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**Insights into ethanol electro-oxidation over solvated Pt(100):
origin of selectivity and kinetics revealed by DFT**

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Abstract

The use of ethanol fuel in direct ethanol fuel cells has been hindered by the slow kinetics of anodic ethanol electro-oxidation reactions over Pt catalysts. We employ *ab initio* molecular dynamics simulations and thermodynamic integrations on the solvated Pt(100) model electrode surface with explicit water molecules, to systematically investigate the ethanol electrocatalytic oxidation mechanisms including partial oxidation to acetic acid and complete oxidation to CO₂. We find that the ethanol decomposition rate does not limit the overall efficiency of the ethanol electro-oxidation reaction. However, the slow oxidation kinetics of surface intermediates to final products, due to the bonding between intermediates and the Pt surface being too strong, is the main obstacle. We suggest that weakening the surface affinity towards adsorption of the intermediates such as CO, for example by engineering the surface structures (e.g. via alloying), could improve the overall catalytic efficiency for ethanol electro-oxidation reaction.

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Keywords: electrocatalysis; ethanol fuel cell; platinum; density functional theory; heterogeneous catalysis;

1. Introduction

Fuel cells are promising clean energy technologies owing to their high energy efficiency and low carbon emission. Among the various types of fuel cells, direct ethanol fuel cells (DEFCs) are particularly attractive for transportation and portable applications because they have the advantage of direct use of liquid ethanol as the fuel, making them comparatively more convenient and with a much higher energy density than hydrogen or even methanol.[1-3] Furthermore, ethanol can be produced from renewable bio-feedstocks, as a carbon-neutral energy source. However, the large-scale implementation of DEFCs has been hindered by the slow kinetics for ethanol oxidation reactions on anodes. The ideal anodic reaction in DEFCs is the complete oxidation of ethanol to CO₂ with the transfer of the maximum twelve electrons per ethanol molecule ($\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$). However, in practice the predominant partial oxidation of ethanol to acetic acid with the transfer of only four electrons ($\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^-$) occurs in most reported catalytic systems.[1-6] To understand the complex surface reactions in the DEFCs, the surface structures of well-defined platinum electrodes have been extensively investigated in past years by using various single crystal planes and well-faceted nanoparticles as model catalysts.[7-9] Regarding the structure-reactivity relationship, it was found that the Pt(100) surface experimentally displays both a higher activity and a higher poisoning rate than Pt(111) and Pt(110).[8, 9]

Despite much theoretical progress in understanding how the surface structures of Pt and Pt-based catalysts may influence ethanol electro-oxidation reactions in terms of both activity and selectivity, most results reported so far have been based on calculations under vacuum conditions without considering the aqueous environment, resulting in a significant gap in relation to real DEFC systems; as such the data obtained under vacuum conditions may not be so relevant to real electrochemical interfaces.[10-13] The explicit inclusion of the solvent water molecules may influence the absolute energetics or revise the presented reaction

mechanisms. Sakong *et al.* reported that solvents could stabilize the reaction intermediates in methanol oxidation containing hydrophilic groups using an implicit solvent model.[14] For catalytic reactions at electrodes, incorporating in the modelling the fluctuations and reorganization of water molecules around the reacting chemical species is a grand challenge. Nevertheless, time consuming but high accurate *ab initio* molecular dynamics (MD) simulation based on density functional theory (DFT) now can precisely evaluate free energies of aqueous reactions by sampling solvent molecules at a given temperature.[15-18] Herron *et al.* concentrated on the role of solvents and electrode potentials on the energetics of the first proton transfer in methanol electro-oxidation on Pt(111) as a model surface by *ab initio* MD simulations.[18]

The reaction mechanisms of ethanol electro-oxidation are much more complex than those of methanol electro-oxidation due to the varieties of intermediates, especially involving the C-C bond breaking process. The latter is a significant issue in utilization of ethanol in fuel cells. Searching for efficient catalysts for ethanol electro-oxidation with both high activity and high CO₂ selectivity at low overpotentials is the most critical task for developing DEFCs. For the rational design of improved catalysts for DEFCs, a comprehensive understanding of ethanol electro-oxidation mechanisms in aqueous surroundings at atomic and free-energy levels is vital to identify the key intermediates, the rate-determining step and the main obstacles. Obtaining these critical data from theoretical calculations can effectively guide the design and synthesis of new catalysts.

In this work, the ethanol electro-oxidation mechanisms on solvated Pt(100) electrode were systematically investigated using constrained *ab initio* MD simulations. These cutting-edge computations reveal comprehensively the whole catalytic cycle, elucidating both the thermodynamics and kinetics of the process of going from ethanol to acetic acid and CO₂. It was found that ethanol decomposition rates are sufficiently high, but the reaction rates of further oxidation of intermediates into final products are

extremely slow, causing rapid poisoning of surface sites and seriously limiting the overall ethanol oxidation efficiency.

2. Computational methods

All calculations were carried out in the VASP code using the Perdew–Burke–Ernzerhof (PBE) functional of exchange–correlation and the projector-augmented-wave pseudopotentials.[19–22] Van der Waals (vdW) interactions were considered using D3 dispersion with zero damping.[23] The water/Pt(100) interface model comprises a four-layer Pt(100) slab with 64 Pt atoms and 48 water molecules with the density of 1 g cm^{-3} (Figure 1), which is kept constant during the MD simulations. A vacuum layer of 6 Å was inserted above the water layer. The cut-off energy was set as 400 eV and a gamma Monkhorst–Pack k-point mesh was used. The reaction free energies were evaluated by constrained *ab initio* MD simulations and thermodynamic integrations.[15] At first, 15 ps (a considerable time) of MD simulations were performed to equilibrate each initial state in elementary steps within the canonical (NVT) ensemble at 300 K (1 fs per step). For each state (per 0.1 Å) along each reaction path, a MD simulation was run for 6 ps to collect 6000 samples. The time-averaged interatomic force from the last 1000 samples was utilized for integrations along the reaction path. All free energy profiles for the elementary steps with key structures are shown in the supporting information (Figures S1–19).

Figure 1. Model of the water/Pt(100) interface including 48 interfacial water molecules presented by the stick model and one ethanol molecule by the ball-stick model. Blue: Pt; red: O; grey: C; white: H. (The same colours are used throughout the paper.)

3. Results

The reaction mechanisms of ethanol electro-oxidation may be divided into two parts: the first part is ethanol decomposition to surface intermediates (CH_3CO^* , CH^* , CO^*) and the second one is further oxidation of intermediates into products of acetic acid and/or CO_2 , whilst also generating free surface sites. Figure 2a shows the free energy profiles for ethanol decomposition over the solvated Pt(100) electrode, and Figure 2b presents the structures of intermediates so formed. The reaction energies and kinetic barriers are listed in Table 1. Note that the ethanol electro-oxidation usually take place under strong acid or alkaline conditions which may play crucial roles on reaction mechanisms. Due to the limitation of computational cost, we only consider the neutral solution using water molecules only. The systematic investigation of pH effects is important but still a huge challenge within explicit water molecules.

3.1. CH_3CO^* formation

One ethanol molecule initially placed on the surface was found to desorb into solution spontaneously after several ps in MD simulations. The OH group in ethanol was solvated by the surrounding water molecules ($\text{CH}_3\text{CH}_2\text{OH}_{\text{aq}}$ in Figure 2b) that is similar to the situation of methanol on solvated Pt(111),[15] suggesting that water molecules can stabilize the OH group and thus reduce its possibility to react with the metal surface. The solvated ethanol can then re-adsorb onto the surface and once there it may be activated by the α -C-H bond cleavage with a free energy barrier of 0.46 eV to yield CH_3CHOH^* on surface; this step is exothermic by -0.19 eV following the Eley-Rideal mechanism (Figure S2). By overcoming a barrier of 0.19 eV, CH_3CHOH^* breaks the second α -C-H

1 bond to produce CH_3COH^* at the top site with an H-down (OH group)
2 configuration (Figure S3). CH_3COH^* is another unstable intermediate due to the
3 O-H bond dissociation barrier being only 0.15 eV to generate CH_3CO^* (Figure
4 S4).
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10 3.2. C-C bond breaking

11 The C-O bond in CH_3CO^* prefers to be parallel to the Pt(100) surface through
12 one C-Pt bond and one O-Pt bond (CH_3CO^* in Figure 2b). For the formation of
13 CH_2CO^* , CH_3CO^* diffuses to the top position firstly ($\text{CH}_3\text{CO}_\text{t}^*$ in Figure 2b)
14 and then breaks the β -C-H bond. The migration of CH_3CO^* to the top position
15 requires only a small energy of 0.24 eV to break the O-Pt surface bond (Figure
16 S5). The latter explains why the C-O bond in CH_3CO^* prefers to bond to the
17 surface rather than being solvated by interfacial water molecules. Afterwards, the
18 β -C-H bond breaking is exothermic by -0.25 eV with a barrier of 0.41 eV (Figure
19 S6). Thus, the overall barrier for CH_3CO^* decomposition to CH_2CO^* is 0.65 eV
20 (0.24 eV for the position migration and 0.41 eV for the bond breaking) and the
21 reaction energy is -0.01 eV. Surface CH_2CO^* is active for further losing its
22 hydrogen to form CHCO^* with a minor barrier of 0.17 eV (Figure S7) rather than
23 breaking its C-C bond with a higher barrier of 0.81 eV (Figure S8). CHCO^* can
24 further break its C-C bond to form hollow CH^* and bridge CO^* with a barrier of
25 0.70 eV; this elementary step is highly exothermic of -0.58 eV (Figure S9).
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43 All elementary steps for ethanol decomposition are reasonably facile in
44 energetics (overcoming a barrier of 0.70 eV or below), suggestive of a fast
45 decomposition rate on solvated Pt(100) at room temperature. The calculated
46 overall barrier for CH_3CO^* formation (that is the ethanol partial oxidation
47 pathway) is 0.46 eV, and that for C1 species formation (including C-C bond
48 cleavage in the ethanol complete oxidation pathway) is 0.70 eV, confirming that
49 the rate limiting step is the C-C bond splitting process in ethanol
50 decomposition.[12]
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Figure 2. (a) Free energy profiles for ethanol decomposition over the solvated Pt(100) surface to C1 species with reaction barriers (in eV). (b) Snapshots of intermediates obtained from *ab initio* MD simulations. The interfacial water molecules were presented by the stick model.

3.3. CH₃CO* oxidation

After studying the initial ethanol decomposition steps, we concentrated on the oxidative processes of intermediates derived from ethanol decomposition; the oxidation reactions require the participation of surface OH* species as oxidants which can be produced from water dissociation. Interestingly, in contrast to the insensitive reactivity of the C-H and C-C bond dissociation over the Pt surface with regards to the presence of water, the C-O bond association would be easily

affected by the aqueous environment due to the negatively charged O atom. The three relevant intermediates oxidation reactions have been calculated, these are CH_3CO^* to acetic acid, CH^* to CO^* , and CO^* to CO_2 . It has been found that water could readily dissociate to OH^* and H^* on Pt(100), having a downhill energy of -0.19 eV with a barrier of 0.39 eV (Figure S1), which indicates that the Pt(100) surface has the ability to activate water to form OH^* without applying extra electrode potentials. Solvated OH^* was stable at the top site that is different from the preferred bridge site of OH^* on Pt(100) in vacuum. It is noted that we have not added or removed any electrons in our theoretical model; such a neutral solvated Pt(100) system thus may be close to the condition at the potential of zero charge (~ 0.4 V). At this potential, the water dissociation can take place to somewhat extent, however, the exact coverage of H^* and OH^* were not considered.

Figure 3 presents the process of CH_3CO^* being oxidized by OH^* to produce acetic acid. It was found that the production of acetic acid is mainly prohibited by thermodynamics ($\Delta G = 0.45$ eV), although the overall barrier (0.60 eV, the free energy difference between $\text{CH}_3\text{CO}^* + \text{OH}^*$ and the transition state from CH_3COOH^* to $\text{CH}_3\text{COOH}_\text{t}^*$ in Figure 3a) is kinetically feasible. The C-O bond coupling barrier between CH_3CO^* and OH^* to form CH_3COOH^* is only 0.53 eV, but this step is endothermic by 0.35 eV (Figure S10). Moreover, the C-O bond making does not induce a concurrent Pt-C bond breaking. Instead, the newly formed CH_3COOH^* (Figure 3b) adsorbs on the surface with two O-Pt bonds and one C-Pt bonds being formed. It needs to overcome a barrier of 0.25 eV to break the C-Pt bond to form $\text{CH}_3\text{COOH}_\text{t}^*$ (Figure 3b) for decreasing the bonding strength of 0.06 eV between CH_3COOH^* and surface (Figure S11). $\text{CH}_3\text{COOH}_\text{t}^*$ bonds weakly to the surface via one O atom in the OH group with a small adsorption energy of -0.04 eV (Figure S12). We also found that the deprotonation of $\text{CH}_3\text{COOH}_\text{t}^*$ can occur to form bidentate CH_3COO^* ($\Delta G = -0.06$ eV) which is more stable than acetic acid on surface with a negligible barrier

of 0.02 eV for the proton transfer (Figure S13); such adsorbed acetic acid usually been experimentally detected out.[2]

Figure 3. (a) Free energy profiles for CH_3CO^* oxidation reaction over the solvated Pt(100) surface with reaction barriers (in eV). (b) Snapshots of intermediates and transition states obtained from *ab initio* MD simulations.

3.4. CH^* oxidation

CH^* oxidized by surface OH^* to form CO^* is energetically feasible; this process is exothermic of -1.13 eV with the overall barrier of 0.91 eV (the energy difference between $\text{CH}^* + \text{OH}^*$ and the transition state from co-adsorbed $\text{CH}^* +$

OH* to CHOH* in Figure 4a), implying that CH* can be converted to CO* by OH*, although the conversion rate is not very fast at room temperature (Figure S14). At first, one hollow CH* occupies four Pt surface atoms and a top OH* stays at another free Pt atom (CH* + OH* in Figure 4b). The distance between O and C atoms can be shortened, with OH* moving to one of the four Pt atoms initially occupied by CH*, thus leading to a repulsive interaction of 0.26 eV with the sharing of a same Pt atom (co-adsorption state in Figure 4b). Next, with further overcoming a barrier of 0.65 eV, the C-O bond formation results in forming CHOH*. This step is slightly exothermic, by -0.16 eV. Afterwards, CHOH*, with a tiny energy barrier of 0.06 eV, rapidly generates CHO* with the release of a proton and electron couple (Figure S15). Further decomposition of CHO* to CO* is very easy both thermodynamically and kinetically, being highly exothermic, releasing -0.91 eV, and a low barrier of 0.15 eV (Figure S16). Experiments only found the conversion of CH* to CO* only above 0.4 V. It is suggested two possible reasons: (i) at very low potentials, ethanol dissociation would produce amounts of surface H*, which may convert CH* into CH₄.^[24] (ii) The increase of electrode potentials can decrease the H* coverage while increase the OH* coverage. The lower H* coverage can suppress the reduction of CH* and the higher OH* coverage may facilitate the oxidation of CH*.

Figure 4. (a) Free energy profiles for CH* oxidation reaction over the solvated Pt(100) electrode with the reaction barriers (in eV). (b) Snapshots of intermediates and transition states obtained from *ab initio* MD simulations.

3.5. CO* oxidation

In contrast to the easy CH* oxidation, further oxidation of surface CO* by OH* was found to be significantly inhibited from both the thermodynamic and kinetic points of view, as shown in Figure 5a. The coupling barrier between CO* and OH* to yield COOH* is as high as 1.04 eV and the reaction energy is uphill, costing 0.68 eV (Figure S17). If the COOH* is produced, it is rather unstable and can be readily converted to CO₂* with the loss of a proton and electron couple. The latter step is exothermic, releasing -0.57 eV and with a tiny proton transfer barrier of 0.03 eV (Figure S18). The formed CO₂* prefers to stay on the interface,

as a bent CO_2^* (Figure 5b) with the adsorption energy of -0.55 eV, rather than desorbing and diffusing into solution. Desorption of the surface CO_2^* is rather difficult since it needs to break a strong C-Pt bond with a kinetic barrier of 0.83 eV (Figure S19).

Because of the highest stability of CO^* among the three intermediates (CH_3CO^* , CH^* and CO^*), some amounts of OH^* formed on the Pt surface at low potentials are more likely to react with CH^* to form CO^* , leading to the rapid formation of CO^* adlayer that was evidenced on the Pt(100) single crystal electrode in experiments.[8] Increasing the potential to above 0.65 V, the CO adlayer starts to be oxidatively removed, so that the Pt(100) surface becomes active for further ethanol electro-oxidation reactions.

Figure 5. (a) Free energy profiles for CO* oxidation reaction over the solvated Pt(100) surface with the reaction barriers (in eV). (b) Snapshots of intermediates and transition states obtained from *ab initio* MD simulations.

Table 1. Calculated free energy barriers (E_a) and reaction free energies (ΔG) in eV of elementary steps in ethanol electro-oxidation over the solvated Pt(100) electrode.

surface reactions	E_a	ΔG
$C_2H_5OH \rightarrow CH_3CHOH^*$	0.46	-0.19
$CH_3CHOH^* \rightarrow CH_3COH^*$	0.19	-0.35
$CH_3COH^* \rightarrow CH_3CO^*$	0.15	-0.58
$CH_3CO^* \rightarrow CH_3CO_l^*$	/	0.24
$CH_3CO^* \rightarrow CH_2CO^*$	0.41	-0.25
$CH_2CO^* \rightarrow CHCO^*$	0.17	-0.44
$CH_2CO^* \rightarrow CH_2^* + CO^*$	0.81	-0.48
$CHCO^* \rightarrow CH^* + CO^*$	0.70	-0.58
$H_2O^* \rightarrow OH^* + H^*$	0.39	-0.19
$CH_3CO^* + OH^* \rightarrow CH_3COOH^*$	0.53	0.35

$\text{CH}_3\text{COOH}^* \rightarrow \text{CH}_3\text{COOH}_{\text{t}}^*$	0.25	0.06
$\text{CH}_3\text{COOH}_{\text{t}}^* \rightarrow \text{CH}_3\text{COOH}_{\text{aq}}$	/	0.04
$\text{CH}^* + \text{OH}^* \rightarrow \text{CHOH}^*$	0.91	0.10
$\text{CHOH}^* \rightarrow \text{CHO}^*$	0.05	-0.29
$\text{CHO}^* \rightarrow \text{CO}^*$	0.15	-0.91
$\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^*$	1.04	0.68
$\text{COOH}^* \rightarrow \text{CO}_2^*$	0.03	0.57
$\text{CO}_2^* \rightarrow (\text{CO}_2)_{\text{aq}}$	0.83	0.55

4. Discussion

The strong bonding between carbon-containing intermediates and the surface can lead to high ethanol decomposition activity because of the notable Bronsted-Evans-Polanyi (BEP) relations, but the intermediates derived from ethanol decomposition then have problems to in turn be further converted into products. It is thus reasonable to suggest that the optimum binding energies of intermediates on surface are critical in determining the total reactivity. For the improvement of ethanol electro-oxidation reaction efficiency, it is essential to balance the initial ethanol decomposition rates and the intermediates further oxidation rates, by finely tuning the binding energies of intermediates. These binding energies of intermediates, with regard to the Pt(100) electrode, are obviously too strong, resulting in the slow kinetics in the overall oxidation process. Therefore, we suggest that weakening the surface affinity towards intermediates adsorption by, for example, engineering the surface structures via alloying, could improve the whole ethanol electro-oxidation activity. Interestingly, it has been evidenced experimentally on methanol system, e.g., the

1 {100}-faceted Pt₃Co nanocubes with the weakened CO adsorption were reported
2 to effectively enhance the methanol electro-oxidation rates.[25] Small Pt₃Co
3 nanoparticles with a Pt skin structure were also found to facilitate ethanol electro-
4 oxidation reactions with a reduced CO formation.[26]
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8 Finally, to further ensure the calculation accuracy for such a multi-step reaction, we
9 calculated the equilibrium potentials for the two products of ethanol oxidation, the
10 partial oxidation product acetic acid and the full oxidation product CO₂, respectively.
11 According to the equilibrium of $H^+ + e^- \rightarrow H^*$ under standard hydrogen electrode (SHE)
12 condition, we converted the binding free energy of H* (-0.33 eV in vacuum, without
13 considering the solvation effects) on Pt(100) into the free energy of ($H^+ + e^-$) under the
14 SHE condition to calculate the theoretical equilibrium potentials. The completed energy
15 profile is presented in Figure 6. The equilibrium potentials were calculated to be 0.076
16 V for acetic acid production and 0.103 V for CO₂ production, which are close to the
17 standard equilibrium values (0.084 V for acetic acid, 0.089 V for CO₂), as listed in
18 Table 2. Such small differences confirm that our calculations are reliable for
19 descriptions of the energetic values in ethanol electro-oxidation reaction.
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Figure 6. Complete free energy profile for ethanol electrooxidation reaction over the solvated Pt(100) electrode.

5. Conclusions

In summary, by performing constrained *ab initio* MD simulations with the explicit aqueous environment, we have provided solid theoretical evidences that the Pt(100) electrode is rather active towards ethanol decomposition; the main bottleneck in controlling the overall ethanol electrooxidation reaction efficiency is further oxidation of the intermediates to final products. The origin of the slow kinetics in ethanol electro-oxidation on Pt(100) was thus identified to be the bonding between intermediates and the Pt surface being too strong. We have proposed that weakening the surface affinity towards adsorption of intermediates such as CO, for example by engineering the surface structures via alloying, could improve the whole ethanol electro-oxidation activity. These findings are of general importance for understanding and solving the key issues surrounding the electro-oxidation of small organic molecules on Pt and Pt-based electrodes, and

the approach could be extended widely for investigations of liquid/solid interfacial heterogeneous catalysis.

Table 2. Comparison of the calculated equilibrium potential (U_{cal} , in V vs SHE) and standard equilibrium potential (U , in V vs SHE) of ethanol partial electro-oxidation to acetic acid and complete oxidation to CO_2 .

reactions	U_{cal}	U
$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^-$	0.076	0.084
$\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$	0.103	0.089

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