Unraveling the Nature of Active Sites in Ethanol Electro-oxidation by Site-Specific Marking of a Pt Catalyst with Isotope-Labeled ^{13}CO

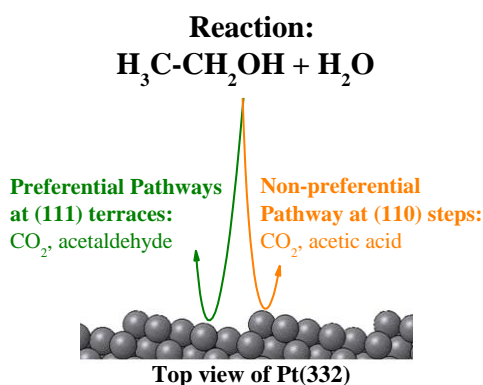Manuel J. S. Farias*[,†], William Cheuquepán[‡], Auro A. Tanaka[†], and Juan M. Feliu[‡]

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Abstract:

This works deals with the identification of preferential site-specific activation at a model Pt surface during a multiproduct reaction. The (110)-type steps of a Pt(332) surface were selectively marked by attaching isotope-labeled ^{13}CO molecules to them, and ethanol oxidation was probed by *in situ* Fourier transform infrared spectroscopy in order to precisely determine the specific sites at which CO_2, acetic acid, and acetaldehyde were preferentially formed. The (110) steps were active for splitting the C-C bond but unexpectedly, we provide evidence that the pathway of CO_2 formation was preferentially activated at (111) terraces, rather than at (110) steps. Acetaldehyde was formed at (111) terraces at potentials comparable to those for CO_2 formation also at (111) terraces, while the acetic acid formation pathway only became active when the (110) steps were released by the oxidation of adsorbed ^{13}CO, at potentials higher than for the formation of CO_2 at (111) terraces of the stepped surface.

Graphical Abstract

Reaction:
$$H_3C\text{-}CH_2OH + H_2O$$

Preferential Pathways at (111) terraces: CO_2, acetaldehyde

Non-preferential Pathway at (110) steps: CO_2, acetic acid

Top view of Pt(332)

Description of the relationships between reaction activation pathways and specific sites at solid surfaces is a demanding task that is necessary for improving understanding of the chemistry of heterogeneous (electro)catalysis at the molecular level. As early as 1925, Taylor[1] pointed out that real solid catalysts possess non-equivalent sites, which today are characterized as steps/defects, close-packed domains, ad-atoms, holes, and so on.[2] These different local surface crystallographic orientations are surrounded by different chemical environments and can vary in activity along the catalyst surface.[3] Consequently, the catalytic activity at the macroscopic scale results from the contributions of sites with different activities. This means that the identification of specific sites in multi-product reactions becomes more challenging, because in the mechanisms of these reactions, different reaction pathways may compete for the same active sites, with the various catalytic activities affecting the overall reaction rate.

Information on the identity of active sites is essential for understanding the nature of factors limiting the efficiency of a catalyst.[4] This is a key issue in energy conversion technology, as in the case of the electrocatalytic oxidation of ethanol, a convenient candidate for use in low temperature fuel cells. The use of infrared spectro-electrochemistry techniques to monitor the products of ethanol electro-oxidation at a Pt single crystal[5] revealed that it is a surface structure-sensitive reaction. From the catalytic viewpoint, one challenge in ethanol electro-oxidation is that almost all catalysts leave the C-C bond intact,[6,7] resulting in reaction products such as acetic acid or acetaldehyde that are associated with lower exploitation of the ethanol energy capacity. So, from the energy conversion perspective, it is desirable to tune the reaction pathway toward CO_2, and

beyond this, as a fundamental scientific question, it is important to understand the factors that favor or hinder it. The pathway to CO_2 requires cleavage of the C-C bond, with this reaction step being more favorable at step/defect sites than at (111) planes.[8,9] Therefore, steps/defects have been proposed to be the only active sites for the formation of CO_2 during ethanol oxidation,[8,10] while the pathway towards acetic acid has been suggested to be highly active on the (111) planes.[11] Additionally, insight into the reaction mechanism of ethanol oxidation has been achieved using isotope-labeled ethanol, evidencing the existence of preferential routes in ethanol dissociation/oxidation.[12-14] However, it is important to note that in previous work, there has been no control over the identity of the active sites and their relationships with specific reaction products or with the activation of the reaction pathway. An elegant methodology to identify active sites involves the selective blocking/marking of sites, but this is not a simple task, because the species used to block/mark active sites may affect the chemistry (reactivity, catalytic activity, etc.) of neighboring sites, as occurs with ad-atoms blocking sites.[15] Ideally, a neutral blocking/marking species should be employed, such as a "marked" reaction intermediate. Here, we overcome that difficulty by selectively marking the (110)-type steps of a stepped (111) Pt surface using isotope-labeled ^{13}CO, followed by examination of the activities of the remaining sites towards different reaction products coming from the ethanol electro-oxidation. In the course of ethanol electro-oxidation, CO_{ads} appears as a reaction intermediate,[5] so the $^{13}CO_{ads}$ deliberately attached at the (110) steps acts as both a site-specific species marker and a neutral/natural intermediate in the CO_2 pathway.

A well characterized Pt(332) stepped surface was employed, consisting of a 5-atom wide (111) terrace, periodically interrupted by monoatomic (110) steps, as shown in the hard sphere model in Figure 1, where the structure corresponding to (110) monoatomic steps is represented by a square, while the structure corresponding to the (111) terraces is

represented by a hexagon. The Pt(332) crystal was prepared as described previously.[16] The selection of this surface was based on its easier CO step sites decoration and its terraces width that was neither too short nor too long. The experimental details are provided in the Supporting Information.
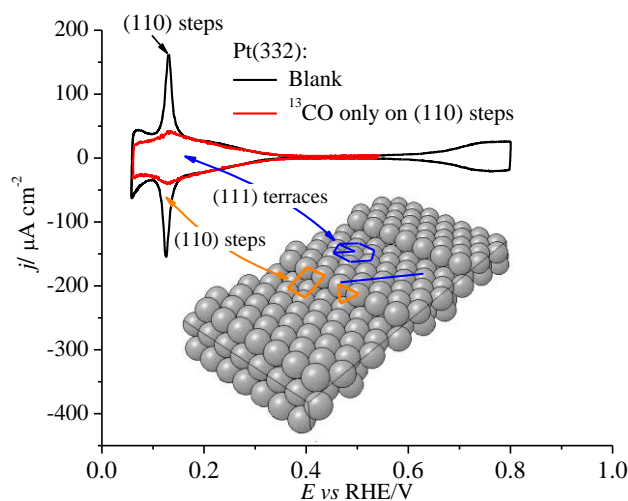

Figure 1. Cyclic voltammograms of Pt(332) in 0.1 M HClO$_4$, obtained at 50 mV s^{-1}. Black line: blank; red line: ^{13}CO only on (110) steps. The data include a hard sphere model of Pt(332).

Figure 1 shows the cyclic voltammogram of Pt(332) in 0.1 M HClO$_4$ (black line) and the voltammogram obtained when the ^{13}C^{16}O (henceforth denoted ^{13}CO) was selectively attached at the (110) steps (red line). The protocol used to obtain ^{13}CO only on the (110) steps consisted of voltammetric partial oxidation of a full ^{13}CO adlayer. Briefly, a full adlayer of ^{13}CO was prepared at the electrode, after which the CO adlayer was oxidized by applying several voltammetric cycles, limiting the upper potential in order to avoid oxidation of the entire ^{13}CO adlayer at once. The oxidation of the CO adlayer at the (111) stepped Pt surface consisting of (110) steps preferentially occurred at the (111) terraces, with the CO oxidation at (110) steps only starting after all the CO at the (111) terraces had been oxidized. Then, since the CO$_{ads}$ in the remaining layer behaved as an immobile species during its oxidation,[17] it was possible to acquire ^{13}CO in the residual ^{13}CO layer

only at the row of (110) steps. In Figure 1, the reversible peaks at ~0.128 V (black line) correspond to hydrogen adsorption/desorption at (110) steps. For the experiment with ^{13}CO only on (110) steps, only these features were suppressed in the hydrogen region. All the features below these processes at ~0.128 V corresponded to hydrogen adsorption/desorption at the (111) terraces. In Figure 1, all these sites were fully freed of $^{13}CO_{ads}$, as shown by comparison of the red line with the black line.

A typical voltammetric profile of 10 mM ethanol oxidation on a stepped Pt surface is presented in Figure 2 (red line), together with a blank voltammogram (black line). The (110) steps were indicative of low adsorption of ethanol at that concentration. All the (111) terraces remained completely unaltered, showing that the (111) terraces were less active for ethanol adsorption/dissociation than the steps, at least at low potentials. The protagonist action of the (111) terraces in ethanol oxidation was evidenced by the experiments shown in Figure 2, which compares voltammograms for ethanol oxidation at bare Pt(332) (red line) and Pt(332) with CO_{ads} selectively attached at the (110) steps (blue line). In order to carry out these experiments, after the preparation of (110) steps decorated with CO (normal CO), the electrode was polarized at 0.100 V and an aliquot of ethanol was added directly into the electrochemical cell, to a concentration of 10 mM. In order to analyze the data in Figure 2, it is opportune to mention that by using stripping voltammetry, in acid media the CO oxidation at the (110) steps of a stepped Pt single crystal with (111) terraces only develops maximum activity at ~0.72 V.[17] In Figure 2 (blue line), all the (110) steps were previously fully blocked by CO_{ads}, so the only sites available to participate in the ethanol oxidation/dissociation were the (111) terraces. However, it can be seen that in the presence (blue line) and absence (red line) of CO previously attached at the steps, the voltammograms were virtually identical between ~0.2 and ~0.5 V. This similarity suggested a predominant participation of (111) terraces in the

overall current density for ethanol oxidation at potentials above ~0.35 V, especially if it is considered that at potentials lower than ~0.72 V, the (110) steps were blocked by CO_{ads}.[17] The molecular factors controlling this behavior are elucidated in Figures 3-4.
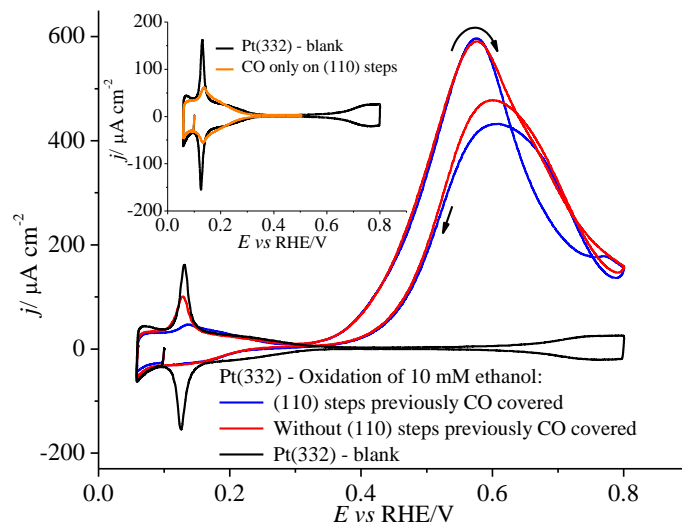

Figure 2. Ethanol (10 mM) electro-oxidation at Pt(332) in 0.1 M HClO$_4$, at 50 mV s^{-1}, in the presence (blue line) and absence (red line) of CO$_{ads}$ previously deposited at the (110) steps. Inset: voltammograms for the blank (black line) and for (110) steps decorated with CO (orange line).

The acquisition of *in situ* FTIR spectra (Figure 3) employed the following experimental protocol. Firstly, the Pt(332) electrode in the FTIR cell was fully covered with isotope-labeled ^{13}CO by bubbling ^{13}CO gas into the cell for 5 min, followed by purging the solution with Ar for 25 min. A partial ^{13}CO stripping experiment was then performed, in which ^{13}CO only remained at the (110) steps. In the experiment of Figure 3, the decorated ^{13}CO surface is that shown in Figure 1 (red line). Then, an aliquot of ethanol was added directly into the solution, to a concentration of 10 mM, while maintaining the potential at 0.100 V. The electrode was pressed against the prismatic optical window (CaF$_2$) to record *in situ* spectra (200 interferograms and resolution of 8 cm^{-1}) from 0.100 to 0.800 V, in intervals of 25 mV. Here, the series of spectra are shown for potentials above 0.400 V.
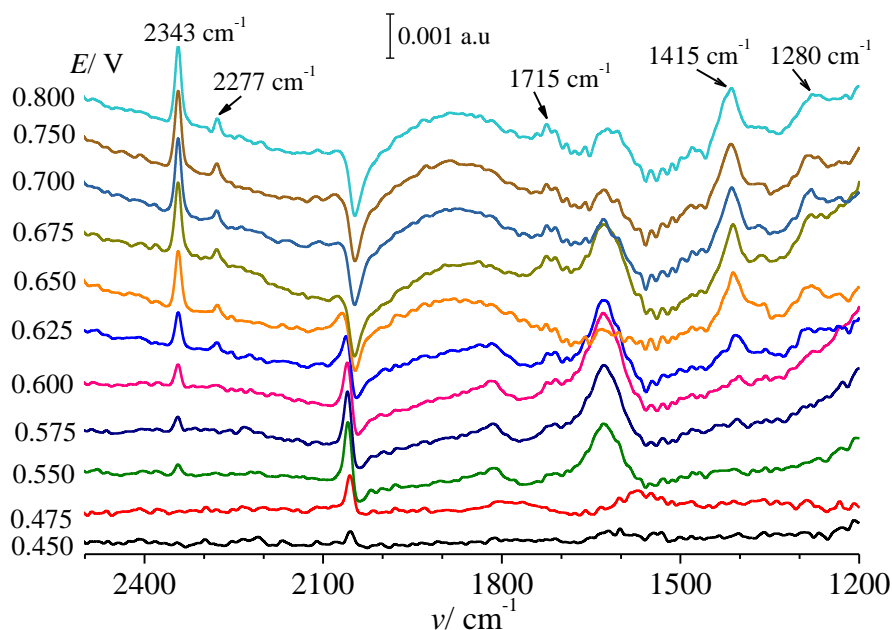
Figure 3. Spectra for ethanol (10 mM) electro-oxidation at Pt(332) with the (110) steps selectively decorated with ^{13}CO. The reference spectrum was recorded at 0.400 V.

Two CO_2 band frequencies can be seen in Figure 3, one at 2343 cm^{-1}, due to the CO_2 coming from the oxidation of CO_{ads} derived from ethanol dissociation, and another at 2277 cm^{-1}, due to the $^{13}CO_2$ coming from the oxidation of ^{13}CO that was previously attached at the (110) step sites. The band at 2343 cm^{-1} appeared at a lower potential (~0.500 V) than the potential at which the band at 2277 cm^{-1} appeared (~0.625 V). This enabled precise discrimination of the preferences for the activation pathways of CO_2 formation at two different active sites, which were the (110) step sites (where the $^{13}CO_2$ was formed) and the (111) terrace sites (where the normal CO_2 was formed) at the same catalyst surface containing these non-equivalent sites. Another important band appeared at ~1280 cm^{-1}, attributed to the combined C-O stretching and OH deformation of the COOH group of acetic acid.[18] This band appeared at ~0.625 V, the same potential at which the oxidation of $^{13}CO_{ads}$ at the (110) steps started. This suggested that the activation pathway of CO_2 formation at the step sites and the acetic acid activation pathway were not independent. In previous experiments, acetic acid was always detected at potentials

after the start of the CO_2 activation pathway,[9] but the reasons for this behavior will be clarified in this work. The band at 1415 cm^{-1}, which appeared at ~0.625 V, was attributed to symmetric O-C-O stretching of the COO$^-$ group. The band at ~1715 cm^{-1} corresponded to C=O stretching of acetaldehyde or acetic acid (CHO or COOH groups).[11] Since the band at ~1715 cm^{-1} appeared at ~0.575 V, before the acetic acid band at ~1280 cm^{-1}, it is reasonable to suppose that the acetaldehyde formation pathway was activated even when all the (110) steps were fully blocked with ^{13}CO, which is consistent with the activation pathway of acetaldehyde formation at the (111) terrace sites of the stepped Pt surface. Bands at ~2030 cm^{-1} and ~2070 cm^{-1} were due to the stretching frequencies of linearly bonded CO at the (111) terraces. The spectra showed dominance of the ^{12}CO band over the ^{13}CO band, with the latter not being detected in the spectra. The spectra for the $^{13}CO/^{12}CO$ mixture evidenced the predominance of dipole-dipole coupling at the CO adlayer,[19] with the intensity of the higher $^{12}CO_{ads}$ band frequency being reinforced at the expense of the $^{13}CO_{ads}$ band.[20,21] This might explain the absence of the $^{13}CO_{ads}$ band in Figure 3. Moreover, using a Pt(533) ≡ Pt(s)-[4(111)×(100)] [22] surface and different proportions of $^{13}CO/^{12}CO$, due to the phenomena of transfer intensity,[20,21] the band intensity related to $^{13}CO_{ads}$ at steps gradually decreased as the CO coverage at (111) terraces increased.[22] Figure S3 shows spectra for the $^{13}CO/^{12}CO$ mixture. In the spectra shown in Figure 3, the bending mode of water appeared at ~1600 cm^{-1}.

Similarly for 100 mM ethanol (Figure 4), all the (110) steps were selectively decorated with ^{13}CO. It can be seen that the spectra exhibited trends similar to those in Figure 3, but with higher band intensities at 2343 cm^{-1}, due to the CO_2 from ethanol oxidation, and at around ~1280 cm^{-1} and 1415 cm^{-1}, because the generation of products was higher.
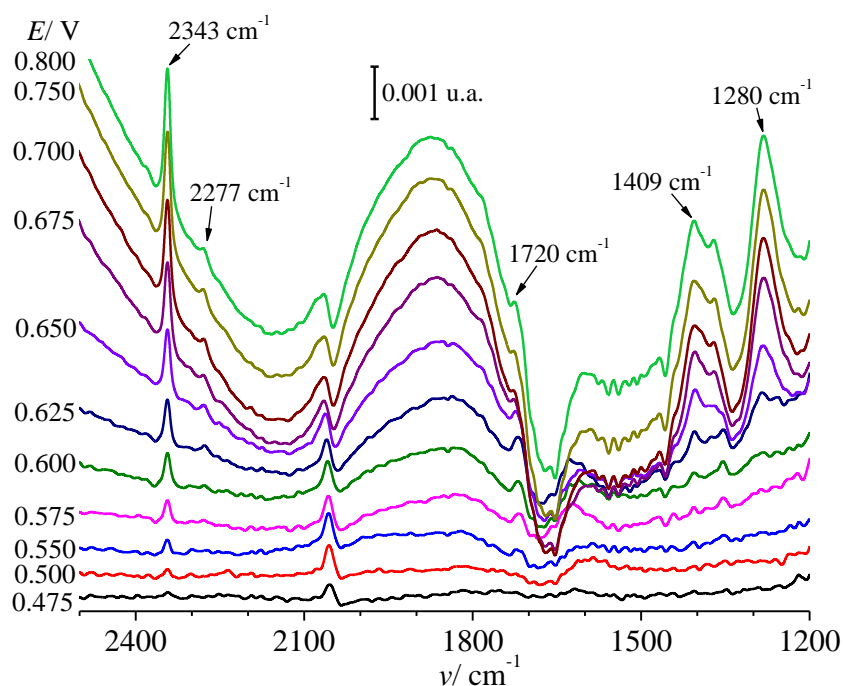
Figure 4. Spectra for 100 mM ethanol electro-oxidation at Pt(332) with the (110) steps selectively decorated with ^{13}CO. The reference spectrum was recorded at 0.400 V.

As described in the literature,[8-10] compared to the (111) terraces, the experiments confirmed that the (110) step sites were more capable of catalyzing cleavage of the C-C bond of the ethanol molecule at low potentials, and calculations suggest that breaking of the C-C bond requires a substantial ensemble of atoms on the surface.[23] Concerning site-specificity, the results revealed other properties of the step sites in ethanol oxidation and the protagonist role of (111) terraces at low potentials. The *in situ* FTIR spectra (Figures 3-4) showed that although the (111) terraces provided only weak C-C bond cleavage, these sites were much more effective in the activation pathway for CO_2 formation at low potential (~0.525 V), compared to the catalytic activity of the (110) step sites (where CO_2 formation started at ~0.625 V). This discrimination of the catalytic activities of non-equivalent sites toward the same reaction product (CO_2) was successfully revealed by the experimental strategy of chemically marking the (110) step sites by attachment of ^{13}CO from the gas phase. This procedure precisely mirrored the attachment of a natural reaction

intermediate at selected active sites (the (110) steps at a Pt(332) stepped surface), leaving all the other sites characterized as (111) terraces free for evaluation of their catalytic properties during ethanol oxidation. According to the spectra shown in Figures 3-4, the pathway to acetaldehyde formation was activated even when all the (110) steps were fully blocked with ^{13}CO, meaning that acetaldehyde was formed at (111) terraces at potentials below ~0.62 V.

The unexpected higher catalytic activity for CO_2 formation at (111) terraces could not be attributed specifically to the terraces themselves. It was previously observed that CO_2 generation at "infinite" (111) planes was low and only occurred above ~0.7 V_{RHE}.[11] In the present case, CO_2 formation at (111) terraces was observed at ~0.525 V, implying that the catalytic properties of "infinite" (111) plane surfaces differed greatly from those at stepped surfaces of the (111) plane. It is likely that the properties of the (111) terraces were modified by the steps, due to the Smoluchwski effect.[24] This involves the charge distribution at the steps, with a lack of it at the top side and accumulation of it at the bottom side, as a surface dipole. The steps probably modified the catalytic properties of the (111) terraces, making them the most favorable locations for activation of the CO_{ads} oxidation pathway. Therefore, although the steps were most effective in cleaving the C-C bond to form CO_{ads}, their ability to convert CO_{ads} to CO_2 was lower, compared to the (111) terraces at the stepped Pt surface. Hence, if CO_{ads} is conceived as a catalytic poison, its adsorption at steps had a greater catalyst poisoning effect than at the (111) flat structure. This easier conversion of CO_{ads} to CO_2 at (111) terraces probably involved the carbon of the alcoholic group, which is more reactive than the ethyl group.[25]

Comparison of the potentials for CO_2 formation at the (111) terraces (Figures 3-4) showed that CO_2 formation unequivocally preceded the appearance of acetic acid. From a mechanistic perspective, both CO_2 and acetic acid formation require the transfer of one external oxygen atom derived from a water molecule. According to the thermodynamics

(Table 1), the acetic acid pathway presents a standard potential $E^0 \simeq 0.058$ V_{SHE}, while for the CO_2 pathway $E^0 \simeq 0.085$ V_{SHE}, and for acetaldehyde $E^0 \simeq 0.246$ V_{SHE}.

Table 1. Standard Potentials [a] (E^0/ V_{SHE}) and the Number of Exchanged Electrons (n_{e^-}) for the Electrochemical Oxidation of Ethanol.

electrochemical reaction	E^0	n_{e^-}
$H_3C\text{-}CH_2OH_{(l)} + 3H_2O_{(l)} \rightleftarrows 2CO_{2(g)} + 12H^+ + 12e^-$	0.085	12
$H_3C\text{-}CH_2OH_{(l)} + H_2O_{(l)} \rightleftarrows H_3C\text{-}COOH_{(l)} + 4H^+ + 4e^-$	0.058	4
$H_3C\text{-}CH_2OH_{(l)} \rightleftarrows H_3C\text{-}CHO_{(l)} + 2H^+ + 2e^-$	0.246	2

[a]Calculated from standard thermodynamic data.[26]

Based on the expected standard potentials, the pathways to acetic acid and CO_2 were almost equally preferable. However, the results showed that the acetic acid pathway was *accidentally* hindered by CO_{ads} poisoning at the steps. At low potentials ($E < 0.6$ V), acetic acid formation apparently did not occur at the (111) plane of stepped Pt surfaces, and only started when the steps were freed. The steps acted to change the mechanism of acetic acid formation at the (111) plane, which was not favored (*at low potentials*) at the (111) planes of the stepped surface.

In conclusion, we show that the protagonist effect of the (111) terraces is induced by the presence of steps. The step sites presented different functionalities at non-equivalent surface sites during the electrocatalysis of ethanol oxidation, modifying the activity of (111) terraces for the CO_2 formation pathway at low potentials, and changing the mechanism of acetic acid formation. The preferential activation of the CO_2 pathway at the (111) terraces indicated that these locations were most suitable for the transfer of external oxygen required for formation of CO_2, rather than acetic acid at (110) steps or even at (111) terraces.

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Supporting Information Available

Additional experimental results, including the cyclic voltammetry and *in situ* FTIR data (PDF).

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