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On-line mass spectrometry system for measurements at single-crystal electrodes in hanging meniscus configuration

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Abstract

We present the construction and some first applications of an On-line electrochemical mass spectrometry system for detecting volatile products formed during electrochemical reactions at a single-crystal electrode in hanging meniscus configuration. The system is based on a small inlet tip made of porous Teflon and a Peek holder, which is brought in close proximity (ca. 10–20 μm) to the electrode surface. The tip is connected to the mass spectrometer by glass and metal tubing. Because of the small amount of gas entering the mass spectrometer, no differential pumping is needed during the measurement. The tip construction and preparation introduced here leads to reproducible voltammetry with very good cleanliness characteristics. The presence of the tip has no significant influence on the blank voltammetry of a Pt(111) in sulfuric acid, and on voltammetric responses for CO adlayer oxidation, methanol oxidation, and hydroxylamine electrochemistry on Pt(111). The formation of gaseous products in these reactions can be followed accurately and is in good agreement with earlier results obtained by other mass spectrometric or spectroscopic techniques. The time response and tailing of the setup is on the order of seconds and mainly determined by the distance between the tip and the electrode.

1. Introduction

On-line mass spectrometry of volatile species involved in electrode reactions is a technique first introduced in electrochemistry by Bruckenstein and Gadde in 1971 [1]. It was subsequently extended and perfected, most notably by the groups of Heitbaum and Baltruschat [2–10], and it is now a routine technique utilized by many groups worldwide. It is the method of choice when on-line quantitative determination of gaseous products during an electrochemical reaction is required, and has proved extremely useful in the study of many electrochemical processes. The technique is commonly termed Differential Electrochemical Mass Spectrometry (DEMS), on account of the differential measurement of the amount of products formed, and uses a differential pumping system to pump down the large amount of solvent (typically water) that would otherwise enter the detection system.

In the original system proposed by Heitbaum, DEMS was used only in combination with electrodes of large surface area, a condition imposed by the rather high detection limit. However, several groups have developed electrochemical cell constructions that allow DEMS to be used in combination with low surface area electrodes, single-crystal electrodes in particular. Baltruschat et al. [7, 10] have developed a flow cell with two compartments connected by a number of capillaries: the working electrode is in the first compartment, whereas the inlet to the mass spectrometer is in the second compartment. Abruna et al. [11] recently described a setup in which the single-crystal electrode is essentially laid on top of a teflon membrane supported by a steel frit that provides the entrance to the mass spectrometer. A disadvantage inherent to both these approaches is that the single-crystal electrode is not studied in its usual configuration, namely the hanging meniscus. In 1994, Kita et al. [12] showed that a teflon-film covered pinhole, some several micrometer in diameter, in contact with the electrode in hanging meniscus mode, enabled detection of gaseous products during the oxidation of acetylene on platinum single-crystal electrodes. Some 10 years later, the tip-based approach introduced by Kita et al. was taken further by Hillier's group [13, 14], who used a membrane covered capillary inlet as the basis of a Scanning DEMS by scanning the probe some 100 μm above the surface of a multi-electrode system. A possible disadvantage of this tip-based setup, as indicated recently by Baltruschat

[7], may be the complex diffusion pattern between the electrode and the tip, leading to “a complicated time dependence and larger response times.” From a more practical point-of-view, we found that, in our attempts to reproduce Kita’s results, it can be very difficult to produce tip-membrane configurations that lead to good, sensitive and reproducible mass responses, and that obtaining (blank) voltammograms that would be of acceptable quality to the electrochemical single-crystal community is a matter that needs thorough attention. Kita et al. did not address these issues, but the voltammogram for CO oxidation on Pt(110) displayed in their Figure 2(a) would suggest that they may have had problems of a similar kind.

In this paper, we report on an on-line mass spectrometry system, based on the approaches of Kita and Hillier, that employs a porous teflon-based tip that can be used to probe gaseous product formation by placing it very close (10–20 μm) to a single-crystal electrode in hanging meniscus configuration. As a first step towards making this setup generally applicable, we have managed to construct tips that produce reproducible mass responses, and combine high sensitivity with reasonable response times. Importantly, the setup leads to very acceptable (blank) voltammetry of the platinum single-crystal electrodes, even when the tip is in very close proximity to the electrode surface. Considering that a sufficiently small amount of gas enters the mass spectrometer system to render differential pumping unnecessary, the technique would be more appropriately called on-line electrochemical Mass Spectrometry (MS) (note that Bruckenstein, in his original paper [1], does not refer to on-line detection but rather to “*in situ*” detection). The design and the details of our on-line electrochemical MS setup will be discussed, and examples of its sensitivity and time response will be illustrated on the examples of carbon monoxide adlayer oxidation, methanol oxidation, and hydroxylamine oxidation and reduction, all at a Pt(111) bead-type electrode. The latter system has not been studied with on-line mass spectrometry before. Elsewhere, we have demonstrated the versatility of the tip-based approach by using on-line electrochemical MS for studying gaseous product formation during nitric oxide reduction on a flat pyrolytic graphite electrode onto which heme groups were immobilized [15].

2. Experimental setup

As illustrated schematically in Figure 1(a), the on-line electrochemical MS setup consists of a mass spectrometer (MS) system, measuring tip, micrometer positioning system, video camera, electrochemical cell, potentiostat and software for measuring the masses simultaneously with the electrochemical parameters. The mass spectrometer is a Balzers Quadrupole (QMS 200) with Quadstar software. The masses are recorded using the analog output of the mass spectrometer. A Leybold turbo molecular pump together with a Leybold trivac D4B prepump make the vacuum. During measurement, the pressure inside the MS must be smaller than 5×10^{-6} mbar.

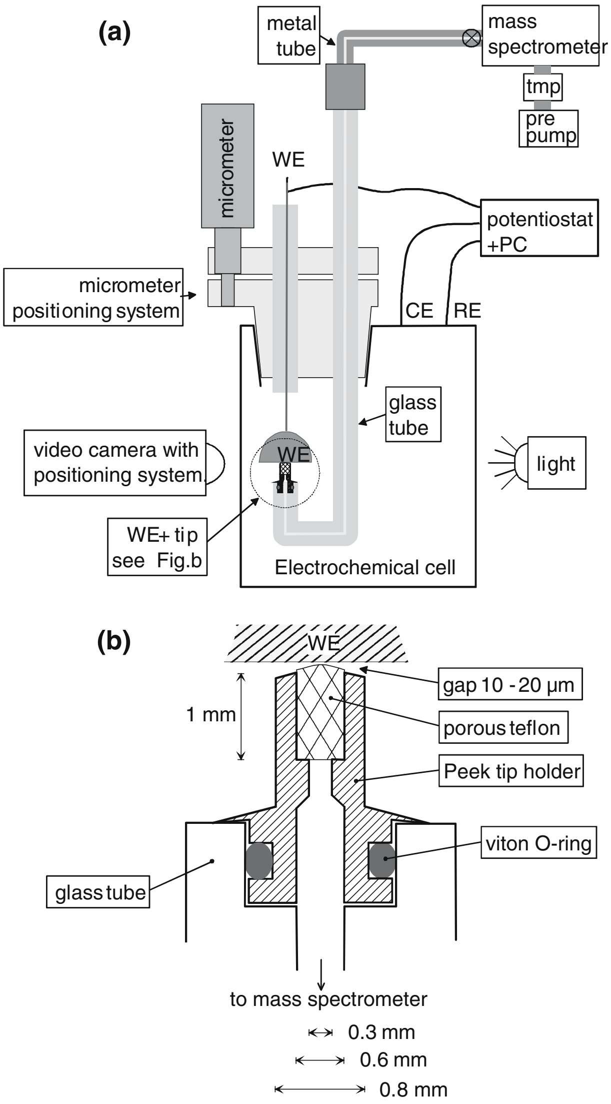

Fig. 1. (a) Schematic drawing of the on-line electrochemical MS setup. WE – Working Electrode, RE – Reference Electrode, CE – Counter Electrode, tmp-turbo molecular pump. (b) Schematic drawing of the on-line electrochemical MS tip.

The small inlet tip (Figure 1(b)) is constructed from porous Teflon (Mupor Ltd.) of 10 μm pore size, a PEEK holder and a glass tube, joined directly to the mass spectrometer with flexible metal tubing. The porous Teflon is a small cylinder of 0.65 mm diameter, squeezed into the PEEK holder, which has a diameter of 0.60 mm. In order to avoid leakage of the Teflon-holder configuration, it is important that the porous Teflon cylinder is perfectly smooth. The inner diameter of the complete inlet system from tip to MS is 0.6 mm. The pore size of the Teflon is also an important factor, although we found that the optimal pore size depends on the Teflon supplier. In our case, the measured signals were too low below 5 μm pore size, and too high for 30 μm pore size.

The electrode-tip assembly is positioned with the aid of a micrometer system (Mitutoyo, 0–25 mm, with a resolution of 10 μm) mounted on two Teflon blocks, which can be placed on the cell. The Teflon blocks have two holes for the working electrode (WE) and the glass vacuum tube, both fixable with plastic screws. During positioning, the distance between the tip and the electrode is monitored using a black and white camera with magnifying lenses and a periscope. It is mounted on a stand, which is adjustable in all directions over a range of a few cm, and which can overturn somewhat to place the camera view in the same plane as the plane of the electrode. The magnification is 50 times and is imaged on a CCTV black and white monitor. Any experiment starts by placing the single-crystal electrode in meniscus mode and measuring the voltammetry in ''tip-retracted'' mode. Next, the electrode is dropped into solution and the tip is placed at ca. 10–20 μm distance from the electrode surface with the help of the micrometer system and the video camera, without touching the electrode surface. Finally the electrode and tip are fixed and are placed simultaneously in hanging meniscus configuration.

The potentiostat used is an Autolab PGSTAT 12 from Ecochemie. Simultaneously with the electrochemical parameters, the vacuum pressure inside the mass spectrometer and maximum four masses are recorded. The electrochemical cell is made of glass and is essentially the same as the cells we use for normal single crystal measurements except for the placement of the working electrode (bead-type single crystal, 2 mm in diameter), which is close to the side of the cell such that the positioning can be followed by the video camera. Glassware is cleaned by boiling in a mixture of concentrated H_2SO_4/HNO_3, whereas the entire tip configuration is cleaned in chromic acid. Both glassware and tip configuration were boiled repeatedly in ultra pure water (Millipore, Milli-Q grade) before use. Solutions were also prepared with Millipore water. Reference electrode employed was $Hg/HgSO_4$, but all potentials are referred to RHE.

Figure 2 shows some photographs of the system as currently used in our laboratory.

3. Results and discussion

3.1. *Carbon monoxide adlayer oxidation on Pt(111)*

Prior to each experiment, the cleanliness of the system and the influence of the tip is checked by recording a blank cyclic voltammogram (BCV) of the Pt(111) electrode in the absence and presence (close proximity) of the tip. The resulting BCVs are shown in Figure 3. The cleanliness of the system is indeed very adequate and, significantly, the presence of the tip has virtually no

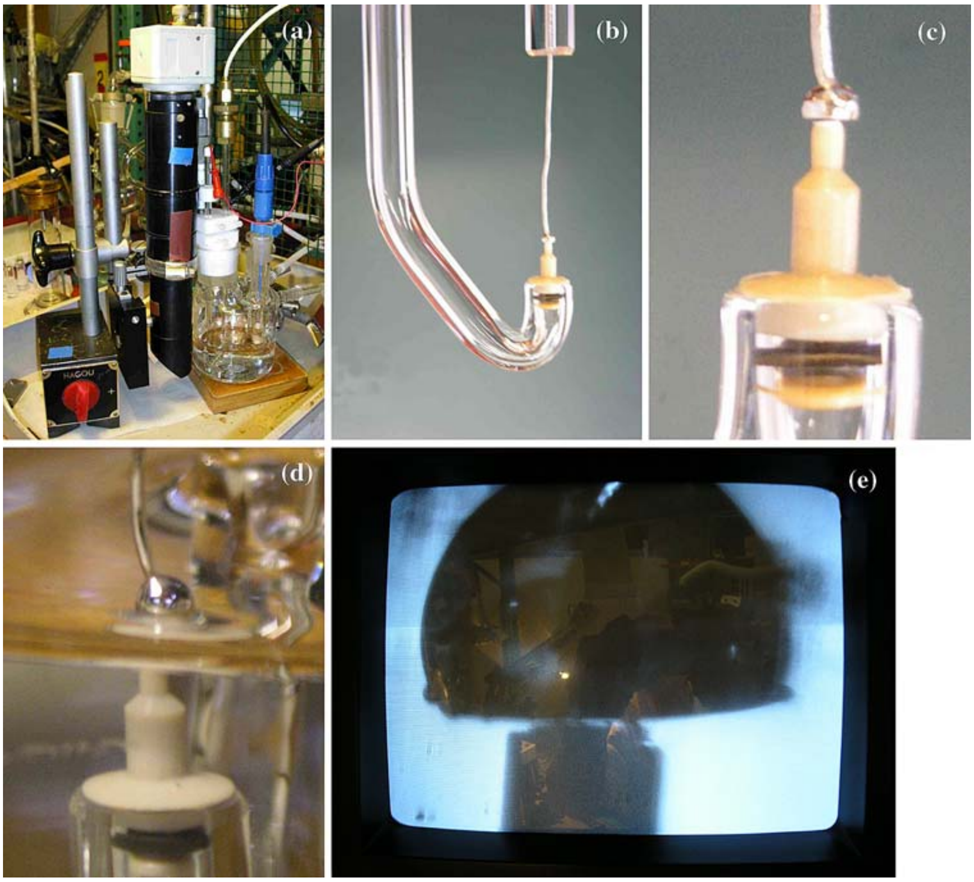

Fig. 2. Photographs of (a) electrochemical cell with the tip configuration and connection to the MS. (b) and (c) Tip – bead-type electrode configuration, (d) tip-electrode in hanging meniscus, (e) view of the tip-electrode configuration on the video screen.

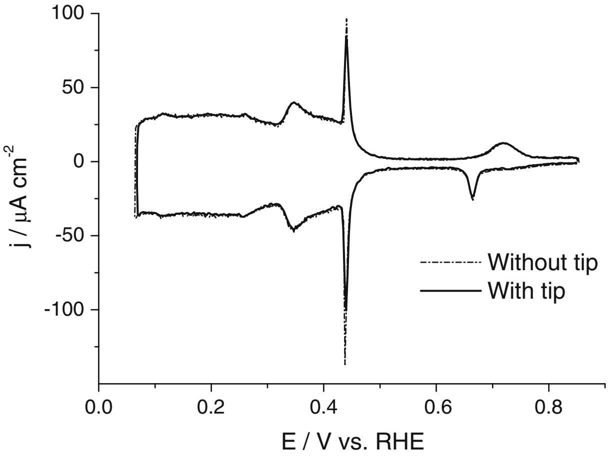

Fig. 3. Blank voltammetry of a Pt(111) electrode in 0.5 M H_2SO_4, 50 mV/s, with the on-line electrochemical MS tip retracted and with the tip in close proximity (10–20 μm) to the electrode.

effect on the quality of the CVs recorded. The maximum current of the characteristic well-developed sharp "butterfly" peak at 0.45 V decreases only slightly when the tip is brought in close proximity of the surface, but satisfies the criteria of system cleanliness proposed by Lebedeva et al. in both cases [16]. Also the small amounts of (110) and (100) defects, visible as the two small peaks in the hydrogen adsorption/desorption region at 0.125 and 0.27 V [17] are largely unaffected by the presence of the tip.

Carbon monoxide adlayer stripping from Pt(111) is the paradigmatic experiment to test the performance of the on-line electrochemical MS setup. It would also serve as a calibration experiment for detecting CO_2, following the procedure outlined by Baltruschat [7]. A monolayer of CO was adsorbed on the electrode in meniscus mode by blowing CO over the electrolyte solution, the electrode and tip were introduced into the solution, followed by flushing the electrolyte with argon for 15 min in order to remove CO from solution. Next, the electrode was positioned close to the on-line electrochemical MS tip, and brought into meniscus mode again. The resulting stripping voltammogram and recorded mass at a scan rate of 2 mV/s are shown in Figure 4. The shape of the CO oxidation peak agrees well with stripping curves recorded previously in our laboratory [16], even if the potential at which the peak is located is shifted to lower potentials as a result of the lower scan-rate. The stripping is complete, as concluded from the clean blank voltammetry obtained after the stripping experiment.

The signal detected by the mass spectrometer shows the expected formation of CO_2 (*m*/*z* 44, most intensive ion of CO_2) as the potential is increased. Comparing CV to the mass signal shows that there is a delay of ca. 10–15 s between the CO oxidation peak and the peak in the recorded mass. This delay results from both the time response of the system (the initial time until a response is measured) and the associated tailing, related to the time dependence of the response. Similar delay times were reported for the tip-based setups of Kita [12] and Hillier [13]. The time delay results from the fact that the CO_2 formed requires some time to diffuse through the electrolyte and the Teflon membrane before it reaches the mass spectrometer. Slow transport is also the cause of the tailing visible for the mass signal for high potentials. In general, we find that the delay time depends on the distance of the tip from the electrode surface as well as on the mass of the detected species, but not on the thickness of the porous Teflon plug or on the length of the tubing connecting the tip to the mass spectrometer. Therefore, achieving a better and more accurate control over the tip-electrode separation should lead to further improvements of the time response and tailing of our system.

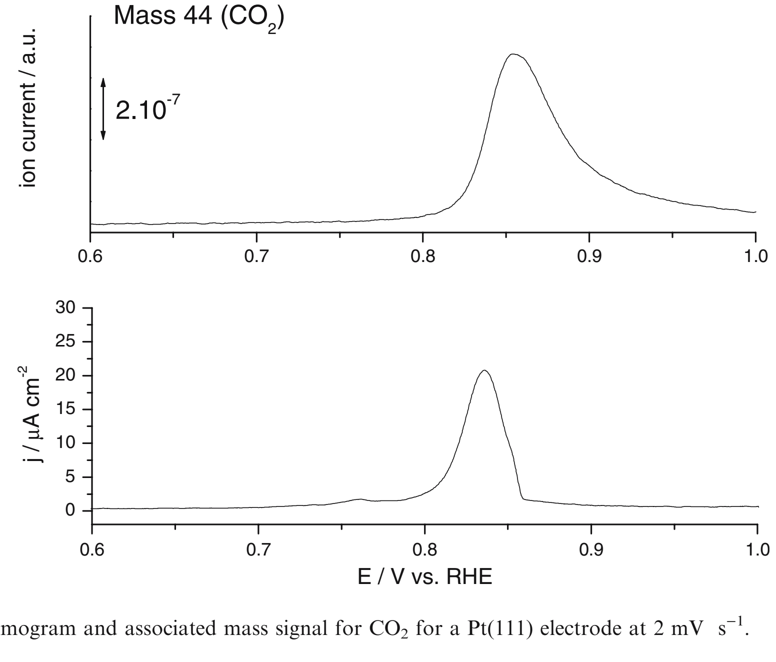

Fig. 4. CO stripping voltammogram and associated mass signal for CO_2 for a Pt(111) electrode at 2 mV s^{-1}.

3.2. *Methanol oxidation on Pt(111) and polycrystalline Pt*

The on-line electrochemical MS was also tested on the oxidation of methanol on single- and polycrystalline platinum electrodes. As shown in Figure 5, the influence of the tip on the cyclic voltammogram in 0.1 M MeOH is small. The cyclic voltammogram for methanol oxidation on Pt(111) at a scan-rate of 2 mV s^{-1} and the corresponding masses *m/z* 44 (CO_2) and *m/z* 60 (methylformate) are shown in Figure 6(a), (b). The figure demonstrates that on Pt(111) a small but detectable amount of methylformate is formed, implying the existence of a "direct pathway" in which species such as formic acid and formaldehyde are formed [18]. More detailed measurements on the oxidation of methanol on single-crystal platinum electrodes probed with the on-line electrochemical MS will be published elsewhere [19].

A similar experiment performed on a bead-type polycrystalline platinum electrode shows that, apart from CO_2 also mass 60 can be recorded (see Figure 7), indicating that on this surface the activity of the parallel pathway is greatly enhanced as compared to Pt(111) (as was also suggested from the DEMS experiments by Wang et al. [20]).

3.3. *Hydroxylamine electrochemistry on Pt(111)*

As a final example, we recently studied in some detail the electrochemistry of hydroxylamine (HAM) at polycrystalline platinum [21] and single-crystalline platinum [22]. One of the oxidation products found was nitrous oxide N_2O. Figure 8 shows a cyclic voltammogram corresponding to the electrochemical transformations of HAM at a Pt(111) electrode in a perchloric acid solution. The solid line corresponds to the voltammetry recorded with the tip retracted; the dotted line corresponds to the tip being in close proximity (ca. 10–20 μm) to the surface. In agreement with our results for the blank voltammetry, CO adlayer oxidation, and methanol oxidation, the tip is found to have a negligible influence on the electrochemical response of reactions for which no diffusion limitations occur.

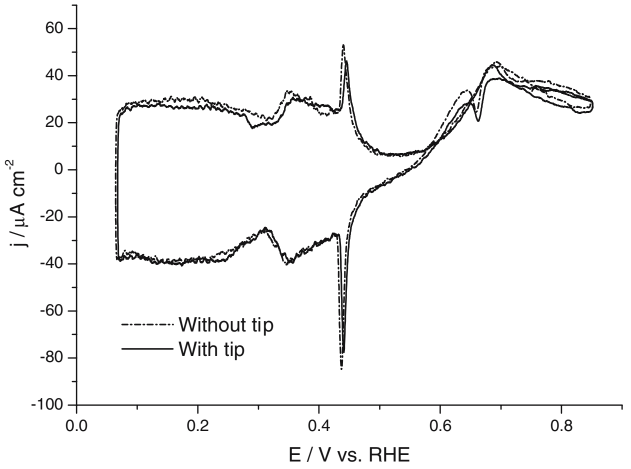

Fig. 5. Cyclic voltammogram for 0.1 M methanol in 0.5 M H_2SO_4, 50 mV s^{-1}, with the tip retracted and with the tip in close proximity to the electrode.

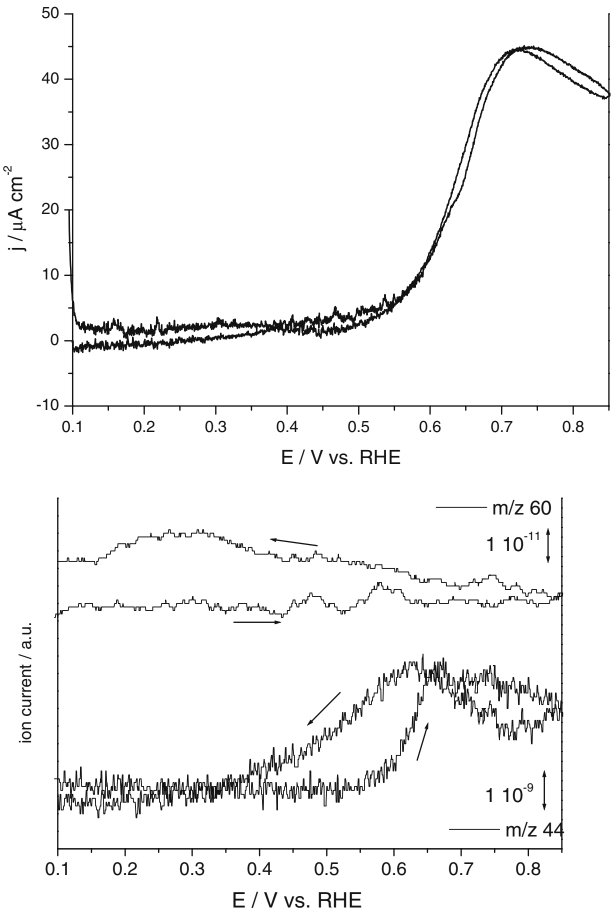

Fig. 6. Voltammetry and associated mass signal for CO_2 (*m/z* 44) and methylformate (*m/z* 60) for 0.1 M methanol in 0.5 M H_2SO_4 at a Pt(111) electrode at 2 mV s^{-1}.

Without going in to the mechanistic details of HAM electrochemistry, we briefly reiterate our interpretation of Figure 8, based on more extensive electrochemical measurements and *in situ* FTIR spectroscopy [22]. Starting at 0.06 V and scanning in the positive direction, the reduction feature E_{R4}^{111} at ca. 0.3 V corresponds to the reduction of HAM to ammonia. Feature E_{R4}^{111} is partially overlapped with feature E_{O1}^{111} at 0.5 V, which corresponds to electro-oxidation of HAM to adsorbed nitric oxide (NO_{ads}). Anodic feature E_{O2}^{111} was assigned to oxidation of the NO adlayer to the adsorbed HNO_2 [22], presumably initiating a reaction between the nitrite formed and HAM. The negative-going scan of the CV in Figure 9 is quite different from the positive-going scan; it exhibits three features (E_{R1}^{111}, E_{R2}^{111} and E_{R3}^{111}), which were shown to correspond to the reductive stripping of saturated (or subsaturated, in case of a lower upper potential limit) NO adlayer [22]. Most significantly for our purposes here, the formation of a small but significant amount of nitrous oxide (N_2O) was observed

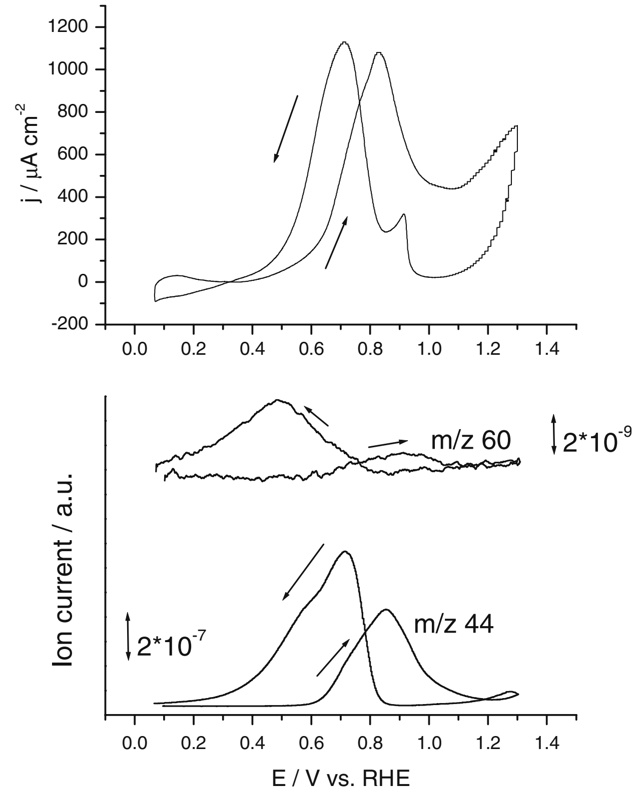

Fig. 7. Voltammetry and associated mass signal for CO_2 (*m*/*z* 44) and methylformate (*m*/*z* 60) for 0.1 M methanol in 0.5 M H_2SO_4 at a polycrystalline electrode at 2 mV s^{-1}.

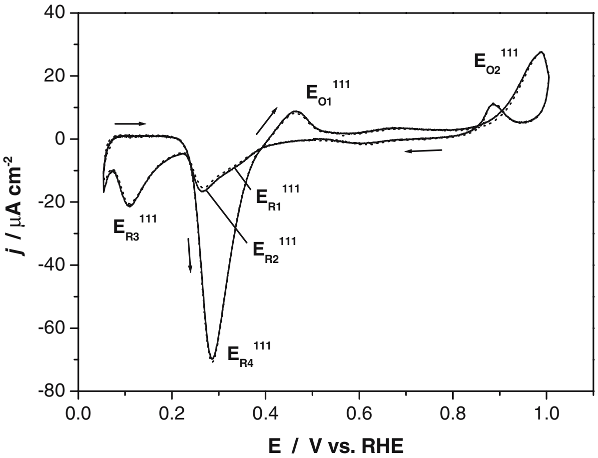

Fig. 8. Electrochemical reduction and oxidation of NH_2OH at a Pt(111) electrode in 0.5 M perchloric acid; the tip far away from the surface (solid line) and close to the electrode surface (dotted line). Experimental conditions: 20 × 10^{-3} M NH_2OH; potential sweep rate 5 mV s^{-1}; starting potential 0.06 V.

spectroscopically starting at potentials as low as ca. 0.4 V. Interestingly, no nitrous oxide was observed in sulfuric acid solution, suggesting the involvement of adsorbed intermediates in the mechanism of N_2O formation.

Figure 9 shows the so-called mass spectrometric cyclic voltammograms (MSCV) for selected *m*/*z* ratios, as recorded in perchloric acid solution. In good accordance with our previous infrared experiments [22], the formation of N_2O (*m*/*z* 44) is observed during the positive-going scan in the potential region between ca. 0.45 and 0.85 V. This formation of N_2O was tentatively explained by a surface reaction, possibly between NO_{ads} and HAM or, alternatively, NO_{ads} and products of partial dehydrogenation of HAM. The further mass signal increase at more positive potentials and subsequently during the negative-going scan coincides with the anodic peak E_{O2}^{111}, thus indicating a second source of N_2O formation, which is most probably a reaction between nitrite formed and HAM. The fragmentation-corrected signal for *m*/*z* 30 (NO) clearly indicates the production of a significant amount of NO in solution at potentials as low as ca. 0.6 V with a maximum at ca. 0.85 V. Significantly, solution NO was not observable with FTIR [22]. The negative-going scan (reversed at ca. 1 V) shows a similar peak-like feature, though with a positive shift of ca. 100 mV. The detection of NO in solution may be tentatively assigned to (i) partial desorption of NO adlayer and (ii) (homogeneous) decomposition of nitrite to NO. We note that we did not observe the formation of N_2, a species that IR cannot detect. Also, in agreement with our earlier studies, in sulfuric acid solution no N_2O formation was observed at Pt(111), whereas NO is observed, but in much smaller quantities than in perchloric acid.

4. Concluding remarks

In this paper, we have presented the construction and some first applications of an on-line electrochemical Mass Spectrometry system for detecting volatile products formed during electrochemical reactions at a single-crystal electrode in hanging meniscus configuration. The on-line electrochemical MS system is based on a small inlet tip made of porous teflon, which is brought in close proximity (ca. 10–20 µm) to the electrode surface. Because of the small amount of gas entering the mass spectrometer, no differential pumping is needed. As a major advancement over previous setups, the tip construction and preparation introduced here leads to reproducible voltammetry with very good cleanliness characteristics, even if the tip is within 20 µm from the surface. The presence of the tip has no significant influence on the blank voltammetry of a Pt(111) in sulfuric acid, and on voltammetric responses for CO adlayer oxidation, methanol oxidation, and hydroxylamine electrochemistry on Pt(111). Note that these are all reactions that are not limited by mass transport. The influence of the presence of the tip on mass transport-limited reactions still needs to be assessed. The time response of the on-line electrochemical MS setup is similar to previous tip-based approaches, and mainly determined by the distance between the tip- and the electrode, which suggests that some significant improvements by improving control over the tip-electrode separation may be expected in the future. The examples considered in the paper also illustrate the utility of the

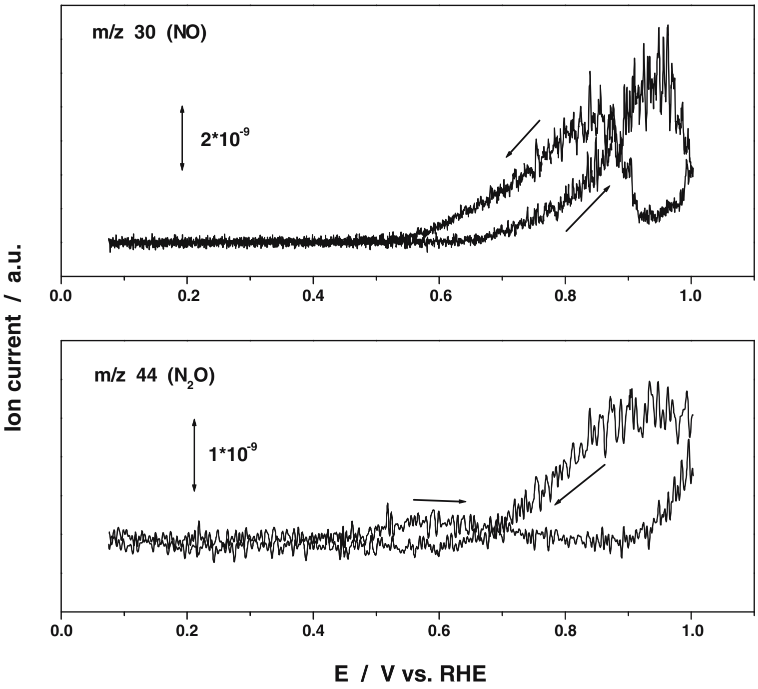

Fig. 9. Mass signals measured for NO and N_2O during cyclic voltammetry of hydroxylamine on Pt(111) in 0.5 M perchloric acid (see Figure 8). Experimental conditions: 20 × 10^{-3} M NH_2OH; potential sweep rate 2 mV s^{-1}; starting potential 0.06 V.

new on-line electrochemical MS setup in studying electrocatalytic surface reactions at single-crystal electrode surfaces.

Acknowledgement

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