

Sean P. E. Smith · E. Casado-Rivera · H. D. Abruña

Application of differential electrochemical mass spectrometry to the electrocatalytic oxidation of formic acid at a modified Bi/Pt electrode surface

Received: 13 December 2002 / Accepted: 2 April 2003 / Published online: 28 May 2003
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Abstract The design and construction of a differential electrochemical mass spectrometry system is presented. This system has been employed in the study of the reaction products and intermediates during the electrocatalytic oxidation of formic acid on Pt(111) and deliberately stepped platinum surfaces, modified with irreversibly adsorbed Bi (Bi_{ad}).

Keywords Bismuth-modified electrodes · Differential electrochemical mass spectrometry · Electrocatalytic oxidation · Formic acid · Platinum surfaces

Introduction

While the use of conventional electrochemical techniques has yielded important information and insights regarding kinetic and thermodynamic parameters of electrochemical reactions, they are not particularly well suited for determining the identities of the intermediates and products formed from such reactions. Rather, the latter studies have, necessarily, relied on the use of techniques capable of providing molecular identity and composition data.

To this end, there has been an increasing effort at determining the identities of the reaction intermediates and poisons formed during the electrocatalytic oxidation of small organic molecules used as potential fuels in fuel cells [1, 2, 3]. Particular emphasis has been placed on spectroscopic techniques such as FT-IR (in its numerous variants) [4, 5, 6], surface enhanced Raman spectroscopy (SERS) [7, 8], second harmonic generation (SHG) [9, 10], sum-frequency generation (SFG) [11, 12], and others.

Moreover, UHV surface structure sensitive techniques [13, 14] have also been employed. Such information can enhance our understanding of the mechanisms involved in such processes, and, thus, provide further insights towards the development and design of more efficient and effective catalyst materials.

A relatively new and powerful technique that has been developed and applied to the determination of species generated during electrochemical reactions is differential electrochemical mass spectrometry (DEMS). This technique was initially developed by Bruckenstein [15] and later enhanced by Heitbaum [16]. Traditionally, this technique has consisted of an electrochemical cell placed at the inlet to a vacuum chamber connected to a quadrupole mass spectrometer. A porous Teflon membrane, onto which platinum (or silver, gold, or other metals) is typically deposited to a thickness of approximately 60–70 nm, served as both the working electrode and the interface between the electrochemical cell, at ambient pressure, and the vacuum chamber, at pressures as low as 10^{-9} Torr. Volatile and/or gaseous intermediates and products formed during the electrochemical reaction at the electrode permeate through the Teflon membrane and into the mass spectrometer, where the flux of the species can be monitored. In the more recent designs, differential pumping has been employed; hence the designation “differential” in the technique’s name.

The use of DEMS could provide extremely valuable mechanistic insights since it could allow one to correlate final products (and their distribution) as a function of electrode surface structure and composition, electrode potential, and charge consumed. Moreover, the judicious use of isotopic labeling could provide additional insights. It is just such information that is necessary for postulating plausible mechanistic pathways, which can then be tested. This will, in turn, provide a rational basis for the design of more effective catalysts.

More recently, DEMS experiments have been applied to studies involving smooth and single-crystal electrodes [17]. As above, a Teflon membrane is still employed as the interface between the electrochemical cell and the

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

S. P. E. Smith · E. Casado-Rivera · H. D. Abruña (✉)
Department of Chemistry, Baker Laboratory,
Cornell University, Ithaca, NY, 14853-1301, USA
E-mail: hda1@cornell.edu

mass spectrometer chamber. However, rather than depositing a metal film on the Teflon membrane, a smooth or single-crystal electrode is arranged in a thin-layer configuration against the membrane. Again, volatile and/or gaseous intermediates and products formed during the electrochemical process will be pulled through the membrane into the mass spectrometer. The very short delay times that can be achieved (< 1 s) for the detection of species in the mass spectrometer allow for the electrode potential to be slowly swept during the reaction, giving potential-dependent species-formation data in real time. This technique, then, provides virtually unambiguous and transient identification of species generated during electrochemical reactions.

Despite the potentially vast amount of information that can be obtained from DEMS, only a relatively small number of groups have applied this technique to the determination of reaction mechanisms and reaction products and intermediates. Baltrusch et al. [18, 19] used DEMS to study the products from the electrocatalytic hydrogenation and desorption of benzene from polycrystalline and single-crystal platinum electrodes, making use of H–D exchange to facilitate the determination of the reaction mechanism. DEMS has also been used to study the identity of the strongly adsorbed residue that forms upon methanol and formic acid adsorption on polycrystalline platinum and platinum/ruthenium dispersed electrodes [20, 21, 22], as well as the products that form upon the oxidation of several species, including ammonia [23], various alcohols and small organic molecules [24, 25, 26, 27, 28, 29], and unsaturated hydrocarbons [30, 31], primarily on polycrystalline platinum and gold and platinum/ruthenium dispersed electrodes. The degradation of organic carbonate electrolyte solutions from lithium-ion batteries has also been studied by DEMS, showing the varied practical applications of this technique [32]. More recently, Hillier [33] has incorporated a scanning capability with a SECM, allowing for studies of heterogeneous electrodes as well as compositionally modulated surfaces. This last example would have clear application in combinatorial screening of electrocatalysts.

We present the design of a DEMS system for the purpose of studying the reaction products and intermediates produced during the electrocatalytic oxidation of small organic molecules, with emphasis on materials that can be employed as fuel cell fuels. Specifically, we present preliminary results of the products from the electrocatalytic oxidation of formic acid on Pt(111) and deliberately stepped platinum surfaces, modified with irreversibly adsorbed Bi (Bi_{ad}). The electrocatalytic oxidation of formic acid at Bi-modified platinum surfaces is one that has been studied extensively in the past and thus represents an attractive model system [40, 41, 42, 43].

When employing polycrystalline Pt surfaces, this system has also been shown to exhibit, under specific experimental conditions, complex oscillatory behavior in the current [38, 39]. However, under our experimental conditions, such phenomena were not observed. In

addition, it is not the intention of the present study to investigate such phenomena.

Experimental

DEMS setup

Cell

The electrochemical cell used in the DEMS experiments (Fig. 1a) consisted of a Teflon block (4.8 cm \times 3.2 cm \times 4.4 cm) into which three holes were drilled to hold the three electrodes and the solution. A closed UHV flange with a hole drilled through the center, into which a stainless steel frit was inserted, served as the bottom of the electrochemical cell. The frit's function was to support the membrane, which was an ethylene-tetrafluoroethylene copolymer membrane (Scimat 200/40/60) or a PTFE membrane (Gore-Tex). The Scimat membrane had a mean thickness of 60 μm , a mean pore size of 0.17 μm , and a porosity of 50%. The Gore-Tex membrane had a mean thickness of 75 μm and a mean pore size of 0.02 μm . The electrochemical cell was press fitted onto the membrane-flange assembly, with the membrane serving as the interface between the mass spectrometer main chamber at high vacuum and the electrochemical cell at atmospheric pressure.

Single-crystal platinum ball electrodes and deliberately stepped surfaces were prepared by the Clavilier method [34]. After flame annealing, they were pressed into a Teflon plunger in order to isolate the desired single-crystal face. This assembly was then inserted into the top of the electrochemical cell, so that the electrode formed a thin-layer configuration against the membrane. Also inserted through the top of the cell were the reference, counter electrodes, and the electrolyte solution. In the case of single-crystal electrodes, a PdH electrode, made by evolving hydrogen at a palladium wire, was used as reference. Its potential was calibrated against an Ag/AgCl reference electrode after every experimental run. Gaseous and/or volatile products produced during the ensuing electrochemical experiments were transported through the Teflon membrane to the main chamber and, ultimately, flowed into the analysis chamber of the mass spectrometer, where they were analyzed.

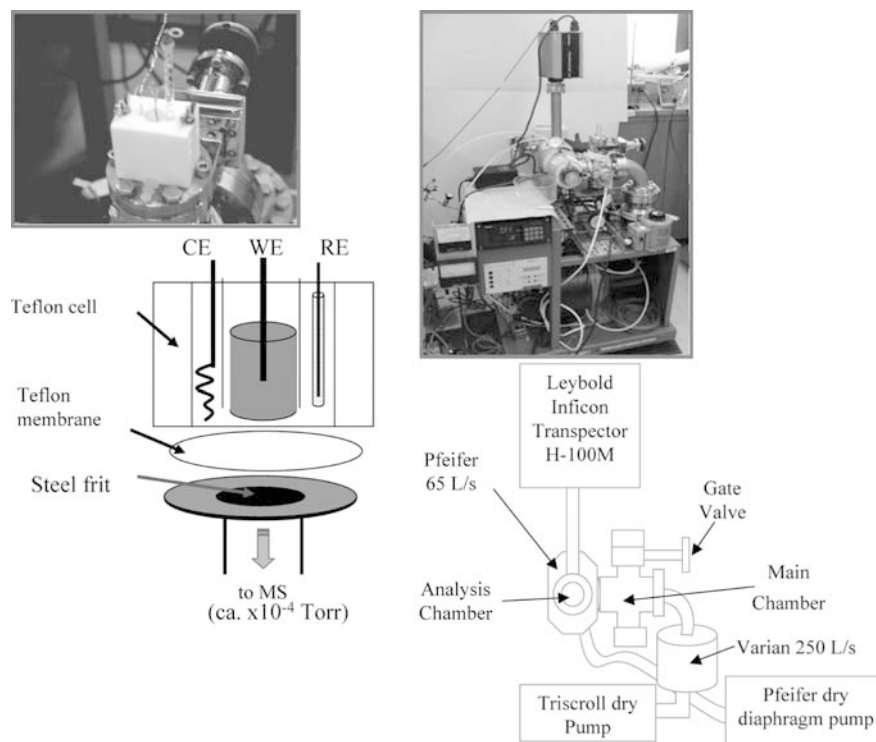
All solutions were prepared with water purified with a Millipore Milli-Q System (18 $\text{M}\Omega\text{ cm}^{-1}$). Acid electrolyte solutions were prepared with the appropriate dilutions of sulfuric acid (Baker ULTREX Ultrapure). Formic acid electrolyte solutions were prepared by diluting formic acid (Fisher, 88%, certified ACS grade) in the sulfuric acid electrolyte. All solutions were degassed for at least 20 min prior to the beginning of the experiments with high-purity nitrogen (4.5 N), which was further purified by passing through oxygen and hydrocarbon traps. Procedures for electrode preparation as well as modification with irreversibly adsorbed Bi (Bi_{ad}) were as described previously [35, 36].

DEMS instrumentation

Figure 1b presents a picture of the DEMS experimental setup and a schematic of the chambers of the mass spectrometer. The main chamber was pumped by a Varian 250 l/s turbomolecular pump, which was backed by a Varian Triscroll dry pump, in order to avoid contamination from oil vapors. In the absence of electrochemical experiments, this chamber was isolated from the membrane-flange assembly via a gate valve, and had a base pressure of approximately 1×10^{-9} Torr. During the electrochemical experiments, the pressure in the main chamber typically reached 10^{-4} Torr, primarily due to the high water vapor background partial pressure from the electrolyte.

Owing to the high pressure in the main chamber during the electrochemical experiments, the mass spectrometer analysis chamber was, itself, differentially pumped by a Pfeiffer 65 l/s turbomolecular pump backed by a Pfeiffer dry diaphragm pump, again to avoid contamination from oil vapor. In addition, this

Fig. 1 Left: electrochemical cell; right: DEMS setup



chamber was isolated from the main chamber through a pressure converter (Leybold Inficon IPC2A), which reduced the pressure from the main chamber via an orifice. However, when the pressure in the latter chamber was less than 10^{-4} Torr, it could be opened completely to allow for the direct sampling of the main chamber.

The quadrupole mass spectrometer (Leybold Inficon Transpector H-100M) was connected to the analysis chamber and contained a Channeltron Electron multiplier/Faraday cup detector with a sensitivity of 100 A/Torr. The time constant of the mass spectrometer was in the millisecond regime, but, in the DEMS setup, was slower due to the diffusion of the gaseous and/or volatile molecules through the membrane. Nevertheless, the time constant still remained considerably less than one second, allowing for the measurement of the mass intensity of a product as a function of the varying electrode potential at slow sweep rates (e.g. 2 mV/s), resulting in the collection of a mass spectrometric cyclic voltammogram (MSCV) in real time.

A demonstration of the time constant of the mass spectrometer is shown in Fig. 2, in which a water/acetone solution was injected into the DEMS cell, and the peak corresponding to acetone ($m/z = 58$) was monitored as a function of time (Fig. 2a). At approximately 7 min, the solution in the cell was replaced with water, and the decay in the signal was immediately apparent. Figure 2b shows this decay, with the replacement of the acetone solution occurring at approximately 1 s on this time scale. While the duration of the signal decay lasted approximately 5 s, this was on the order of the time scale that was required to replace the acetone solution. It was shown previously, moreover, that the delay time for the detection of nitrogen upon arresting its flow through the DEMS setup was on the order of 12 ms [16].

Results and discussion

Formic acid oxidation at bismuth-modified single-crystal platinum electrodes

We have previously carried out extensive studies of the electrocatalytic oxidation of formic acid on bare and

bismuth-modified deliberately stepped platinum surfaces with (111) terraces of varying width and monatomic (110) [35] or (100) steps [36]. The use of platinum surfaces is advantageous since the voltammetric profile provides unambiguous information as to which sites are blocked (modified) and the extent of such blockage (modification). Moreover, the Bi adlayer on the (111) terraces has a well-defined redox response, which can also be employed in a diagnostic way providing additional information.

The data from those studies suggest that, for Bi-modified deliberately stepped platinum surfaces, the electrocatalytic activity increases significantly once the step sites are blocked/modified with Bi. In addition, the electrocatalytic activity for stepped surfaces is dependent on both the terrace width and the nature of the step with current densities, being higher for surfaces with (110) steps [relative to (100) steps] as long as they are modified with Bi. Moreover, whereas for Bi-modified deliberately stepped Pt surfaces the electrocatalytic current increased with increasing step density, for the unmodified surfaces the currents were not only significantly smaller, but also the trend was completely opposite. That is, the current decreased with increasing step density. We have employed the DEMS system described above to study the electrocatalytic oxidation of formic acid at Bi-modified Pt single crystals and deliberately stepped surfaces.

Figure 3 shows a cyclic voltammogram for formic acid oxidation at a Bi/Pt(111) ($\Theta_{\text{Bi}} = 0.27$) electrode along with the simultaneous monitoring of the intensity at $m/z = 44$, which corresponds to CO_2 . As can be seen, the mass spectrometric response tracks the

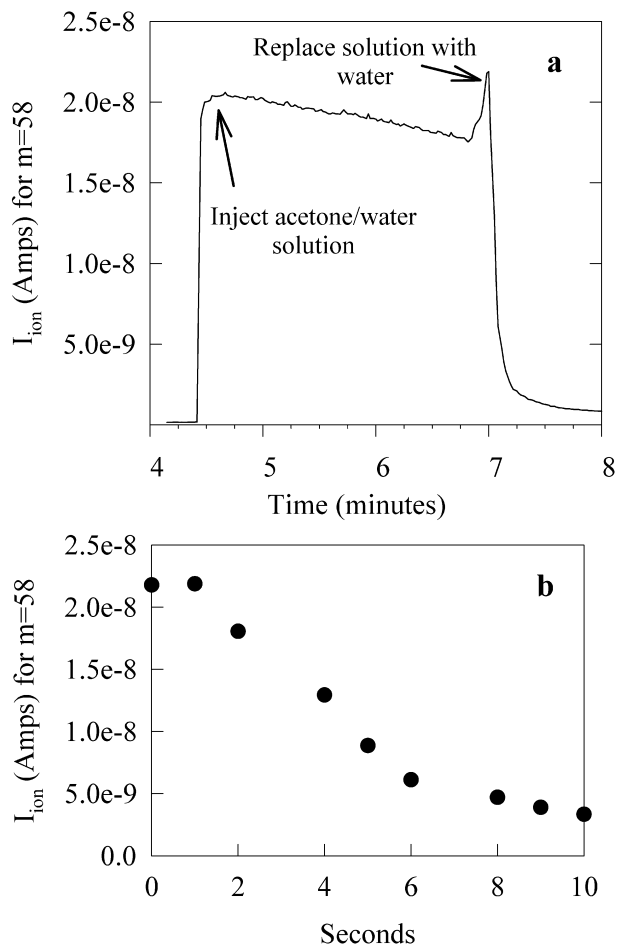


Fig. 2 **a** Detection of acetone ($m/z=58$) upon the injection of a water/acetone solution in the DEMS electrochemical cell as a function of time, and **b** the decay time of the acetone peak upon replacing the solution with water

electrochemical response with virtually no time lag. Moreover, the features in the voltammetric scans are reproduced in the ion intensity profile. Except for the mass peak associated with CO_2 , no other reaction products were detected, besides those associated with the molecular fragments and the isotope and double-ion contributions of CO_2 . These results are also in accordance with work by Weaver et al. [37], who employed vibrational spectroscopy.

It is clearly evident in Fig. 3 that the mass intensity for the detection of CO_2 (Fig. 3b) in the mass spectrometer closely follows the voltammetric profile (Fig. 3a). This not only shows that the voltammetric response arises from the production of CO_2 from the direct oxidation of formic acid and/or the oxidation of the surface poison, but also shows the very short delay time of the mass spectrometer. Moreover, the sensitivity of the mass intensity to the splitting of the peaks in the voltammetric profile is clearly evident here, and more so for the analogous case on bismuth-modified Pt (755), as shown in Fig. 4.

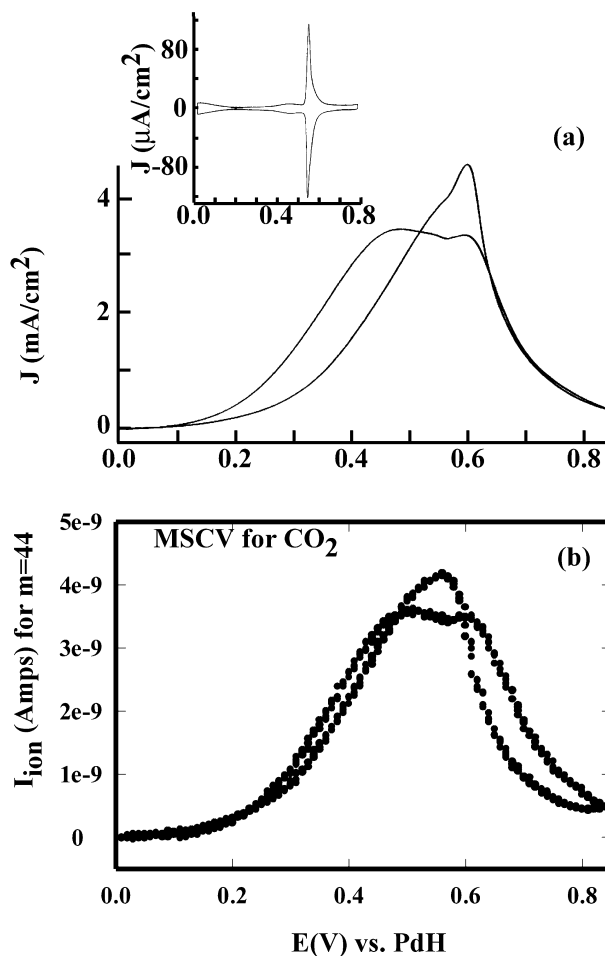


Fig. 3 **a** Voltammetric profile in 0.25 M $\text{HCOOH}/0.1$ M H_2SO_4 (sweep rate, 2 mV/s) of Bi/Pt(111); bismuth coverage, 0.27; *inset* shows the voltammetric profile in 0.1 M H_2SO_4 . **b** The mass spectrometric cyclic voltammogram (MSCV) for the detection of CO_2 ($m/z=44$) from the above electrode

Figure 5 shows an analogous experiment for a Bi/Pt (221) electrode with all step sites blocked with Bi and a coverage of Bi on the terraces of 0.04. Again, there is a clear correlation between the electrochemical and mass spectrometric responses. Closer inspection reveals the presence of a sharp feature in the voltammetric scan (see arrow) that has no counterpart in the ion intensity profile. Such a voltammetric feature has been previously observed and it was speculated to be due to the rearrangement of anions. The fact that no peak in the ion current profiles is observed is consistent with this and provides additional mechanistic information.

It should be emphasized that these data were obtained on a single voltammetric scan at a slow (2 mV/s) sweep rate. This, combined with the complementary spectroscopic information of FT-IR measurements, will provide a wealth of information on the reaction pathways involved, which will, in turn, be extremely useful for providing mechanistic details. Moreover, our DEMS instrument has the capability of monitoring 18 different masses simultaneously, which will allow us to follow the

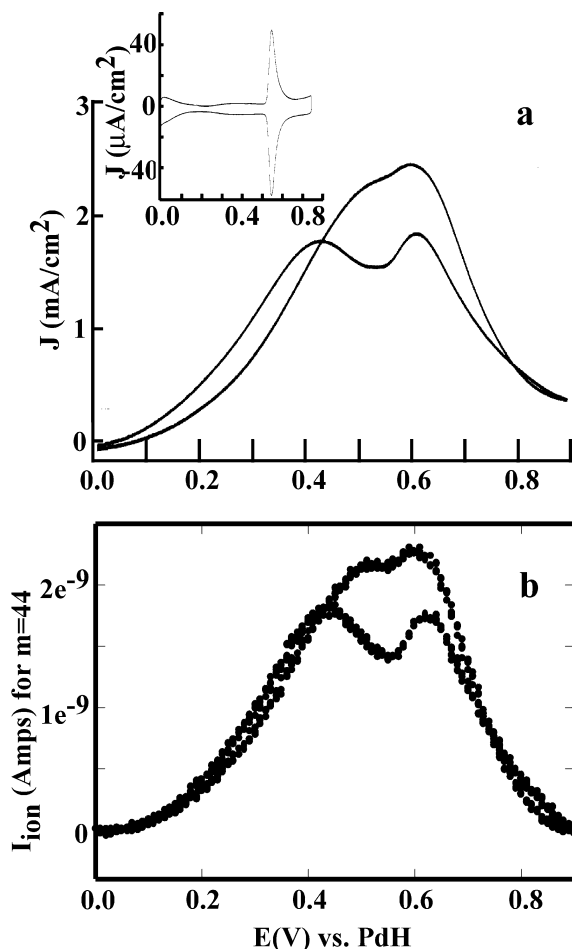


Fig. 4 a Voltammetric profile in 0.25 M HCOOH/0.1 M H₂SO₄ (sweep rate, 2 mV/s) of Bi/Pt(755); bismuth coverage, 0.20 on the (111) terraces with the (100) steps blocked with bismuth; *inset* shows the voltammetric profile in 0.1 M H₂SO₄. **b** The MSCV for the detection of CO₂ ($m/z=44$) from the above electrode

generation (and quantification) of virtually all postulated reaction products.

Conclusions

The coupling of a mass spectrometer to an electrochemical chamber has been shown to result in the ability to detect, in real time, the products formed during electrochemical reactions as a function of the applied potential. Results show that the voltammetric responses observed for Bi-modified deliberately stepped platinum surfaces arise from the production of CO₂ from the direct oxidation of formic acid and/or the oxidation of the surface poison. Moreover, the sensitivity of the mass intensity to the splitting of the peaks in the voltammetric profiles and the very short delay time of the mass spectrometer were clearly evident.

This is precisely the type of information that will be needed for the further advancement of determining the mechanisms of electrochemical and, specifically,

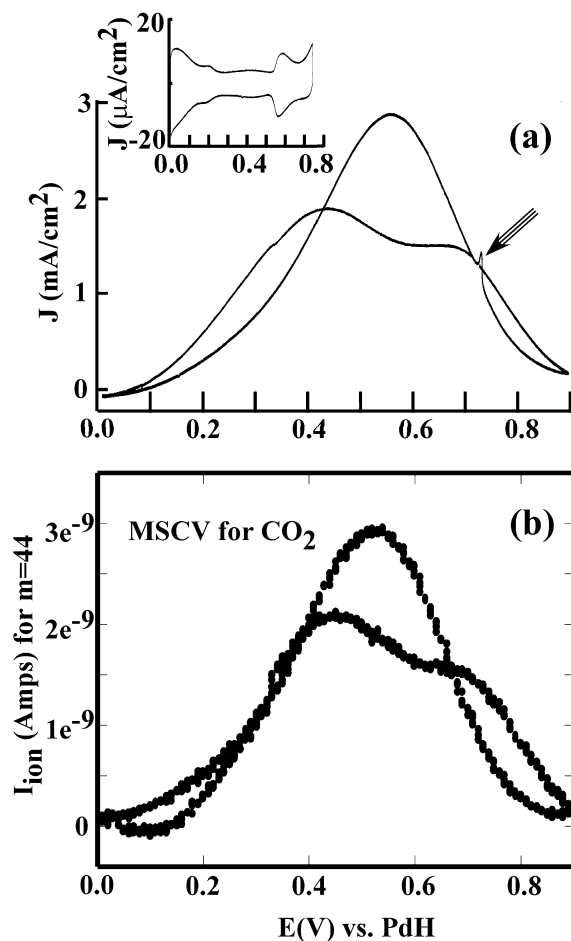


Fig. 5 a Voltammetric profile in 0.25 M HCOOH/0.1 M H₂SO₄ (sweep rate, 2 mV/s) of Bi/Pt(221); bismuth coverage, 0.04 on the (111) terraces with the (110) steps blocked with bismuth; *inset* shows the voltammetric profile in 0.1 M H₂SO₄. **b** The MSCV for the detection of CO₂ ($m/z=44$) from the above electrode

electrocatalytic reactions such as those involved in fuel cells.

Acknowledgements This work was supported by the National Science Foundation and the Office of Naval Research. E.C.-R. acknowledges support by a Provost's Diversity Fellowship from Cornell University. We also gratefully acknowledge the help and support by Prof. R. Vielstich and Prof. T. Iwasita during the early parts of this work.

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