, compared to the experimental value (137 cm⁻¹). From Table 1, it is noticeable that, in the IR spectrum of CH₃COOH adsorbed on a Pd(100), the asymmetric vibration is also red-shifted by 80 cm⁻¹, compared to the one of CH₃COOH using a continuum model for the water solvent. In addition, the two other peaks are much weaker than in solution. Thus, the comparison of the DFT simulations and the PM-IRRAS spectra shows that the “surface” species signal obtained experimentally corresponds mainly to solvated species in the interfacial water zone.

There is a remarkable difference between surface species and bulk solution species in the regions of 1620–171 cm⁻¹ and 3648 cm⁻¹, which also highlights the utility of the PM-IRRAS technique. It is evident that the species absorbing at 1726 cm⁻¹ is mainly available in the bulk solution but not on/or near the electrode surface. This peak corresponds to C=O stretching vibrations of an aldehyde/ketone or acetic acid. Our DFT simulations for acetaldehyde show a strong peak at 1720 cm⁻¹ (C=O) but also two weak peaks between 1300 and 1400 cm⁻¹ (C–H bending), overlapping with the weaker peaks of acetate and one strong peak at 2812 cm⁻¹ (C–H stretch), overlapping also with a broad band centered at ~2600 cm⁻¹. The origin of the broad peak at 2600 cm⁻¹ would be due to the accumulation of a combination of various intermediates (ethoxy, acetaldehyde and its hydrate form, and acetic acid) in the thin cavity, as shown in Figure S3 in the Supporting Information. Figure S3a shows the simulated spectra for ethoxy (CH₂CH₂O), acetaldehyde (CH₃CHO), hydrated acetaldehyde (CH₃CHOOH), and acetic acid (CH₃COOH), which confirms that ethoxy and hydrated acetaldehyde have bands near 2600 cm⁻¹. Although the simulated spectrum for acetic acid (Figure S3a in the Supporting Information) does not show any peak between 2400 cm⁻¹ and 2700 cm⁻¹, the experimental spectrum (Figure S3b) shows that acetic acid has three overlapping peaks within the region. Therefore, the potential candidates for the broad peak at 2400–2700 cm⁻¹ would be ascribed to a combination of ethoxy, geminal-diol, and acetic acid, as a result of the changing pH during the electro-oxidation. Further studies are underway to confirm the experimental peak centered on 2600 cm⁻¹. The absence of the peak at 1726 cm⁻¹ on the surface spectra is probably due to the low concentration of acetaldehyde and/or its interaction with the electrode surface. The negative peak at 3648 cm⁻¹ on the surface species spectra is the evidence for the consumption of water molecules at the electrode surface. Note that, at higher potential (i.e., 0.96 V), where the catalyst surface is deactivated, the product accumulation decreases with time but there is no evidence for the formation of CO₂. This observation proves that acetate is indeed the dead end for EOR in agreement with the acetate CV in Figure 1a. Therefore, cleavage of the C–C bond is only possible at lower potentials.

To summarize, the PM-IRRAS spectra show that, at lower potential, it is possible to break the C–C bond of ethanol on Pd/C in alkaline media to form CO₂. However, the selectivity is poor, because of competition toward the formation of acetate, which gets worse at higher potentials. In addition, traces of acetaldehyde are found in the bulk solution. Based on these experimental insights, we now explore the most likely intermediates involved in the reaction path using DFT computations, as presented in the next sections.

3.3. Reaction Mechanism. The reaction network involved in ethanol electro-oxidation is quite complex, as presented above, even after simplifying it by considering only proton-coupled electron transfers as electrochemical steps. There are 12 electrons to be recovered through 9 proton abstractions and 3 OH additions. Our simulations do not include explicitly the influence of the water-based electrolyte on the intermediates structures. However, the main determining factor is the role of OH⁻ as a proton acceptor on the thermochemistry, and this is included in the computational hydrogen electrode approach.

Furthermore, the reaction only proceeds to completion if the C–C bond can be broken. Hence, we must at least consider the following elementary reaction steps, with specific examples given for illustration in eqs 10−13:

C–H scission:

\[
\text{CH}_3\text{CH}_2\text{OH}^\bullet + \text{OH}^- \rightarrow \text{CH}_3\text{CHOH}^\bullet + \text{H}_2\text{O} + e^- 
\]

(10)

O–H scission:

\[
\text{CH}_3\text{CH}_2\text{OH}^\bullet + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{O}^\bullet + \text{H}_2\text{O} + e^- 
\]

(11)

C–OH formation:

\[
\text{CH}_3\text{CHOH}^\bullet + \text{OH}^- \rightarrow \text{CH}_3\text{CH(OH)}_2^\bullet + e^- 
\]

(12)
 acetate formation. Then, in order to obtain a relative energies and the most likely reaction pathway until electro-oxidation on Pd(111). The structures are consistent of the most important intermediates involved in ethanol cleavage of the C bond is di 

\[ \text{CH}_3\text{CH}_2\text{OH@Pd} + \text{Pd} \rightarrow \text{CH}_4@\text{Pd} + \text{CH}_2\text{OH@Pd} \] (13)

To break up the complexity into smaller manageable parts, we proceed as follows: PM-IRRAS data demonstrates that the electro-oxidation of ethanol over Pd leads to identifiable acetate and traces of CO$_2$. Therefore, for simplicity, we start by studying the intermediates that lead to acetate on the dominant Pd(111) and the more reactive and still sufficiently abundant Pd(100) surface. A brief description of the geometric features in the Supporting Information; we discuss here their relative energies and the most likely reaction pathway until acetate formation. Then, in order to obtain a “complete” picture, we have searched the most stable C$_1$ and C$_2$ intermediates at each oxidation state until CO$_2$ is formed. Based on this overview, we shed more light on the reason why the reaction stops at the acetate level and why the selective cleavage of the C–C bond is difficult.

3.3.1. From Ethanol to Acetate. 3.3.1.1. Pd(111). Figure S8 in the Supporting Information shows the adsorption structures of the most important intermediates involved in ethanol electro-oxidation on Pd(111). The structures are consistent with the literature and, thus, we focus here on the relative energies of the intermediates at a given oxidation state and their involvement in the oxidation path toward acetic acid. Figure 3a shows the reaction energy profile for ethanol oxidation on Pd(111) at a potential of 0.26 V, based on the computational hydrogen electrode (see the Computational Methods section). This potential corresponds to the thermodynamic equilibrium potential for the oxidation of ethanol to CO$_2$. In reality, overpotentials are necessarily observed but with an onset potential of ~0.4 V, Pd is rather promising. Each column in the reaction coordinate corresponds to intermediates at a given oxidation state. Intermediates below and above the dotted line are due to exothermic and endothermic processes, respectively.

The ethoxy (CH$_3$CH$_2$O) species is higher in energy than the \(\alpha\)-dehydrogenated intermediate CH$_3$CHOH in agreement with previous reports. However, Hibbitts and Neurock have modeled the oxidation of EtOH by O$_2$ in which the catalyst surface was precovered with O and OH species and have shown that the formation of ethoxy has the lowest activation barrier under these conditions, proving that it is an important intermediate. The CH$_3$CH$_2$OH is intermediate in energy. A second proton-coupled electron transfer leads to an oxidation state, which is particularly challenging to describe realistically. Three adsorbed intermediates are connected through well-known solution equilibria: acetaldehyde, its hydrate (the geminal diol), and the enol. A fourth intermediate considered (CH$_3$COH) is strongly bound to the metal surface and can only indirectly participate in the equilibrium.

On the surface, acetaldehyde and its enol are almost iso-energetic. Since the CH$_3$C$_x$ intermediates at the following oxidation states are significantly higher in energy than the CH$_3$C$_x$ intermediates, we consider the enol to be a dead end, i.e., it just participates in the equilibria if formed. In fact, instead, it is the hydrate that is the dominant intermediate: it is the lowest energy intermediate, is connected to the previous lowest energy intermediate, and can form either in solution through acetaldehyde or on the surface by a surface OH-assisted process.

The oxidation of the hydrate does not lead to the lowest energy intermediate in the +3 oxidation state. The lowest energy intermediate in the +3 oxidation state is the acetyl (CH$_3$CO) and it is only accessible from higher-energy intermediates of the previous oxidation state +2. Oxidation of CH$_3$CO or CH$_3$C(OH)$_2$ invariably yields acetic acid, through a OH addition and a dehydrogenation, respectively. Acetic acid is, by far, the lowest energy intermediate on the surface in the +4 oxidation state (the second lowest fragment is CH$_3$CO at 0.86 eV higher in energy), and can desorb easily into solution. Then, in alkaline solution, the formation of CH$_3$COO$^-$ is straightforward. This reaction network satisfactorily explains the observed formation of acetic acid (or acetate at high pH values). After a quick comparison of the acetic acid formation on the Pd(100) surface, the following sections investigate the prospects to split the C–C bond in ethanol.

3.3.1.2. Pd(100). Figure S9 in the Supporting Information shows the adsorption structures of the most important intermediates involved in the ethanol electro-oxidation on Pd(100). The geometry of the adsorbates is very similar to that on Pd(111) and is therefore not discussed any further.

Figure 3b shows the reaction energy profile for the ethanol electro-oxidation on the Pd(100) surface at a potential of 0.26 V. Here, we highlight the differences between the Pd(100) surface and the Pd(111) surface. One difference is that the reaction energies are shifted to lower energies by ca. 0.1–0.2
eV, meaning that the (100) surface is more reactive than the (111) surface, which is consistent with previous reports.\textsuperscript{73--75} The second difference is that the relative stability of acetaldehyde (CH\textsubscript{3}CHO) and 1-hydroxyethylidene (CH\textsubscript{3}COH) is reversed: on the 100 surface, CH\textsubscript{3}CHO is 0.02 eV more stable than CH\textsubscript{3}COH. However, it is doubtful that these very small energy differences are representative of the situation under electrocatalytic conditions where the solvent and the potential may easily change the relative energies by more than this difference. In any case, the gem-diol is the lowest intermediate at this oxidation state for both surfaces. Therefore, we conclude that investigating the Pd(100) or Pd(111) surface is qualitatively the same. Nevertheless, since the (100) surface is more active for bond formation and splitting reactions,\textsuperscript{75} and these reactions are key and highly activated on this surface (vide infra), only results for Pd(100) in the remainder of this article. Based on our DFT results, we can also predict the overpotential to produce CH\textsubscript{3}COOH from EtOH on Pd catalysts and this overpotential is in agreement with the onset potential observed experimentally. The lowest energy path is represented at various potentials in Figure 4. It starts with the generation of CH\textsubscript{3}CHOH, which is an endothermic step at 0.26 V. It yields the gem-diol CH\textsubscript{3}CH(OH)\textsubscript{2} at the +3 degree of oxidation that is further dehydrogenated into CH\textsubscript{3}C(OH)\textsubscript{2}, which is a step that is also endothermic at this potential. The last step is strongly exothermic and gives CH\textsubscript{3}COOH. At 0.45 V, all the steps along the most stable path to CH\textsubscript{3}COO\textsuperscript{−} are predicted to be endothermic. At that potential, even the generation of acetaldehyde starts to be exothermic. Those potentials are in line with our experimental results (CV in Figure 1 and the PM-IRRAS spectra in Figure 2), where the reaction starts at \sim 0.45 V and where traces of acetaldehyde are identified at 0.65 V/RHE and are more intense at 0.72 V.

### 3.3.2. Intermediates beyond Acetate and Breaking the C−C Bond

The chemical viability of DEFCs relies on two related aspects. First, the fuel must be completely oxidized in order to obtain a realistically useful energy and current density. In other words, catalysts that oxidize ethanol to acetate (acetic acid in acidic media) are not useful in practice, as they would liberate only 4 out of 12 possible electrons. Second, the kinetics must be efficient at a reasonably low overpotential. According to the Butler−Volmer equation, a proton-coupled electron transfer is directly accelerated by the overpotential. Furthermore, the barriers for formal dehydrogenation reactions are fairly small on Pd (in the order of 0.7 eV). While the C−OH formation could be somewhat more activated, it can equally be considered an electrochemical step and, therefore, its barrier is likely to be heavily lowered by the overpotential and the presence of surface hydroxyls. If the C−C dissociation were coupled with the formation of the C−OH bond, in a concerted mechanism with the hydroxide anion attacking from the solvent, this dissociation would also be strongly dependent on the electrochemical potential. However, modeling such a process would required a full description of the solvent and a complete inclusion of the electrochemical potential, which is beyond the scope of this study. The direct C−C bond splitting, in contrast, is a chemical step and thus hardly affected by the electrochemical potential as extrapolated from our findings for the electrocarboxylation of ethene.\textsuperscript{76} Hence, investigating the feasibility of C−C bond splitting is key in order to understand

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**Figure 4.** Reaction energy profiles for ethanol electro-oxidation on the Pd(100) surface, showing the effect of the electrochemical potential (0.26, 0.56, and 0.72 V vs RHE) for the most likely C\textsubscript{2} reaction path.

**Figure 5.** Global reaction energy profile of the most stable intermediates during ethanol electro-oxidation process on Pd(100) at 0.26 V/RHE. To guide the eyes, a solid line has been added when the intermediates are connected from one oxidation state to the next and a dotted line has been added when the intermediates are not connected. Legend: curve a (black square), representing the most stable C\textsubscript{2} species at each oxidation state whose intermediates are indicated at the top; curve b (black cross), representing the C\textsubscript{1} fragments generated from the most stable C\textsubscript{2}; curve c (red cross), representing the most stable C\textsubscript{1} fragments; and curve d (red square), representing the parent C\textsubscript{2} species of the most stable C\textsubscript{1} fragments, which are shown at the bottom.
both incomplete oxidation and sluggish kinetics, and this can be done without the inclusion of the electrochemical potential.

Let us start by addressing the first question: which is the most likely possible path that would lead from ethanol to CO$_2$ instead of acetic acid, based on thermodynamics? Figure 5 summarizes our effort to identify the lowest-energy intermediates at each of the 12 oxidation states, accounting for C−H, O−H, and C−C bond activations as well as C−OH bond formation. The intermediates below the zero horizontal dashed line in Figure 5 are due to an exothermic process, while those above the line are due to an endothermic process at the potential of 0.26 V, i.e., the minimum potential for which ethanol oxidation is energetically feasible, in terms of free energy. At each oxidation state, we indicate the most stable C$_2$ intermediate and the energy of its C−C bond broken C$_1$ analogue. Of course, at any given oxidation step, the lowest intermediate before the C−C bond breaking does not need to yield the lowest two C$_2$ fragments at that oxidation step, which is indicated by the presence of red symbols on Figure 5. Note that we did not consider additional “pure” chemical steps, which further complicate the reaction network, e.g., by introducing formic acid (HCOOH) at the same oxidation state as CO. Similarly, the lowest energy intermediate at each oxidation state “n” is not necessarily directly related to the intermediate of oxidation state “n + 1” (e.g., CH$_3$CH$_2$(OH)$_2$ is the most stable intermediate at oxidation state +2, but at +3, CH$_3$CO is the most stable intermediate), which is indicated by broken black lines instead of the full lines.

As mentioned in the Introduction, the ethanol electro-oxidation mechanism is best presented in a “dual path mechanism scheme”. The C$_2$ path does not involve the breaking of the C−C bond, whereas, in the C$_1$, the C−C bond yields C$_1$ fragments. In agreement with previous reports, we found a reasonably well-connected C$_2$ pathway up to CH$_3$COO (+5 oxidation state). However, from +5 to +6, the lowest-energy intermediate changes dramatically from CH$_3$COO to CHCOOH. Furthermore, the process is endothermic by 0.6 eV at the thermodynamic equilibrium potential for the overall reaction. This implies that a potential of at least 0.6 V would be necessary to drive the oxidation beyond acetate (acetic acid). The fact that these intermediates are not connected would mean a further increase of the overpotential. This is in agreement with the CV experiments, demonstrating that acetic acid is inert for further oxidation, i.e., no current transfer was observed in the CVs with 1 M (KOH + CH$_3$COOH) solution, as shown in Figure 1a. To conclude, Figure 5 indicates that it would be ideal to split the C−C bond before reaching acetate (acetic acid in acid media), which is the dead end of the reaction with the current catalysts. On the other hand, on thermodynamic grounds, the C−C bond splitting is “constant” beneficial from the +6 oxidation state onward and, generally, passing to the C$_1$ pathway is more likely when the C$_2$ fragment can be split through a decarbonylation, generating a highly stable CO moiety.

Turning to the second limitation, i.e., the sluggish kinetics, we investigate the reasons for which the C−C bond is not split before reaching acetic acid. Both for ethanol and for the first oxidative intermediates, the C−C bond breaking is highly unlikely as the thermodynamics are fairly unfavorable. However, at the +2 and +3 oxidation states, the breaking of the C−C bond could occur based on thermodynamic grounds. So why is it barely observed experimentally? To answer this question, we have identified transition states for breaking the C−C bond in the key intermediates at the +2 oxidation state (Figure 6a) and the +3 oxidation state (Figure 6b).

In general the activation energies are quite high (∼1.3 eV), even on the Pd(100) surface, which is more active than the Pd(111) surface. There are two barriers that differ significantly. First is the highest activation barrier for breaking the C−C of the hydrate, CH$_3$CH(OH)$_2$ (+2 oxidation state) ($E^T = 2.1$ eV). This large barrier is probably due to the fact that the carbons of the reactant are not interacting with the catalyst surface; hence, they are not activated. Besides, the steric crowding, which destabilizes both the transition state and the product, barely affects the reactant, which does not adsorb through a carbon atom but rather through the two lone-pairs electrons of the oxygen atoms. In support of this argument, we find that the energy barrier for the dehydrogenated geminal diol is significantly lower (1.4 eV). In this case, the steric crowding in the reactant and product is similar, since both adsorb through the unsaturated carbon atom, hence benefiting from less destabilization.

Second, the lowest barrier for breaking the C−C bond is found for acetyl (CH$_3$CO) with an activation energy of “only” 0.9 eV, which is attributed to the very stable CO product on Pd surface. Note, however, that this is still a significant barrier at room temperature that cannot be lowered by the application of a potential. Furthermore, the C−C splitting is in competition with the thermodynamically favorable C−OH bond formation that yields acetic acid. Playing on the structure of the catalyst, one may favor the C−C bond splitting since this is a structure-sensitive reaction that is favored on low-coordinated facets: the
Scheme 1. General Reaction Scheme Based on Our Results

C–C bond splitting in CH₃CO decreases from 1.4 eV on Pd(111) to 0.9 eV on Pd(100) and 0.7 eV on Pd(110).

The reaction selectivity toward acetic acid is better understood from the aforementioned reaction energy profiles, keeping in mind the C–H and O–H bond breaking in ethanol catalyzed by Pd have a barrier of <0.8 eV. These steps can be even further activated by the presence of surface hydroxyls, as shown in previous DFT studies. However, the thermodynamic impact of the recombination of H⁺ and OH⁻ is also included in our present study, through the use of the computational hydrogen electrode. At the +2 oxidation state, the most stable intermediate (the gem-diol CH₂CH(OH)₂) does not undergo C–C splitting (E° = 2.1 eV) and also higher-lying intermediates only react slowly toward C₁ products and face a strong competition with C–OH bond formation. Hence, the hydrate gets oxidized, despite the fact that this does not lead to the lowest-energy intermediate at the +3 oxidation state. At the +3 oxidation state, there are three processes in competition. In one process, the CH₃C(OH)₂ is quickly oxidized to acetic acid (E° < 0.8 eV) and the C–C bond remains intact. In the second process, the most stable but kinetically less accessible intermediate CH₂CO can undergo slow C–C bond splitting (E° = 0.9 eV) and the fragments eventually be oxidized to CO/CO₂. In the third process, CH₃CO can be oxidized to acetic acid as explained above, which is an electrochemical process that is favored by oxidative potentials. In other words, the necessary potentials and the unfavorable “connection” between the most stable intermediates lead to the dominance of acetic acid as a product and to the small probability of splitting the C–C bond at an early stage of the oxidation process. These results show how challenging and complex it is to design a catalyst for complete electro-oxidation of ethanol to CO₂.

3.4. Ethanol Electro-oxidation Mechanism. In this section, we summarize the reaction scheme that results from our joint experimental and theoretical study, as shown in Scheme 1.

Ethanol is converted to acetaldehyde by oxidative dehydrogenation on Pd. This is a two-step processes that has been studied in details by DFT simulations including coadsorbed species and water solvent. To be able to screen a much larger part of the reaction network of ethanol electro-oxidation into CO₂, we had to simplify our model to a Pd/vacuum interface.

The effects of the coadsorption of water are not included but expected to be negligible on the relative energies. Indeed, even if the details differ, our study leads to the same conclusion at the +2 oxidation state: acetaldehyde is in equilibrium with its hydrate, the gem-diol. Then, two routes are in competition. First, the gem-diol is the most stable adsorbed species at its degree of oxidation. The α-C–H bond breaking is particularly facilitated in electrochemical conditions and leads to CH₃C(OH)₂ that easily yields acetic acid. In the second route, acetaldehyde is dehydrogenated into acetyl, CH₃C=O. Since acetaldehyde is less stable on the surface than its gem-diol, this route is disfavored. However, the acetyl is a pivotal intermediate. Its degree of oxidation is the first along the path where the key C–C bond scission can occur exothermically from the most stable C₂ fragment. Moreover, among all the intermediates with an oxidation state of +2 and +3, it is the one that exhibits the lowest activation barrier for the C–C bond scission (0.9 eV). Hence, even though a chemical step, CH₃CO decarbonylation could compete with the C–H, O–H, and C–OH rearrangements that are facilitated by electrochemical potential. Thus, the CO₂ traces we have observed experimentally at low potentials by PM-IRRAS are probably generated from adsorbed acetyl. This is consistent with the ATR-SEIRAS experiments of Yang et al. However, the acetyl can also easily lead to acetic acid by the formation of a C–OH bond, which is a process that is accelerated by oxidative potentials. This explains the experimental observation that the selectivity toward CO₂ decreases at higher potential.

In summary, the C–C bond scission that is essential to open the route to a full oxidation of ethanol can occur at the +3 oxidation state. However, it is a slow process and in competition with the faster oxidation to acetic acid. For oxidation states greater than +5, the C–C bond splitting is exothermic, opening the road to the C₁ pathway. However, there is a strong disconnection on the C₂ pathway between the most stable species at the +5 oxidation state (CH₃COO) and the most stable species at the +6 oxidation state (CHCOOH) that hinders the oxidation of acetate (Figure 5), which is consistent with the experimentally observed impossibility to oxidize acetic acid in KOH under our conditions (see Figure 1).
4. CONCLUSION

We have presented a comprehensive study of the reaction mechanism of ethanol electro-oxidation over Pd surfaces, combining cyclic voltammetry (CV), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and density functional theory (DFT) computations. The PM-IRRAS information (identification of surface and bulk solution species) simplified the number of possible intermediates considered in the DFT modeling, while DFT insights provided invaluable information on the elementary reaction intermediates and kinetic parameters, which was not accessible experimentally. This strategy can be easily extended to other alcohols or organic molecules on other metal surfaces.

In this work, we have solved two of the long-debated puzzles: the path leading to the formation of acetate, the product obtained over a Pd catalyst under alkaline conditions, and the most likely intermediates where the C–C bond can be broken. For the formation of acetic acid, we have identified two converging paths: the most stable path, going through the gem-diol (hydrate of acetaldehyde), and the second-most-stable path going through the acetyl (CH₃CO). Unfortunately, acetate cannot be oxidized further over Pd, according to our CV and DFT results, closing the door to the C₁ path and thus the complete oxidation of ethanol. Hence, to contribute to the second debate, we have determined the most likely intermediates where the C–C bond can be broken before reaching acetate. We have demonstrated that acetyl (at oxidation state three) has by far (>0.3 eV) the lowest activation energy for the C–C bond breaking (ΔF° = 0.9 eV). However, the overpotentials required for reasonable current densities strongly accelerate the electrochemical oxidation process. This favors the C–OH formation over the C–C splitting reaction. Therefore, CH₃CO is quickly oxidized to acetic acid, thereby suppressing the C–C bond breaking, explaining the negligible amount of CO₂ detected at higher potentials. In other words, CH₂CO plays a pivotal role, since it can either undergo a C–C bond splitting, eventually yielding CO₂ or be oxidized toward CH₃COOH, a dead end in the reaction scheme. Through this analysis, our work has determined the conditions for a better selectivity toward CO₂: destabilize the gem-diol, stabilize the acetyl, and facilitate its splitting to CH₃ and CO. A large descriptor-based search of catalysts has been started to determine in silico alloy formulations that would obey these conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00289.

The physical characterization of the Pd/C nanoparticles; the PM-IRRAS background/reference and data processing and interpretation details; FTIR transmission spectra for KOH and (KOH + acetic acid, sodium acetate, sodium carbonate, and ethanol); most stable geometric ethanl oxidation intermediates structures and some of the key POSCAR files (PDF)

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Notes

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