

CO_{AD} COVERAGE AND CURRENT EFFICIENCY OF METHANOL OXIDATION STUDIED BY DEMS AND POTENTIAL STEP

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in: Direct Methanol Fuel
Cells, S. Narayanan, T.
Zawodzinski, S. Gottesfeld
(eds), Electrochemical
Society Proceedings,
Pennington 2001, PV 2001-4,
p. 50 – 60

ABSTRACT

The determination of the current efficiency for CO₂ formation during formaldehyde oxidation on Pt under forced convection yields values of 20 to 50 %. The independence of flow rate is interpreted by a parallel path mechanism. The rate of CO₂ formation is given by the rate of adsorbate oxidation, which is independent of coverage.

Ru as a cocatalyst does not only lead to an increased oxidation rate of the adsorbate, but also to an increased adsorption rate, probably due to electronic effects. This explains the markedly increased current efficiency in the presence of Ru.

INTRODUCTION

Despite its importance for fuel cells, there seems to be no general agreement about the mechanism of methanol oxidation on Pt electrodes. Whereas recent experiments showed that methanol oxidation takes place at potentials well below the onset of the oxidation of adsorbed CO, and were also interpreted on the basis of a complete oxidation of methanol to CO₂ at these potentials (1-3), DEMS experiments showed that CO₂ is only formed at potentials at which also adsorbed CO is oxidized(4).

We therefore reexamined product formation during the electrooxidation of methanol using a DEMS equipment with a high sensitivity and by exactly quantifying the observable products CO₂ and methylformate and the faradaic current.

EXPERIMENTAL

The experiments were performed with a QMG 511 quadrupole mass spectrometer and a DEMS setup as described in (5). For some experiments, a porous Teflon membrane with a sputter deposited 50 nm Pt layer was used as the electrode in a conventional DEMS cell. For most experiments, a newly designed dual thin layer cell (6) was used (fig. 1). Here, a massive Pt electrode forms the wall of a first thin layer cell. The

electrolyte flows constantly from this cell into a second thin layer cell, in which a porous teflon membrane (70 μm thickness, porous width 0.02 μm), mechanically supported by a steel frit, forms one of the walls and simultaneously the interface to the vacuum system. The flow rate is adjusted by a peristaltic pump.

Small coverages of Ru on polycrystalline platinum were achieved by depositing Ru at 0.6V (RHE) for 5 min. from $5 \cdot 10^{-3}\text{M}$ RuCl_3 in 0.5M H_2SO_4 . A coverage of 25 to 35% should thus be achieved(7). As a control, the actual Ru coverage on polycrystalline platinum was determined using the method of Motoo(8).

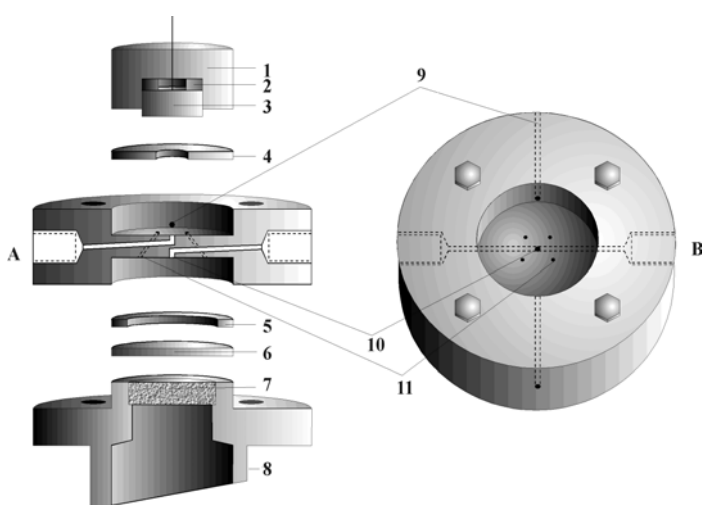


Fig.1. Dual thin-layer flow-through cell (Kel-F). 1, Kel-F holder; 2, Kalrez tightener; 3, electrode; 4 and 5, Teflon tighteners; 6, porous Teflon membrane; 7, stainless steel frit; 8, stainless steel connection to the vacuum system and the mass spectrometer; 9, capillaries for flushing with Ar; 10, inlet-outlet capillaries; 11, connecting capillaries. (A) Side view of Kel-F body of the cell; (B) top view of the cell

RESULTS AND DISCUSSION

It has been shown before that not only CO_2 , but also methylformate is produced during methanol oxidation and can be well detected by DEMS. This is shown by the cyclic voltammogram (CV) and mass spectrometric cyclic voltammogram (MSCV) for $m/z=44$ (CO_2) and $m/z=60$ (methylformate) in fig. 1, which were obtained at a much higher sensitivity than those published before. It can be clearly seen now that (in the anodic sweep) formation of methylformate, which is formed from formic acid and methanol, starts well below that of CO_2 . This effect is even more pronounced when using HClO_4 as the supporting electrolyte as in fig. 2 than when using sulfuric acid (cf. ref. (9)). A peak in the ion current for $m/z=60$ is visible at 0.75 V, whereas for the $m/z=44$ signal and the faradaic current only a shoulder is visible.

The use of the thin layer cell also allowed us to quantify the amount of CO_2 and methylformate: The average current of methylformate is only 1/40 that of CO_2 (as compared to 1/27 in sulfuric acid under otherwise identical conditions). The current efficiency for CO_2 , as given by the ratio of charge due to formation of CO_2 from methanol according to Faraday's law to the experimental change is with 30% identical to that in sulfuric acid for the averaged complete cycle. This means that 70% of the current are

used for the formation of other species, most probably formaldehyde and formic acid, which cannot be detected by DEMS. Methylformate is not just a by-product, but since it is most probably formed in a reaction between formic acid and methanol, an indicator of the former species. This is also indicated by the fact that at 1.2 V the ion current for CO₂ drops to zero, whereas both the faradaic current and the signal for methylformate are significant. Please note the additional shoulder at 0.5 V in the first sweep (inset of fig. 2), which is due to the adsorption of methanol. The shift for the usual adsorption peak potential at 0.3 V observed in 0.1 M HClO₄ is due to the higher acid concentration.

In the cathodic sweep, methylformate is still produced at potentials where the signal for CO₂ already decreases to zero. This effect, which is more drastic in sulfuric acid, is not due to the time constant of the detection, since at a flow rate of 5 μL/s and a volume of the thin layer cell of 15 μL, the time constant is 3 s (which was experimentally verified by varying the flow rate), corresponding to only 30 mV.

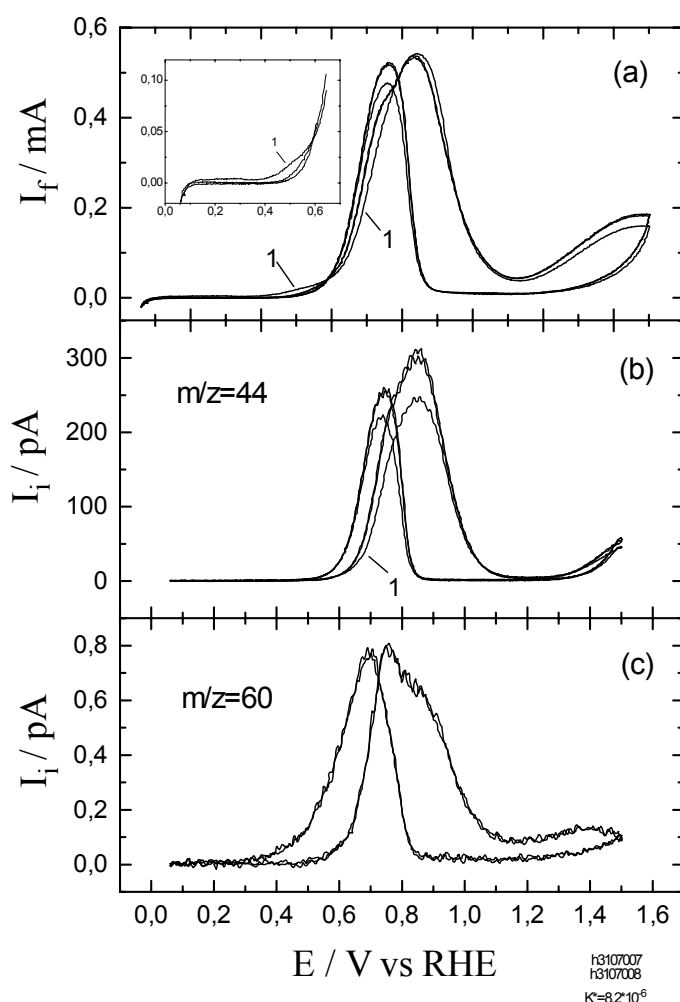


Fig. 2. Simultaneously recorded CV (a), MSCV for $m/z=44$ (b) and MSCV $m/z=60$ (c) on smooth polycrystalline Pt in 0.1M methanol + 0.5M HClO₄ solution. Scan rate: 10mV s⁻¹, electrolyte flow rate: 5μL s⁻¹. 3 cycles are shown, “1” indicates the first cycle. Inset: expanded view of the faradaic current at low potentials.

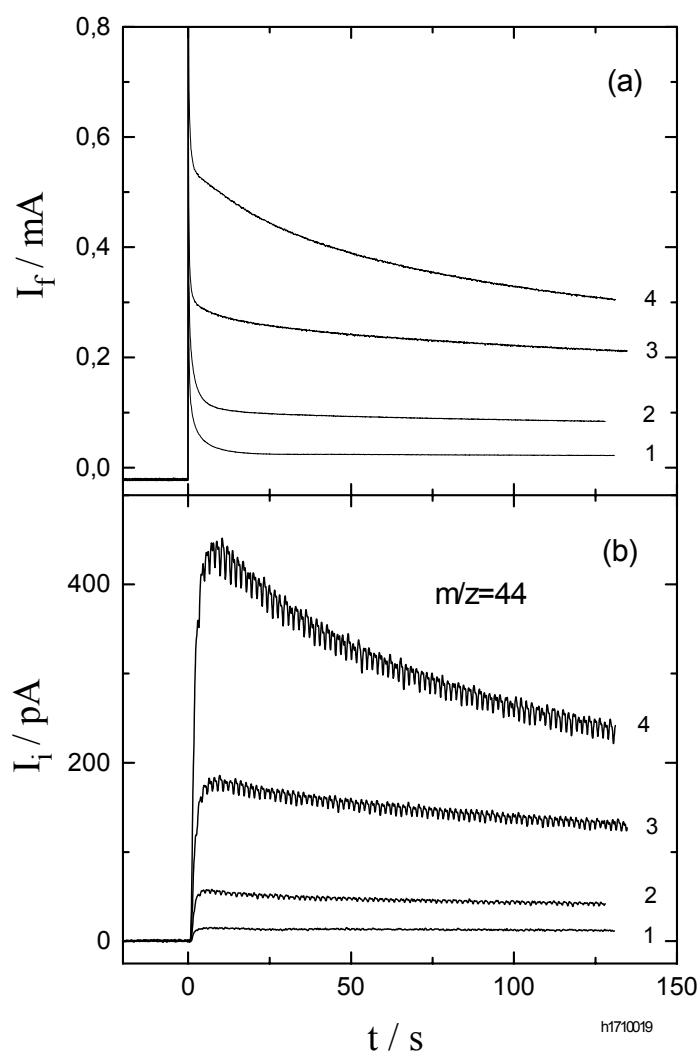
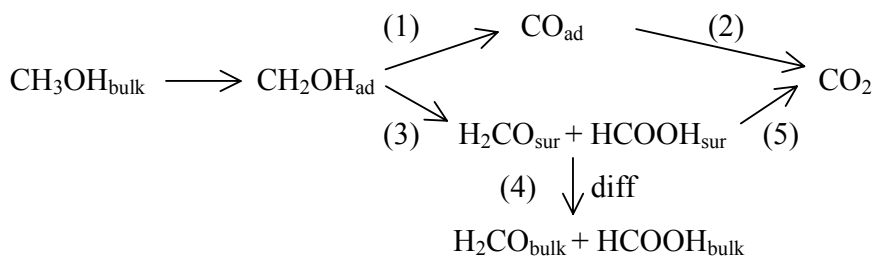


Fig. 3. Simultaneously recorded transients of faradaic current (a) and ion current $m/z=44$ (b) on smooth polycrystalline platinum in 0.1M methanol + 0.5M H_2SO_4 solution after the step of potential from 0.05V to E_{step} . (1) $E_{step} = 0.6V$, (2) $E_{step} = 0.65V$, (3) $E_{step} = 0.7V$, (4) $E_{step} = 0.8V$. Electrolyte flow rate: $5\mu L s^{-1}$.

In order to obtain more detailed information on the potential dependence of the methanol oxidation under stationary conditions, we performed potential step experiments, some of which are shown in fig. 3. As shown in the subsequent table, a variation of the flow rate over more than one order of magnitude does not have an influence on the current efficiency.

This independence of the current efficiency on the flow rate shows that the dissolved products (formaldehyde and formic acid) are not intermediates under these conditions, i.e. they do not react further to CO_2 because of their fast diffusion away from the electrode. If they reacted with a rate comparable to their diffusion, the current efficiency would strongly depend on the flow rate or be 100%. Of course, if there is no convection

at all, diffusion is so slow that these species react as well. These results therefore suggest a parallel path mechanism:



Here, the current efficiency is determined by the ratio of the reaction rates via step (1) and (3). Alternatively, the results can be interpreted by a reaction sequence

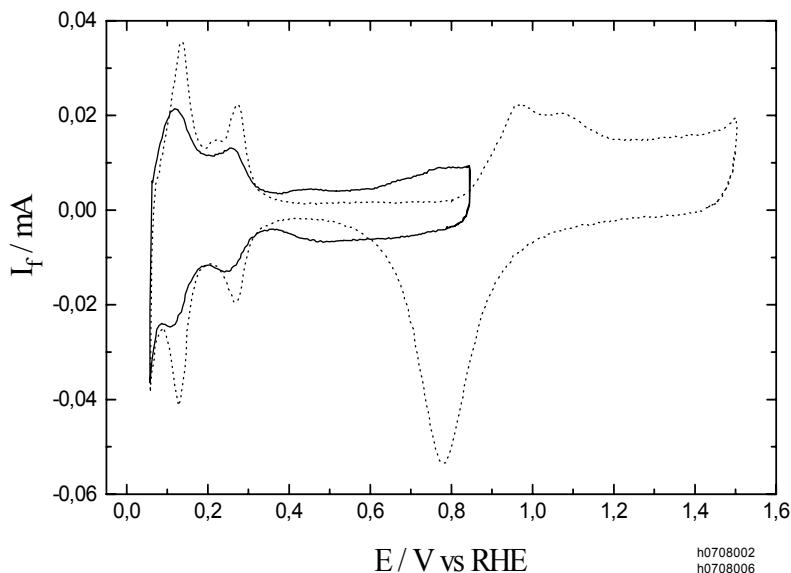
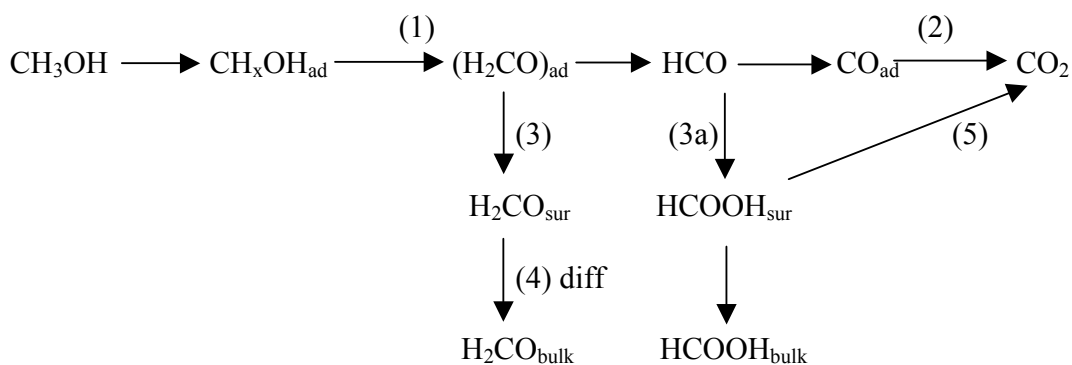


Fig.4. Cyclic voltammogram of Ru modified smooth polycrystalline platinum ($\vartheta_{\text{Ru}} \approx 0.35$) (—) in 0.5M H_2SO_4 solution. Scan rate: 50mV s⁻¹. For comparison the cyclic voltammogram of smooth polycrystalline platinum (.....) is also shown.

Here, the current efficiency under strong convection is determined by the ratio of the desorption rates to the oxidation rate of CO_{ad} . Here, the parallel paths only occur in the last sequence of steps. Theoretically, instead of reaction (5) also a back adsorption (reverse of (3a)) might occur in the absence of convection; however, this is very unlikely, since this would be a reductive adsorption followed by oxidation. Alternatively, one might also discuss reversible desorption of CO_{ad} as HCOOH (instead of (3a) and (5)), but this reaction has never been observed.

Fig. 4 shows the cyclic voltammogram of Ru modified polycrystalline Pt in 0.5M H_2SO_4 solution. Compared to pure Pt, due to Ru the double layer charge becomes larger because of OH adsorption / desorption, while the hydrogen adsorption/desorption peaks are diminished.

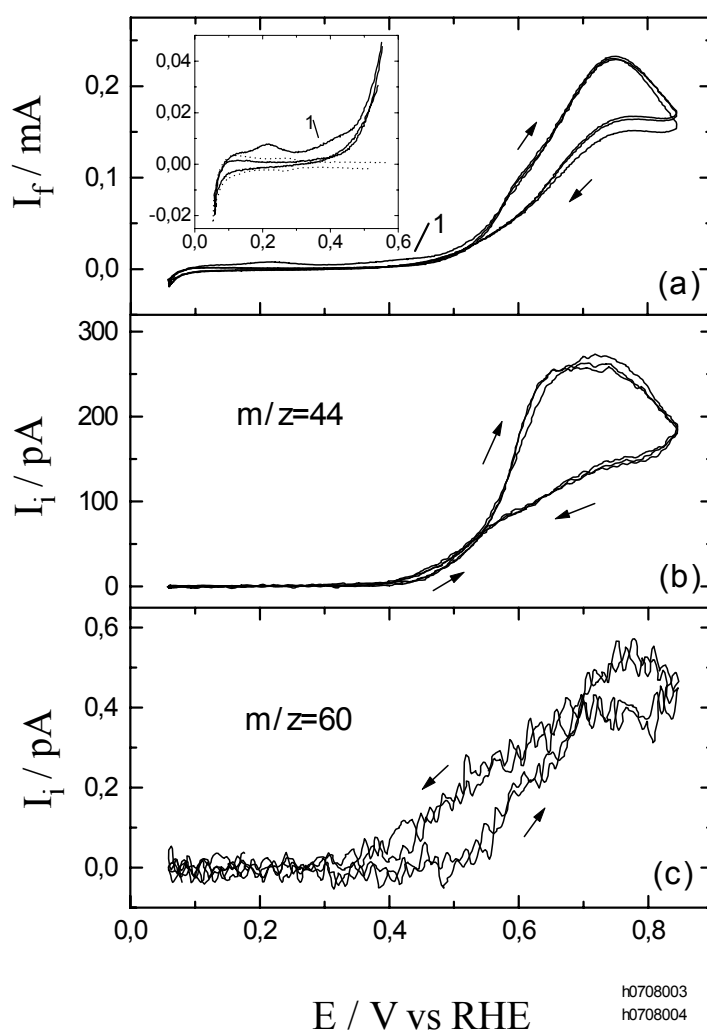


Fig. 5. CV (a) and MSCV for $m/z=44$ (b) and 60 (c) on Ru modified smooth polycrystalline platinum ($\theta_{\text{Ru}} \approx 0.35$) in 0.1M methanol + 0.5M H_2SO_4 solution at 10 mV s^{-1} , electrolyte flow rate: $5 \mu\text{L s}^{-1}$. (.....):CV in 0.5M H_2SO_4 solution. Inset is an expanded view of the faradaic current in the low potential range.

The cyclic voltammogram for methanol oxidation on such a Ru modified polycrystalline platinum in 0.1M methanol+0.5M H₂SO₄ solution and the corresponding mass spectrometric cyclic voltammograms for $m/z = 44$ (CO₂) and $m/z = 60$ (methylformate) are shown in fig. 5. In the first sweep a peak at 0.22 V and a shoulder at 0.4 V are observed, which are not paralleled by the formation of CO₂. Therefore, as in the case of pure polycrystalline Pt, it is due to the oxidative adsorption of methanol. But compared with Pt, the adsorption of methanol occurs at a more negative potential. Since methanol is not reactive at pure Ru, it must be assumed that a combined effect of Pt and Ru promotes the rate of formation of the adsorbate. Therefore, in addition to the bifunctional mechanism active for the oxidation of adsorbed CO, there is another cocatalytic effect of Ru. This effect is examined in more detail below.

The formation of CO₂ on Ru modified polycrystalline platinum starts at 0.4V, i.e. over 150mV more negative than that on polycrystalline platinum. At the potentials of above 0.65V the ion intensity for CO₂ does not continually increase, whereas the faradaic current and ion intensity for methylformate increase continuously until 0.75V. The formation of methylformate starts at 0.5V, which is same as the case of polycrystalline platinum, but increases steeper directly above 0.5V. At higher potentials, the relative amount ratio of methylformate to CO₂ is larger than at low potentials (0.6 V). The average amount ratio of methylformate to CO₂ in a cycle is 1:46. The average current efficiency for CO₂ reaches to 39%. It is independent of the flow rate.

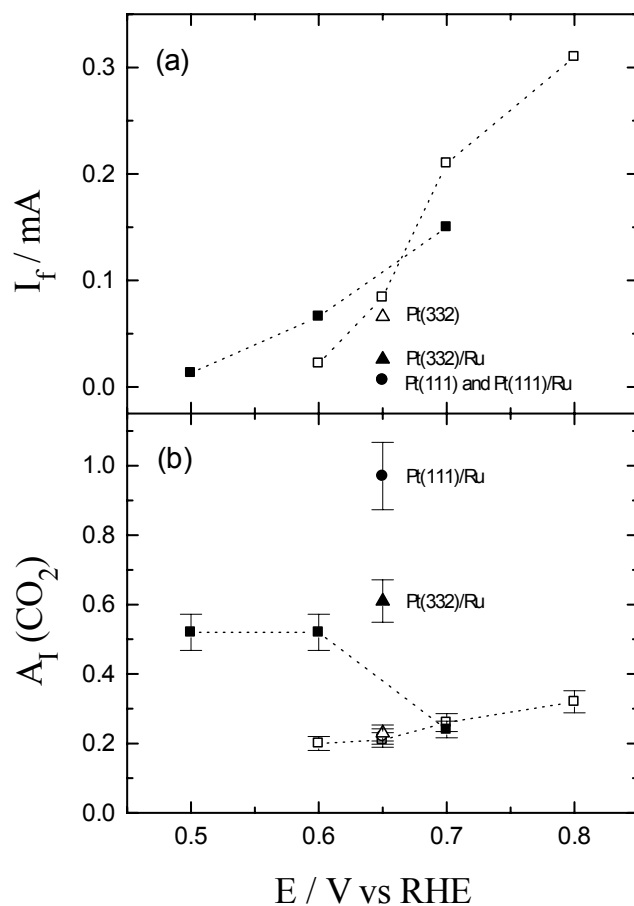


Fig. 6. Potential dependence of the faradaic current and the current efficiencies for Pt and Ru modified Pt. Also included are values for single crystal electrodes.

We also performed similar potential step experiments as in fig.3 on this surface. Compared to unmodified polycrystalline Pt, at 0.6 V the faradaic current and also the current efficiency (52%) is larger. The absolute amount of methylformate is also larger, but only 2% that of CO₂ (compared to 10% in the case of Pt).

In fig. 6, the current efficiencies as a function of the potential are compared for Pt and Ru modified Pt. Please note that for pure Pt, the current efficiency does not depend on the surface structure. The current efficiency for the Ru modified electrode drops at higher potentials (0.7 V) to the same value as that on pure Pt. Above this potential, also the faradaic current on PtRu is lower than on pure Pt. Ru loses its cocatalytic properties because oxygen is too strongly bound.

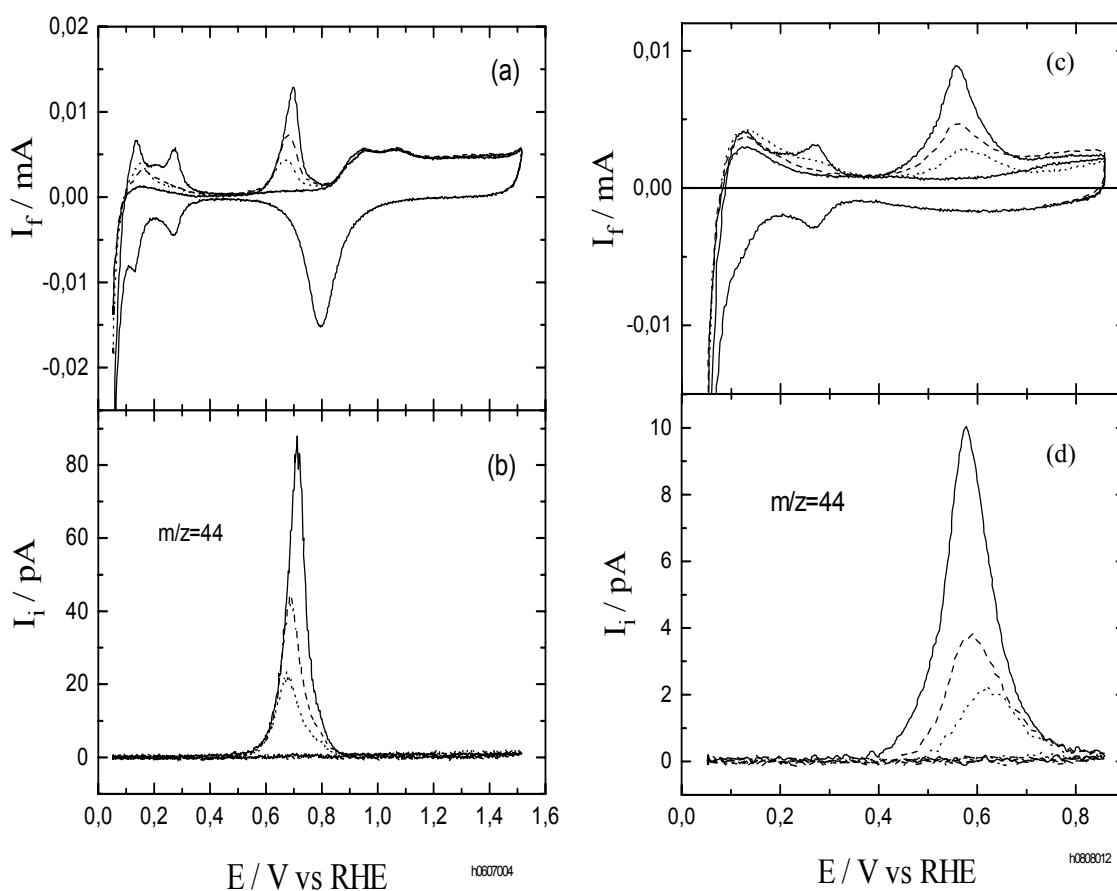


Fig. 7. CV(a) and corresponding MSCV of CO₂ (b) during oxidation of the methanol adsorbate on smooth Pt in 0.5M H₂SO₄ solution. Methanol adsorption for 2 minutes at 0.5V (—), 0.3V (·····), 0.7V (-----). Scan rate: 10mV/s, flow rate of electrolyte: 5 μ L/s..

(c) and (d): same for Ru modified Pt ($\theta_{Ru} \approx 0.35$), 0.4V (—), 0.7V (·····), 0.2V (-----)

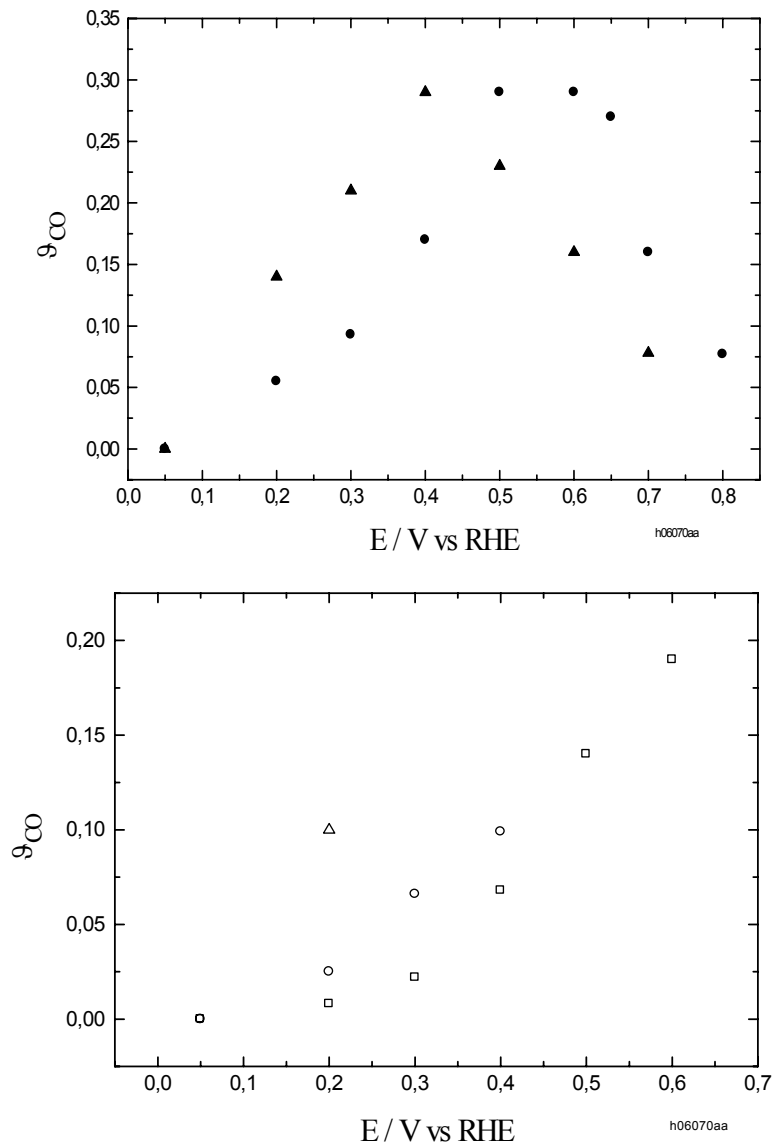


Fig. 8. (a) saturated coverages (CO molecules per Pt sites) at different adsorption potentials on smooth polycrystalline Pt (●) and Ru modified Pt ($\theta_{Ru} \approx 0.35$) (▲). The adsorption of methanol was carried out for 2 minutes. (b). same as (a) for an adsorption time of 1 sec, smooth polycrystalline Pt (□), Ru modified Pt ($\theta_{Ru} \approx 0.35$) (○) and ($\theta_{Ru} \approx 0.2$) (△).

An information on the stationary coverage with the adsorbate and the adsorption rate was obtained by adsorbing methanol for 2 min or 1 sec, resp., at a given potential and then stepping back to 0.05 V, where no adsorption occurs. In control experiments with different adsorption times it was checked that after 2 min saturation is achieved indeed. After an electrolyte exchange with pure sulphuric acid, the adsorbate was oxidized. Fig. 7

shows the corresponding cyclic voltammograms together with the formation rates of CO_2 . In the case of pure Pt, the initial desorption rates are independent of the coverage, pointing to a reaction order of zero. This may suggest that the adsorption of OH (with which the adsorbed CO reacts) is the rate determining step in the overall reaction. This is different on Ru modified surfaces, where the initial oxidation rate of the adsorbate depends very much on the coverage. The reason for this difference is the well-known fact that Ru as a cocatalyst for CO oxidation acts by enhancing the adsorption of OH.

The coverage is shown as a function of the adsorption potential in fig. 8. Obviously, both the adsorption rate and the stationary coverage are increased by the presence of Ru. The cocatalytic effect of Ru, which leads to higher current densities and higher current efficiencies, therefore is not only due to an increased oxidation rate of CO, but also an increased adsorption rate. The fact that the stationary coverage starts to decrease at lower potentials than on the unmodified surface, is of course due to the first of these effects.

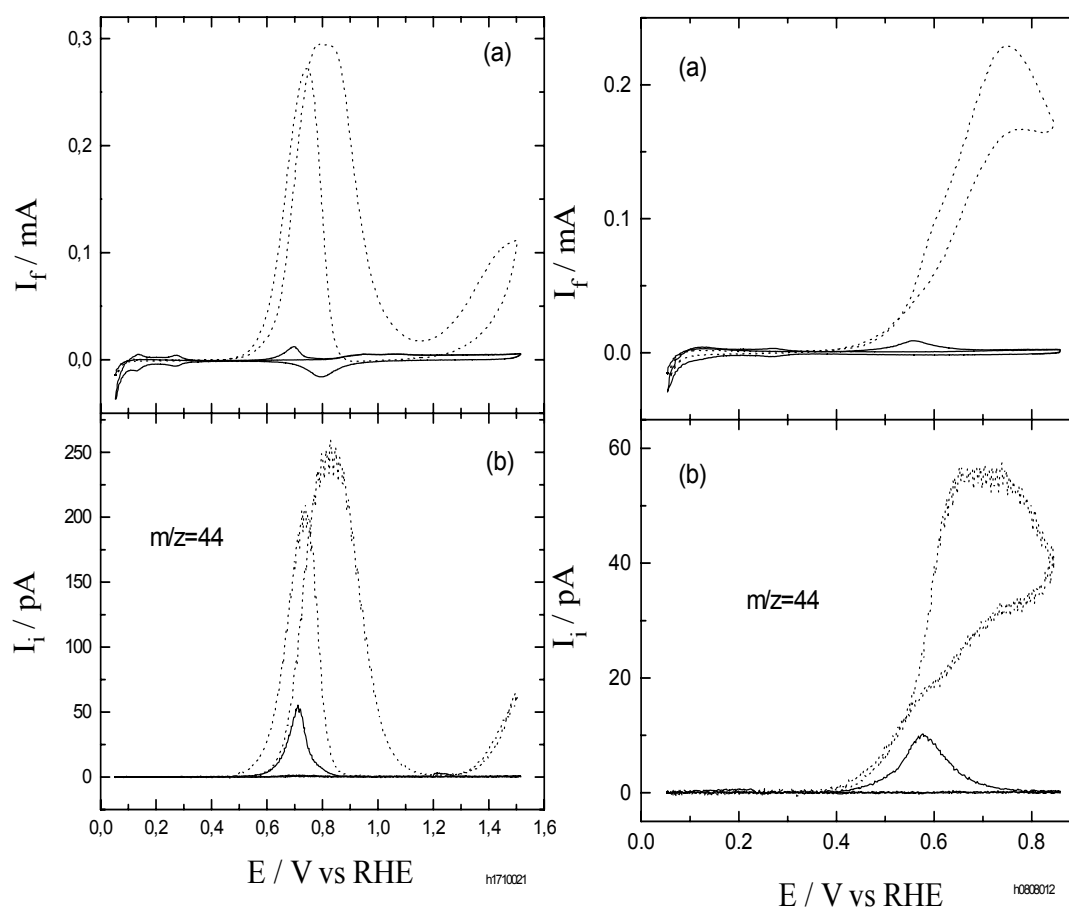


Fig. 9 (left). Comparison of methanol bulk oxidation at smooth polycrystalline platinum in 0.1M CH_3OH + 0.5M H_2SO_4 solution with the oxidation of adsorbed methanol. Methanol is adsorbed from 0.1M CH_3OH + 0.5M H_2SO_4 solution at 0.5V for 2 minutes. Scan rate: 10mV/s. The flow rate of electrolyte: 5 $\mu\text{L/s}$. (—) adsorbate oxidation, (·····) bulk oxidation.

Fig. 10 (right). same as fig. 9 for Ru modified Pt. Adsorption at 0.4V for 2 minutes.

Finally, in fig. 9 the oxidation of the adsorbed CO formed from methanol is compared to the direct methanol oxidation rate. Whereas for pure Pt, the faradaic current is much larger for bulk methanol oxidation than for the oxidation of the adsorbate, the formation rates for CO₂ are interestingly identical. Together with the results of fig. 7 this leads to the conclusion, that not only formation of CO₂ during bulk methanol oxidation is limited by the oxidation of the adsorbate (under enforced convection), but also it is limited by the adsorption of OH. Again, this is different for Ru modified Pt, where the CO₂ formation rate is larger for bulk oxidation than that of the adsorbate even for the highest CO coverages obtained.

In the light of the above mentioned reaction mechanisms, the action of Ru therefore is an enhancement of the reaction steps (1) and (2) (mechanism I) or (6) and (2) mechanism (II), where only the enhancement of (2) is, as in the case of CO oxidation, due to the promotion of OH adsorption. The increased adsorption rate (formation of CO_{ad}) has to be ascribed to an electronic effect.

ACKNOWLEDGEMENTS

Thanks are due to the DFG and to the MSWWF, NRW ("Nakab") for financial support.

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