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## On the effect of tungsten on CO oxidation at Pt electrodes

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**Abstract** The co-catalytic effect of W on the oxidation of CO and methanol is investigated by using differential electrochemical mass spectrometry (DEMS). DEMS reveals that CO oxidation starts at 120 mV, overlapping with W oxidation. The action of W consists in shifting the pre-peak from 450 mV (as observed on pure Pt) to 200 mV. In this shifted pre-peak only 2% of the total adsorbed CO is oxidized independently from the W coverage, as compared to 10% on pure Pt. A correlation between the surface coverage of W as determined by XPS with the W oxidation peak charge in cyclic voltammetry suggests that the oxidation is a six-electron process.

**Keywords** Tungsten · UPD · CO oxidation · Pt electrode · XPS · DEMS

### Introduction

Adsorbed CO formed from methanol has a large detrimental effect as a poisoning intermediate in both direct and indirect methanol fuel cell. In previous studies W has been found to show a promoting effect for the oxidation of methanol [1, 2]. The same effects were shown when W was used as a co-catalyst in combination with Pt/Ru [3]. In fuel cell measurements, the co-catalytic effect was observed both for methanol and for methanol reformat gas [4, 5, 6].

Concerning the origin of the co-catalytic effect, it is usually believed that it is due to the easier adsorption of

an oxygen species, which is needed according to the bifunctional mechanism at the less noble metal [7]. In the case of Mo, which is chemically similar to W, we have recently shown by anodic stripping experiments and detection of the produced CO<sub>2</sub> by differential electrochemical mass spectrometry (DEMS) that the co-catalytic effect is only observed for the weakly adsorbed state of CO, i.e. at low potentials, whereas the oxidation peak of strongly adsorbed CO is hardly shifted with respect to pure Pt. This proved the assumption made in [8], that on PtMo electrodes only small amounts of adsorbed CO are oxidised below 0.5 V. This was ascribed to a catalytic activity of Mo only in its “low” oxidation state, whereas the Mo(VI) at higher potentials is no longer catalytically active [9].

Also in this work DEMS [10] is used in order to distinguish the oxidation of adsorbed CO from pseudocapacitive currents due to oxidation of the adsorbed W.

### Experimental

UHV experiments were carried out in a modified Perkin-Elmer 548 system. It consists of a main chamber equipped with an AES/XPS spectrometer, a LEED optics, a quadrupole mass spectrometer for residual gas analysis, and a pumping chamber with an ion getter pump and titanium sublimation pump. The base pressure after bake-out is about  $1 \times 10^{-10}$  Torr and rises to  $3 \times 10^{-9}$  Torr after a few electrochemical experiments. An antechamber, attached through a gate valve, allows one to move in an electrochemical cell through a second gate valve after transferring the electrode and filling back to the ambient pressure with argon 5.0. For the experiments in the UHV system a Pt(111) crystal (diameter 1 cm) was used, which was cleaned by sputtering ( $8 \times 10^{-5}$  Torr Ar 5.0) without subsequent annealing; its surface morphology therefore is close to that of polycrystalline Pt. Integration of the hydrogen region in cyclic voltammetry showed that the roughness factor is 1.1. Cleanliness was checked by XPS.

From the XPS data, the coverage of the electrode with W ( $\theta_W = N_W/N_{Pt}$ ,  $N$  = number of atoms) was determined using an ordered iodine adlayer for the calibration of the XPS spectrometer. The iodine adlayer was obtained by covering the (annealed) Pt(111) single-crystal electrode with iodine from dilute sulfuric acid containing  $10^{-4}$  M KI which led to an ordered  $(\sqrt{7} \times \sqrt{7})R19.1$

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

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iodine adlayer with an iodine coverage of  $\vartheta_{I,cal}=0.42$ . The coverage of the adsorbate deposited on the electrode is then calculated by:

$$\vartheta_W = \vartheta_{I,cal}^* (I_W/S_W) / (I_{I,cal}/S_I) \quad (1)$$

Here  $I_{I,cal}$  and  $I_W$  are the areas of the corresponding XPS peaks of I ( $3d_{5/2}$ ) or W ( $4f_{7/2}$ ) respectively, and  $S_I$  and  $S_W$  are tabulated atomic sensitivity factors of the elements for the spectrometer. Since this calibration is done for Pt(111) and since the atomic density of surface Pt atoms on a polycrystalline electrode is lower by 10%, the coverage (which refers to the number of surface Pt atoms) as determined by Eq. (1) has to be multiplied by 1.1 for the sputter-roughened surface.

For DEMS, the “classical” setup was used with a working electrode consisting of a 52 nm thick Pt layer sputtered onto a porous PTFE membrane with diameter of 6 mm (approximately 3 cm<sup>2</sup> real surface). The solutions are made out of Millipore water and analytical grade chemicals from Merck and de-aerated with argon 5.0 or saturated by CO from Air Products.

W deposition is done from different concentrations of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The potential was cycled between 50 mV and 800 mV with a scan rate of 10 mV/s until no further changes in the CV were observed. Since the standard potential for W deposition from W(VI) is -0.09 V, only submonolayer amounts are deposited under these conditions. The solution containing W is replaced again by a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a potential of 50 mV and the potential sweeps between 50 and 600 mV were applied until the cyclic voltammetry did not change any more.

CO is adsorbed at a potential of 80 mV from a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution saturated with CO (ca. 10<sup>-3</sup> M). After 15 min the solution is replaced by 0.5 M H<sub>2</sub>SO<sub>4</sub> under potential control. After that the anodic scan of the potential goes up to 1.6 V. In the case of the CO adsorption on W-modified platinum electrodes the upper potential limit is 1.0 V. CO coverages were calculated from the amount of CO<sub>2</sub> formed. The CO oxidation on pure Pt is done for comparison and also serves for the determination of the calibration constant  $K^*$  [11].  $K^*$  is the ratio between the integrated ionic ( $Q_i$ ) and the faradaic current ( $Q_f$ ) when the current efficiency is 100%, taking into account the number of electrons ( $z=2$  for the oxidation of CO).

$$K^* = zQ_i/Q_f \quad (2)$$

The measurement setup consists of the electrochemical cell with a sputtered platinum membrane which is connected to the mass spectrometer. Data are collected by a PC using the Quadstar software. In these DEMS measurements the ion current ( $m/z=44$ )

and faradaic current are recorded simultaneously as a function of the potential.

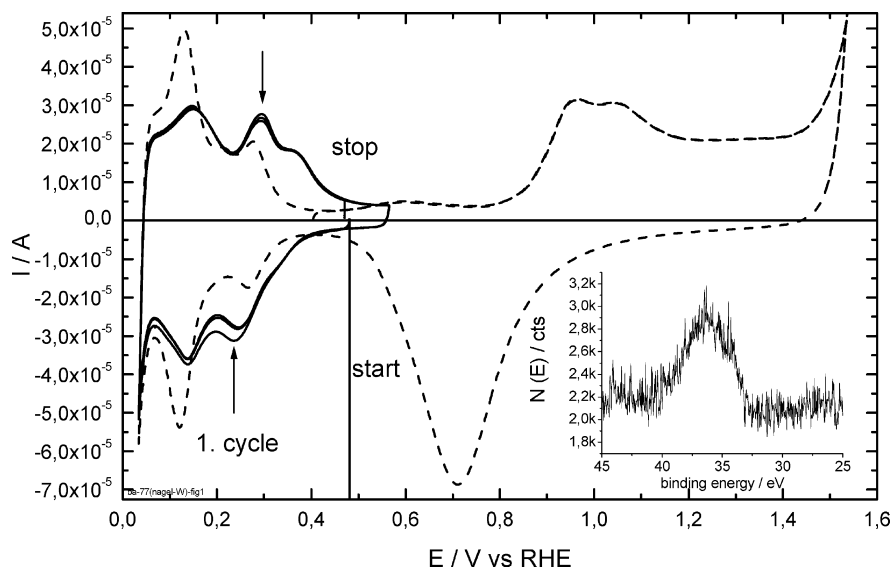
## Results and discussion

Cyclic voltammetry of the sputter-roughened Pt(111) is shown in Fig. 1. For the clean surface, the more anodic of the two hydrogen adsorption peaks is a little smaller than usual for polycrystalline Pt, which is due to the preferential formation of (110) steps (as compared to steps with a local (100) geometry) upon roughening a Pt(111) surface [12]. The cyclic voltammogram after deposition of W reveals a new peak at around 310 mV (versus RHE) due to oxidation of adsorbed W, and another peak at 260 mV strongly overlaps with the more positive of the hydrogen adsorption peaks. The more cathodic hydrogen peak is partially suppressed. These peaks change only slightly during prolonged cycling. From XPS we obtain a coverage of only  $\vartheta=0.044$ ; in other measurements using the same W concentration in solution  $\vartheta$  was always between 0.038 and 0.05. The shape of the W 4f peak is due to a superposition of different oxidation states, the position corresponding to W<sup>6+</sup> and W<sup>5+</sup>, independent of the emersion potential. This, however, should not be over-interpreted, since W may be oxidized after emersion and loss of potential control, e.g. by sulfate ions [13, 14].

The evaluation of the charge due to oxidation of adsorbed W is more difficult than in the case of adsorbed Mo due to the overlap with hydrogen adsorption. We therefore integrated the anodic peak between 250 mV (RHE) and 550 mV(RHE) ( $Q_W=158 \mu\text{C cm}^{-2}$ ) and subtracted the background charge of the CV of the clean Pt electrode ( $82.5 \mu\text{C cm}^{-2}$ ). With the coverage of 0.044 this leads to a number of 7.8 electrons per adsorbed W atom. Taking into account that hydrogen does not adsorb on W and taking into account that W blocks two

**Fig. 1** Cyclic voltammograms and XPS signal of a sputter-roughened Pt(111) surface:

..... clean Pt in 0.1 M H<sub>2</sub>SO<sub>4</sub>; —, after modification in 1×10<sup>-5</sup>-M Na<sub>2</sub>WO<sub>4</sub> + 0.1-M H<sub>2</sub>SO<sub>4</sub> solution recorded in pure 0.1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate 35 mV/s. Inset: detail of the XPS spectrum showing the W 4f peak (excitation: Mg K<sub>α</sub>)  $R_f=1.1$



adsorption sites as Mo, only the hydrogen adsorption charge on the uncovered surface should be taken into account for the background subtraction leading to even  $N_{e^-} = 8.5$  electrons per adsorbed W atom. Here, the equation

$$N_{e^-} = [Q_W - (1 - 2\vartheta_W)Q_b]/(220 \mu\text{C cm}^{-2} \times \vartheta_W) \quad (3)$$

was used where  $Q_b$  is the background charge obtained in the same integration range as  $Q_W$ . This value is even higher than expected for an oxidation from the zero-valent state to the +6 state, as in the case of adsorbed Mo [9]. Alternatively, the whole hydrogen region can be used for the evaluation of the charge. Integration between 55 mV (RHE) and 580 mV (RHE) yields a charge of  $322 \mu\text{C cm}^{-2}$  ( $288 \mu\text{C cm}^{-2}$  for the background, including double layer contribution). Inserting this into Eq. (3), we obtain 6.0 electrons per adsorbed W. This implies that W is in the zero-valent state at low potentials, which may seem astonishing. Similar to Mo, however, the reason may be the usual UPD situation where the metallic state is stabilised due to interaction with the substrate. Concerning the difference of the workfunctions ((111) plane) from Pt and W of 1.55 eV and a standard potential of  $-0.09$  V (SHE) for the reaction:  $\text{WO}_3 + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{W} + 3\text{H}_2\text{O}$  it is feasible to assume a UPD-like deposition process for W [15]. The large decrease of the more cathodic hydrogen adsorption state compared to the small coverage of W signifies that part of the hydrogen desorption (and adsorption) is shifted to more positive potentials, which is in accordance with the too high charge obtained by integration between 250 mV (RHE) and 550 mV (RHE). It should be noted that this number of 6 electrons was reproducibly obtained also when performing experiments in very dilute sulfuric acid and also in preliminary experiments involving a smooth Pt(111) surface.

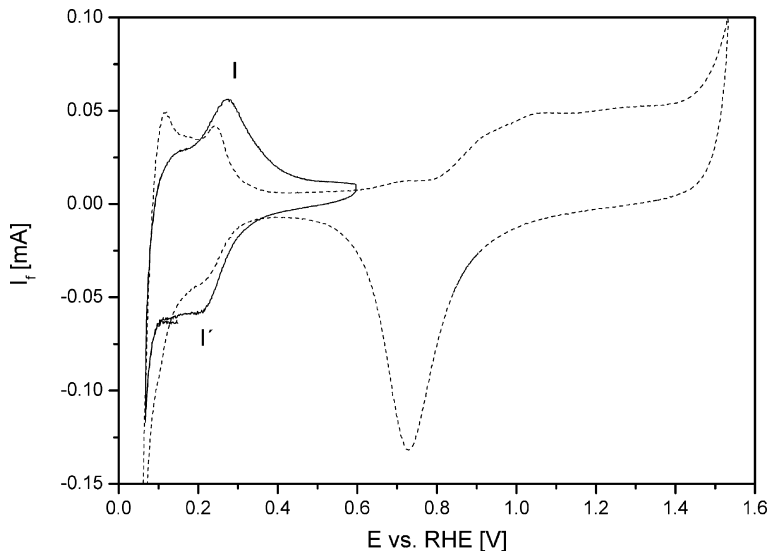
In Fig. 2, the cyclic voltammograms for sputter-deposited Pt on a Teflon membrane and W-modified Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  are compared. The more

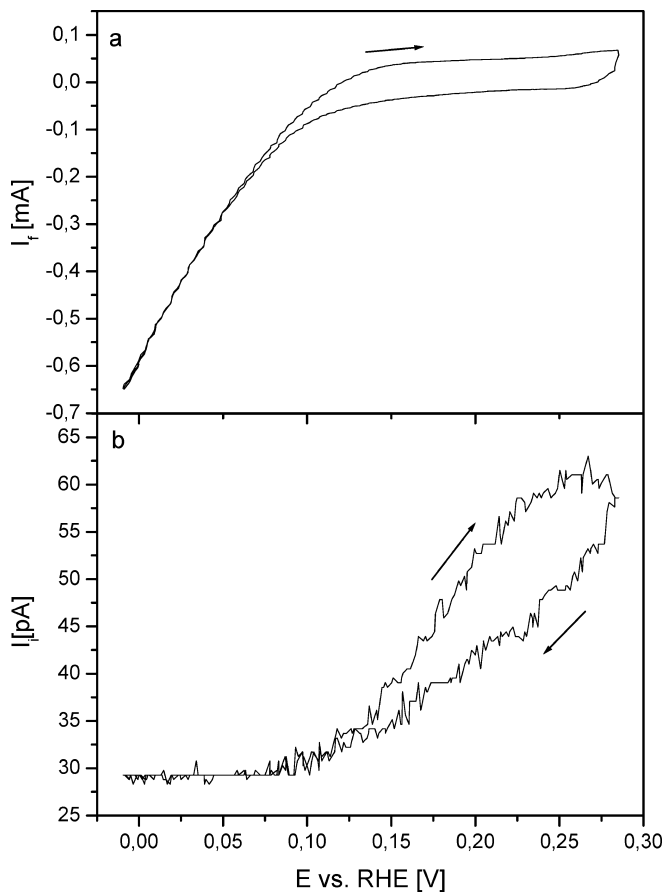
cathodic hydrogen adsorption peak is partially suppressed by W and a new peak evolves at 0.26 V (peak I) and at 0.21 V in the cathodic sweep (peak I') [2]. Contrary to the case of Mo with a peak at 0.4 V in the anodic sweep [9] these peaks are more negative and completely overlap with the hydrogen adsorption peaks. (Please note that at the porous Pt electrode hydrogen evolution starts at a more positive potential than at the massive Pt due to removal of  $\text{H}_2$  by evaporation into vacuum.) Compared to the UHV experiments, no two peaks are resolved which is due to some residual single crystalline behaviour of the latter.

Cyclic voltammetry at a Pt electrode partially covered by W ( $\Theta_W \approx 0.25$ , see below) in a CO-containing electrolyte suggests that there is no obvious oxidation of CO occurring below 0.3 V (Fig. 3). (The cathodic electrode current increases with decreasing potential (negative from 0.1 V) due to the formation of hydrogen.) The ion current for  $\text{CO}_2$ , however, shows that the oxidation of bulk CO starts at 0.12 V. This is one of the lowest onset potentials for CO oxidation ever measured, but also shows that CO can be adsorbed at 100 mV without any significant oxidation to  $\text{CO}_2$ .

The oxidation of the pre-adsorbed CO on the sputtered platinum electrode and on the electrode modified with different coverages of W is shown in Fig. 4. Figure 4a shows that the size of the main CO oxidation peak decreases with an increasing W oxidation peak at 0.3 V. The reason is that CO does not adsorb on W and therefore an increased coverage with W leads to a decreased number of sites available for CO adsorption. Compared to the clean Pt, a new peak at 250 mV (II in Fig. 4b) for the oxidation of CO is visible in the MSCV, which replaces the so called "pre-peak" at pure Pt oxidation of the weakly adsorbed state of CO (with a peak maximum at 0.43 V). The onset of the CO oxidation on the W modified electrode starts at 0.12 V. This onset is more than 150 mV more negative than at pure platinum. After background subtraction, integration of the ion

**Fig. 2** Cyclic voltammograms of sputtered deposited platinum electrode in 0.5 M  $\text{H}_2\text{SO}_4$ :  
 ..... clean Pt;  
 — electrode modified in 0.1 mM  $\text{Na}_2\text{WO}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution and 0.5 M  $\text{H}_2\text{SO}_4$ . Scan rate 10 mV/s





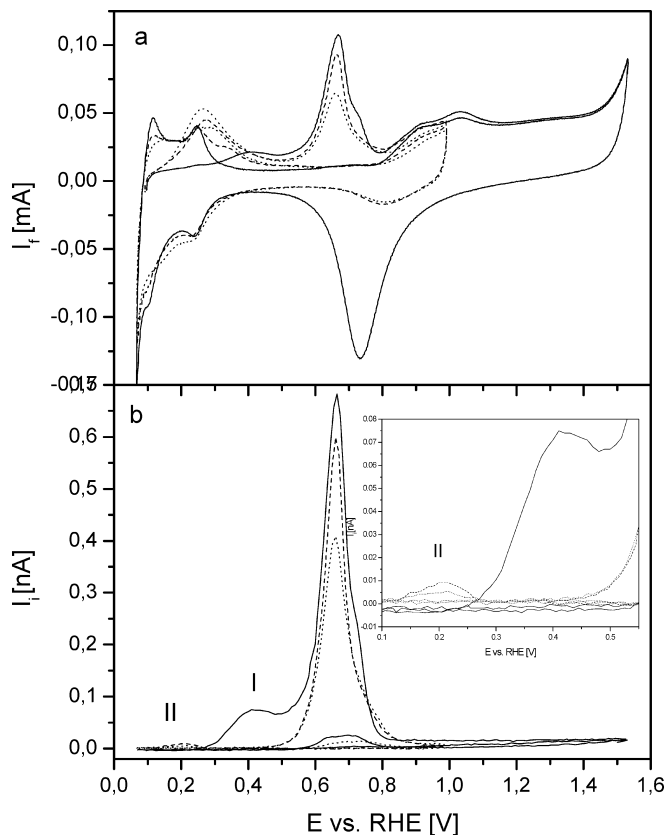
**Fig. 3** Simultaneously recorded CV (a) and MSCV  $m/z=44$  (b) of oxidation of dissolved CO at the sputtered Pt electrode modified in 0.06 mM  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  ( $\Theta_{\text{W}}=0.25$ ) in 0.5 M  $\text{H}_2\text{SO}_4$  solution. Scan rate 50 mV/s

current shows that the relative amount of CO oxidized in the pre-peak at 430 mV (peak I, Fig. 4b) is 12% for clean Pt and sharply decreases already with small coverages of W (Fig. 5). In contrast to this decrease the new peak (peak II, Fig. 4b) has nearly a constant size when related to the total oxidation peak (roughly 2%). This correlates well with the adequate observations made with Mo modified Pt electrodes; there the pre-peak is a little larger (roughly 4% [9]).

The relative W coverage cannot be calculated from the suppression of the hydrogen adsorption peak because of the overlap with the W redox process. Assuming that no CO is adsorbed on W, but on all other Pt sites, the surface covered by W is given by the surface which is not covered by CO, i.e. the suppression of CO adsorption, and its coverage therefore is given by [9]

$$\Theta_{\text{W}} = \frac{Q_{\text{i,CO}}^0 - Q_{\text{i,CO}}^{\text{W}}}{Q_{\text{i,CO}}^0} \quad (4)$$

where  $Q_{\text{i,CO}}^0$  is the mass spectrometric charge of  $\text{CO}_2$  during the oxidation of pre-adsorbed CO on pure platinum and  $Q_{\text{i,CO}}^{\text{W}}$  the same charge after W deposition. Please note that  $\Theta$  refers to the blocking of sites (for CO



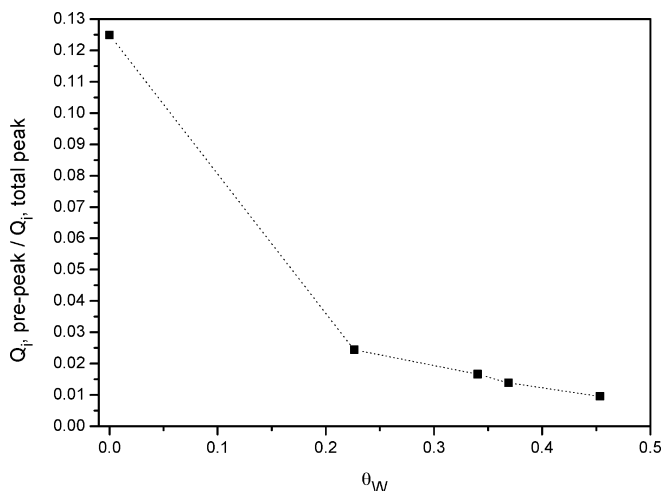
**Fig. 4** Simultaneously recorded CV (a) and MSCV  $m/z=44$  (b) of the oxidation of the pre-adsorbed CO on porous Pt (—) and porous Pt with adsorbed W species in 0.5-M  $\text{H}_2\text{SO}_4$ . W was deposited from  $x$ -mM  $\text{Na}_2\text{WO}_4 + 0.5$ -M  $\text{H}_2\text{SO}_4$  solutions. ....,  $x=0.1$  mM ( $\Theta=0.34$ ); ..... ,  $x=0.5$  mM ( $\Theta=0.45$ ). Scan rate 10 mV/s.  $R_{\text{f}}=10.7$

or H adsorption) whereas the coverage  $\vartheta$  used earlier denotes the ratio of surface W atoms or CO molecules to the Pt surface atoms.

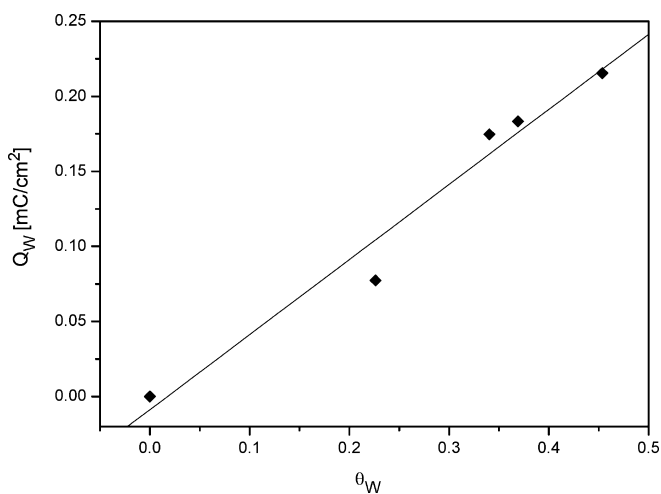
The tungsten oxidation charge can be best evaluated from a CV in which adsorbed CO is oxidized since adsorbed CO on the Pt surface suppresses the hydrogen adsorption. The small contribution of the faradaic current to the beginning CO oxidation in that potential range (0.07–0.55 V) can be determined from the ion current for CO (expression in round brackets in equation 5). Furthermore, the corresponding background current for the unmodified, but CO-covered Pt electrode is subtracted, again after correction for the corresponding CO oxidation charge. Therefore:

$$Q_{\text{W}} = \frac{\left[ Q_{\text{f,CO}}^{\text{W}} - \left( Q_{\text{i,CO}}^{\text{W}} \frac{2}{K^*} \right) \right] - \left[ Q_{\text{f,CO}}^{\text{Pt}} - \left( Q_{\text{i,CO}}^{\text{Pt}} \frac{2}{K^*} \right) \right]}{A} \quad (5)$$

with  $Q_{\text{f,CO}}^{\text{W}}$  the faradaic charge for the W and CO oxidation and  $Q_{\text{i,CO}}^{\text{W}}$  the mass spectrometric charge for the CO oxidation on the W-modified electrode;  $Q_{\text{f,CO}}^{\text{Pt}}$  the faradaic charge for the CO oxidation on the clean Pt electrode;  $Q_{\text{i,CO}}^{\text{Pt}}$  the mass spectrometric charge for the CO oxidation on the W-modified electrode;  $K^*$  a



**Fig. 5** Plot of the ratio between the integrated ion current of the pre-peak and the peak of the total CO oxidation. It was obtained from the corresponding MSCV



**Fig. 6** Plot of the W oxidation charge versus the W coverage. The former was obtained from the first anodic scan after Co adsorption from the corresponding CV and corrected from the charge of the CO pre-peak

calibration constant;  $A$  the real surface. The true surface area of the polycrystalline Pt electrode was determined from the hydrogen adsorption charge by integration from 90 to 400 mV after correction for the double layer charging.

The resulting charges are plotted versus the coverage of W (Fig. 6). The linear behaviour verifies the assumption that no CO adsorbs on the W and that the calculation of the relative W coverage can be performed evaluating the CO coverage (Eq. 4).

The number of electrons per platinum site ( $n_{\text{eps}}$ ) is given by Eq. 6

$$n_{\text{eps}} = \frac{Q_{\text{W}}}{\Theta \times 210 \frac{\mu\text{C}}{\text{cm}^2}} \quad (6)$$

and is calculated as 2.5 in these measurements. For measurements with Mo the  $n_{\text{eps}}$  was calculated to be 3

[9]. Together with the number of 6 electrons per adsorbed W, we obtain the site occupancy of W which is  $6/2.5 = 2.4$  CO adsorption sites per adsorbed W atom which justifies the factor 2 on the correction term of Eq. (3).

As in the case of Mo, the main CO adsorption peak is hardly influenced at all [16]. Therefore, the bifunctional mechanism is not effective for all CO or it is not effective in the whole potential range. As for Mo [9], we assume that W is not catalytically effective in its +6 valent state on the surface. Adsorbed W in the metallic state below 0.3 V acts according to the bifunctional mechanism by offering favourite adsorption sites for an oxygen species, which is not too strongly bound and can react with CO. This effect shifts CO oxidation roughly by 200 mV to lower potentials. This is not enough for the main peak to be shifted to potentials where W is still in its metallic state.

As reported below for the case of Mo, it may seem astonishing that W has such a beneficial effect on the performance of fuel cell anodes, although only a few percent of adsorbed CO are oxidized at low potentials. Obviously, a few sites thus freed are sufficient for an efficient oxidation of  $\text{H}_2$  (but certainly not methanol). Furthermore, at high temperature, typical for fuel cells, the effect of W certainly may be larger.

In addition, W and Mo have shown the largest effect when combined with Ru. As already discussed for Mo in [9], this may—at least in part—be due to the easier formation of a few free sites on the Ru surface on which OH can adsorb.

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