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Electrocatalysis

ISSN 1868-2529

Volume 5

Number 1

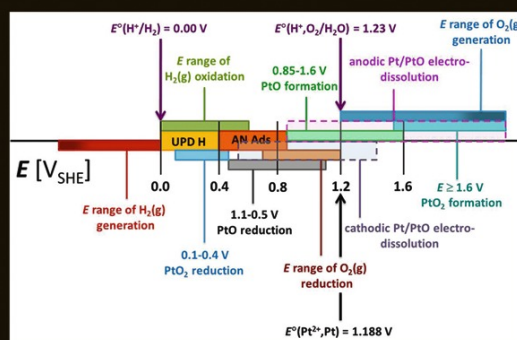
Electrocatalysis (2014) 5:1-4

DOI 10.1007/s12678-013-0170-1

Volume 5 • Number 1

January 2014

Electrocatalysis



 Springer

12678 • ISSN 1868-2529
5(1) 1-112 (2014)

 Springer

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How Reactive are Metal Surfaces in Solution? A Comparison of the Electrochemical Adsorption of Organic Molecules on Pt At Low Potentials

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Published online: 13 November 2013
© Springer Science+Business Media New York 2013

Introduction

Transition metal surfaces are widely employed as catalysts of chemical reactions, both at the metal/gas [1] and at the metal/solution [2] interfaces. Well-known examples are ceramic-supported catalysts used in gas exhausts of vehicles to oxidize partially burnt fuels [3] and metal-based catalysts used in fuel cell devices to promote electrochemical oxidation of organic molecules for direct conversion of chemical energy into electrical energy with high efficiency [4].

In this context, the electrochemical oxidation of alcohols has been extensively studied in the last decades [5] due to their potential for practical applications in fuel cells. Direct alcohol fuel cell (DAFC), especially direct ethanol fuel cell (DEFC), is becoming a very attractive alternative energy source for fossil fuel combustion engines due to several advantages, including its high theoretical efficiency, high energy density of alcohols (comparable to gasoline) [6], and the possibility of energy production from renewable sources [7]. However, for the DEFC to become commercially attractive, a few issues must be overcome. One of the difficulties is that the current state-of-the-art anodes are not capable of fully oxidizing ethanol to CO₂. Even at low ethanol concentrations, the CO₂ production is small compared to partially oxidized products [8], reducing

the overall efficiency of the fuel cell. This is one of the most critical drawbacks of this reaction and suggests that present catalysts are not able to effectively cleave the C–C bond of ethanol. Another general problem of catalysis is the poisoning of their surface by strongly adsorbed species (usually reaction intermediates). In the case of electrooxidation of ethanol, the main poison to the surface reaction, at low overpotentials and at room temperature, is believed to be carbon monoxide (CO) or CO-like species and CH_x-like species [9]. Overcoming these issues will therefore demand a thorough understanding of the reaction mechanism and of the metal–molecule interaction in a liquid environment, which is a formidable task for both experimental techniques and theoretical modeling.

Given the great complexity of the ethanol electrooxidation reaction on Pt, which is the major catalyst for electrochemical oxidation of small organic molecules and regarded as a model catalyst in electrocatalysis, numerous experimental techniques have been used to try to identify adsorbed intermediates and to elucidate the reaction mechanism. Among these techniques are in situ Fourier transform infrared spectroscopy (FTIR) [10], differential electrochemical mass spectrometry (DEMS) [10, 11], and, more recently, sum-frequency generation (SFG) spectroscopy [12]. Although it is well-known that ethanol oxidation on Pt electrodes follows parallel reaction pathways yielding the formation of acetaldehyde, acetic acid, and CO₂ [13], the detailed mechanism of this reaction remains unclear. Previous studies have contributed significantly to the understanding of ethanol oxidation on Pt. Nevertheless, they were mostly based on linear spectroscopic techniques, which cannot completely discriminate features from adsorbates and contributions from bulk species. SFG spectroscopy can be used as a powerful tool to obtain vibrational spectra of adsorbed species without contribution from the bulk [14]. Very recently, we reported an extensive study about adsorbed intermediates of ethanol electrooxidation on Pt in acidic medium investigated by SFG spectroscopy [15].

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Here, we study by SFG spectroscopy the adsorption of acetaldehyde, acetic acid, and methanol on Pt in acidic medium in the fingerprint region at low potential (0.05 V vs. reversible hydrogen electrode (RHE)). We compare these results with that of ethanol at the same experimental conditions. The main goals of the present investigation were to confirm the spectral assignments proposed previously [15] and to gain insights on the detailed reaction pathways for the electrooxidation of ethanol. Specifically, since acetaldehyde and acetic acid are products of the ethanol electrooxidation on Pt in acidic medium, investigating the adsorption of these molecules on Pt (at low potentials) could help clarifying the assignment of the different bands in the SFG spectrum for the ethanol solution/Pt interface. Also, by replacing ethanol with methanol, we intended to identify among the peaks observed in the spectrum for the ethanol solution/Pt interface those related to the C–C stretches, as we expected they would be absent for the Pt/methanol solution interface. However, our data indicate that a pristine Pt surface is extremely active for bond breaking and rearrangement of the fragments, even at potentials as low as 0.05 V vs. RHE, producing similar adsorbates independent of the original molecules. Since it is generally believed that the reaction mechanism of small organic molecules (such as: ethanol, methanol, acetaldehyde, and acetic acid) on Pt in aqueous environment depends specifically on the reacting molecule, the results presented here represent a change in paradigm for the role of a metal catalyst, suggesting that electrochemical reactions on metal surfaces may be much more complex than could be presumed from their reactants and products, taking place with multiple and similar reaction pathways simultaneously.

Materials and Methods

Similar to previous work [12], SFG experiments were performed in a three-electrode spectro-electrochemical cell covered by a 2-mm thick CaF_2 window. The working electrode was a polished polycrystalline Pt disk (12-mm diameter). A platinized Pt wire and an RHE were used as the counter and reference electrodes, respectively. Before each experiment, the working electrode was annealed in an H_2 flame for approximately 15 min, cooled down to room temperature in an inert N_2 atmosphere, and then protected with a drop of water to prevent contamination before being transferred to the spectro-electrochemical cell. The working electrode was then introduced at open circuit potential to the spectro-electrochemical cell containing $0.5 \text{ mol L}^{-1} \text{ HClO}_4$ and subsequently polarized to 0.05 V vs. RHE. Ethanol, acetaldehyde, acetic acid, or methanol were added to the cell to attain a 0.1-mol L^{-1} concentration, with the working electrode polarized at 0.05 V in $0.5 \text{ mol L}^{-1} \text{ HClO}_4$ medium. SFG spectra were taken into the region between $1,000$ and $1,500 \text{ cm}^{-1}$ at 0.05 V. During the

acquisition of the SFG spectra, the working electrode was pressed against the CaF_2 window to obtain a thin liquid film in order to minimize the absorption of the infrared beam by the electrolytic solution. From $1,250$ to $1,000 \text{ cm}^{-1}$, the IR transmittance for a 2-mm thick CaF_2 window decreases from 95 to 60 % due to bulk IR absorption. Our spectra were not corrected for these effects. Details of our SFG spectrometer and data acquisition procedure can be found elsewhere [15].

Results and Discussion

The SFG spectrum for the ethanol solution/Pt interface is shown in Fig. 1a. With at least 14 peaks in this narrow spectral range, the most striking feature of this spectrum is its complexity, especially if we recall that only vibrations that are simultaneously IR and Raman active (with the IR transition dipole perpendicular to the metal surface) can be detected in the SFG spectrum [14]. Since the peaks are so numerous and appear to be regularly spaced, at first, one could imagine that they could result from interference effects in the thin liquid film sandwiched between two reflective surfaces: the CaF_2 window and the Pt electrode. This is ruled out by the spectrum for the pure electrolyte/Pt interface shown in Fig. 1e, where most of the resonances disappear, except for a narrow peak at $1,408 \text{ cm}^{-1}$

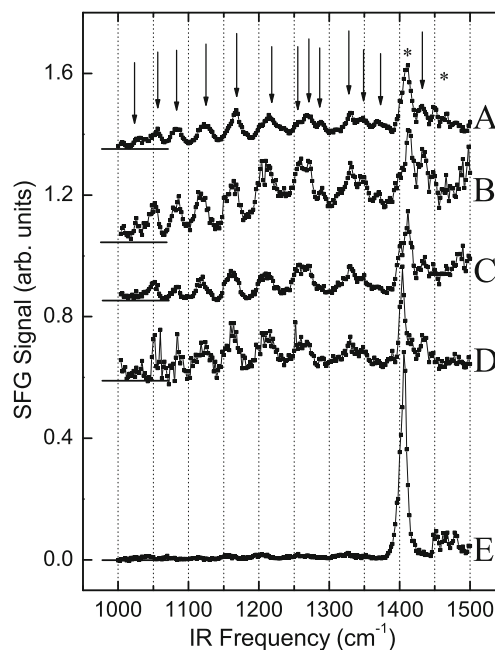


Fig. 1 SFG spectra of Pt in $0.5 \text{ mol L}^{-1} \text{ HClO}_4$ and 0.1 mol L^{-1} A ethanol, B acetaldehyde, C acetic acid, D methanol, and Pt in $0.5 \text{ mol L}^{-1} \text{ HClO}_4$ (E) at 0.05 V vs. RHE with PPP polarization combination (P-polarized SFG, visible and infrared beams). A, B, C, and D are vertically offset for clarity, and their zero intensities are indicated by horizontal lines. Arrows indicate similar peaks in the spectra A–D. The peak at $1,408 \text{ cm}^{-1}$ and a broad feature between $1,445$ and $1,490 \text{ cm}^{-1}$ are labeled with (asterisk) and are not related to any molecular vibrational transition

and a broad and weak resonance above $1,450\text{ cm}^{-1}$. Additional evidences for the absence of interference effects in the thin liquid film are presented in detail elsewhere [15], together with a discussion on the possible origin of the peaks observed in Fig. 1e. These two features are not related to any molecular resonance since they also appear without any liquid when the clean electrode is pressed against the clean window.

Consequently, the SFG spectrum of Fig. 1a (except for the peak at $1,408\text{ cm}^{-1}$ and broad band at $\sim 1,470\text{ cm}^{-1}$ shown in Fig. 1e) is attributed to adsorbed intermediates of the ethanol electrooxidation at low potentials. The bands observed in the region between $1,000$ and $1,500\text{ cm}^{-1}$ correspond to C–OH [16], C–C [16], C–C–O [17] stretching vibrations, to CH_2 and CH_3 deformations [18], CH_2 wagging and twist [19], and CH_3 rocking modes [19] of the adsorbed species. However, if we consider only one type of adsorbate, for instance, an adsorbed ethoxy group, theoretical calculations of the vibrational spectrum [15] indicate that there are only about four modes that are simultaneously strong in the IR and Raman spectrum in this frequency range. Therefore, such a rich spectrum is likely to come from a superposition of modes from several different adsorbates. Therefore, a detailed assignment of this spectrum is quite difficult for two main reasons: (1) the interaction with the underlying metal can significantly perturb the vibrational resonances of the organic adsorbates, and (2) there are contributions from many possible adsorbates. A tentative assignment of the spectrum of Fig. 1a is given in ref. [15], based on experiments with isotopically labeled ethanol, DFT calculations, and data in the literature, and it is consistent with the presence of several one- and two-carbon molecular fragments. This indicates that the Pt surface is quite reactive and is capable of binding ethanol molecules (and their derivatives) with different adsorption geometries.

Figure 1b–d shows the SFG spectrum for Pt in contact with electrolyte solutions containing the same concentration (0.1 mol L^{-1}) of (B) acetaldehyde, (C) acetic acid, and (D) methanol. Surprisingly, at 0.05 V vs. RHE, the spectra with ethanol, acetaldehyde, acetic acid, or methanol in solution are remarkably similar, suggesting that they all lead to nearly the same set of adsorbed species. This implies that the Pt surface is highly active for breaking the molecules into several possible fragments and also rearranging them since apparently, even methanol is able to give more complex adsorbates containing a C–C bond (suggested by the presence of bands in the $1,015$ – $1,065\text{ cm}^{-1}$, which is a characteristic of C–C stretches [19]; for instance, the C–C stretch of ethanol appears at $1,017\text{ cm}^{-1}$ [19]). This interpretation is consistent with the results of Koper and co-workers [20], who evidenced the formation of ethylene (C_2 species) as a coproduct of carbon dioxide (C_1 species) reduction on copper electrodes. Other studies also support our interpretation about the high activity of the Pt toward breaking molecules into fragments and rearranging them [21, 22]. In particular, a recent SFG study

of ^{13}C -labeled ethanol electrooxidation on Pt shows cleavage of the C–C bond upon electrochemical adsorption [22]. Additionally, by using deuterium labeled reagents, Pastor and Iwasita [21] showed that considerable exchange of H atoms from methyl and hydroxymethyl groups of ethanol occurs upon the electroreduction reaction toward the formation of methane and ethane. Therefore, independent of the original molecule we used, a similar set of adsorbates is obtained at low potentials. It should be mentioned that a very recent SFG study by Braunschweig et al. [23] has investigated acetic acid electrochemical adsorption onto Pt and Au electrodes in this IR frequency range, but they only found adsorbed acetate ions, as in ref. 22 by the same group. We attribute the discrepancies to different experimental methodologies (electrode preparation and SFG spectral acquisition).

On this basis, we suggest that the mechanisms of ethanol, acetaldehyde, acetic acid, and methanol electrooxidation on Pt present similar reaction pathways at low potential. These experimental results are in agreement with density functional theory calculations [24]. Kinetic studies on the reactivity of ethanol and acetic acid over Pt(111) predict that it is possible that the ethanol/Pt(111) and acetic acid/Pt(111) reaction pathways are connected by similar adsorbed intermediates [24]. Although electrooxidation of ethanol, acetaldehyde, acetic acid, or methanol over Pt seems to present similar adsorbates at 0.05 V , the kinetics of these reactions and their final products are relatively different [13, 25, 26]. Probably the reaction intermediates of their electrooxidation on Pt change with increasing applied potential, as previously observed for the electrooxidation of ethanol on Pt [15]. This interesting possibility will be the subject of future studies.

Conclusions

In summary, we have investigated the electrochemical adsorption of ethanol, acetaldehyde, acetic acid, and methanol on polycrystalline Pt at 0.05 V vs. RHE by sum-frequency generation spectroscopy. We have obtained for the first time the complete vibrational spectrum of the adsorbed species in the fingerprint region. Its complexity indicates that each reactant produces several different adsorbates, but the similarity among the spectra for different reactants suggests that a pristine Pt surface is extremely active for bond breaking and rearrangement of the fragments, even at potentials as low as 0.05 V vs. RHE, producing similar adsorbates independent of the original molecules. These results represent a change in paradigm for the role of a metal catalyst in aqueous environment, suggesting that electrochemical reactions on metal surfaces may be much more complex than could be presumed from their reactants and products, taking place with multiple reaction pathways simultaneously. This has important implications to the development of catalysts for fuel cells, for

example. Theoretical calculations with realistic models could perhaps capture this feature and help develop insights to allow a rational optimization of metal catalysts for a given reaction.

Acknowledgments The authors thank FINEP, CNPq, CAPES, and FAPESP for financial support. K.B. acknowledges FAPESP for a post-doctoral fellowship (2005/02284-0).

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