

# **CO oxidation and CO<sub>2</sub> reduction on carbon supported PtW bimetallic catalysts**

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*Submitted to Electrochimica Acta*

February 2006

## CO oxidation and CO<sub>2</sub> reduction on carbon supported PtW bimetallic catalysts.

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### *Abstract*

The activity of a bimetallic carbon supported PtW (PtW/C) catalyst in the CO oxidation and CO<sub>2</sub> reduction reactions was evaluated with the help of cyclic voltammetry in sulfuric acid solution. PtW/C catalyst was prepared using reductive co-precipitation with formic acid as reducing agent. Elemental analysis of the synthesized PtW/C material using energy dispersive X-ray spectroscopy (EDX) showed that the bulk composition of the prepared catalysts deviates slightly from the targeted Pt<sub>0.6</sub>W<sub>0.4</sub>/C due to the loss of W. X-ray photoelectron spectroscopy (XPS) showed that in as-prepared material W is present in the form of its trioxide, WO<sub>3</sub>, while Pt is fully reduced to Pt<sup>0</sup>. XPS also revealed that the W concentration at the surface of the catalyst is higher than that in the bulk. Although CO oxidation on a PtW/C electrode commences at rather low overpotentials, ca. 0.3 V vs. RHE, it involves only a minor fraction of the CO adlayer, the major part of the adsorbed CO layer being oxidised at the potentials as high as those for pure Pt catalysts – ca. 0.8 V vs. RHE. The reduction of CO<sub>2</sub> on PtW/C leads to the formation of an adsorbate – presumably CO – on the Pt sites of the catalyst. Although the rate of the adsorbate build-up on PtW/C at 0.1 V is lower than that on pure Pt/C, our results indicate that upon a prolonged exposure of the PtW/C electrode to a CO<sub>2</sub>-saturated solution a complete poisoning of the Pt sites with the adsorbate is likely to occur at room temperature.

**Keywords:** anode catalysts for PEMFC, bimetallic catalyst, PtW, CO<sub>2</sub> reduction, CO oxidation

### *1. Introduction.*

In the decades-long quest for a more CO- and reformate-tolerant catalyst for proton-exchange membrane fuel cells (PEMFC) as well as for methanol-tolerant catalyst for direct methanol fuel cells (DMFC) many elements have been tested either as platinum alloys or as adsorption layers on platinum [1]. PtRu catalysts are presently recognised as the state of the art materials for the anodes for both reformate-fed PEMFC and DMFC [1]. Although the specific activity of the PtRu/C catalysts is acceptable for many applications, high price of the components constantly stimulates further search for cheaper alternatives, mainly among transition metals. Numerous studies demonstrated that the addition of Ni, Co, Fe, Sn and Mo to Pt significantly improves its CO tolerance [1,2,3]. Addition of W to either pure Pt

[2,3,4,5,6] or as a third component to PtRu [3,7,8] was also shown to improve CO- and methanol-tolerance of the catalysts and in some instances a better performance than the widely used PtRu/C was reported [3,5,6,8].

An important selection criterion in the screening of the anode electrode materials for reformat-fed PEMFC is their ability to catalyse the reduction of CO<sub>2</sub> – one of the major components of the reformat gas – by H<sub>2</sub> as this process usually results in additional polarisation losses [9,10,11,12]. Despite this fact, the reactivity of W-modified Pt or PtRu materials in CO<sub>2</sub> reduction is seldom investigated and reported.

Another crucial characteristic of the anode catalysts for PEMFC, which seems to be somewhat underexposed in literature, is their stability. Instability of the anode catalyst, i.e. leaching out of the metal ions, can be detrimental to the cell. First of all, loss of functionality at the anode results in yet higher overpotentials, but also other parts of the cell can be affected. Metal ions dissolved in the membrane cause drying-out and eventually deposit on the cathode leading to its deterioration [13].

As mentioned above bimetallic PtMo and PtW materials have long been recognised for their excellent catalytic activity in the electro-oxidation of CO and methanol. Unfortunately, PtMo catalysts seem to be inherently unstable and suffer from the leaching of Mo due to the solubility of MoO<sub>3</sub>·xH<sub>2</sub>O at low pH [14]. Contrary to molybdenum trioxide, tungsten trioxide is known to be hardly soluble even in very strong and oxidising acids [15], hence stability question for a bimetallic PtW/C catalyst supposedly would not arise.

In this work we present a study of the reactivity of the bimetallic PtW/C catalyst, prepared via the so-called formic acid route, developed by the group of Ticianelli [16,17,18], in CO oxidation and CO<sub>2</sub> reduction. Stability of the catalyst is also addressed. Physical characterisation of the surface and bulk composition of the material provides a link between its structure and electrochemical performance.

## ***2. Experimental.***

### ***2.1. PtW/C catalyst preparation.***

Preparation of the PtW bimetallic catalyst with Pt:W ratio of 6:4 and the total metal loading of 20 w% involved reduction of Pt and W precursors with formic acid in the presence of a carbon support suspension according to the procedure described by the group of Ticianelli [16,17,18] and used earlier by the authors for the synthesis of carbon supported PtMo [14].

Formic acid (pro analysi, Merck) was added in five times excess of the stoichiometric amount necessary to reduce both Pt and W to a vigorously stirred aqueous slurry of Vulcan XC-72. The slurry was heated to 50°C. The appropriate amounts of H<sub>2</sub>PtCl<sub>6</sub> (40% Pt, for

synthesis, Merck) and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (pro analysi, Merck) were dissolved in a minimum amount of water and these solutions were slowly dropwise added to the Vulcan XC-72 slurry. The progress of the reduction of  $\text{H}_2\text{PtCl}_6$  was periodically checked with saturated KI solution [18]. If unreacted Pt-species were detected, the addition of the Pt and W precursors was stopped till the reduction of  $\text{H}_2\text{PtCl}_6$  was complete and then resumed again. Then the slurry was stirred further for about 16 hours at room temperature, filtered, washed on the filter with water and dried at  $80^\circ\text{C}$  under nitrogen flow for at least 2 hours.

## **2.2. Characterisation of PtW/C catalyst.**

The elemental bulk composition of the prepared PtW/C catalyst was verified with the help of energy dispersive X-ray analysis (EDX) using a JEOL JSM-6330F field emission scanning electron microscope. The surface composition of as-prepared catalysts was investigated using X-ray photoelectron spectroscopy (XPS). The XPS measurements were done with a VG ESCALAB hemispherical electron energy analyser with five channeltron detection and a VG XR3 twin anode (Al/Mg) X-ray source. Spectra were obtained with the aluminium anode ( $\text{AlK}_{\alpha}=1486.6$  eV) used at the power of 240 W with constant pass energy of 20 eV. Background pressure of the vacuum system was ca.  $2 \cdot 10^{-9}$  mbar.

## **2.3. Preparation of the PtW/C electrodes.**

For testing of the electrochemical performance of the synthesised material, a catalytic ink was prepared as follows: an aliquot of propanol-1 (pro analysi, Merck) and of 5 w.% solution of Nafion (EW 1100, DuPont) were added to a certain amount of PtW/C catalyst so that the resulting ink would have 1.3 w.% content of total metal and 2 w.% of Nafion. The slurry was dispersed using T25 B homogeniser (IKA Labortechnik, Germany) at 24000 rpm for a few minutes.

For the electrochemical tests in a standard three-electrode cell with liquid electrolyte the PtW/C ink was applied on a smooth Pt electrode and dried at  $130^\circ\text{C}$  under the flow of nitrogen for 30 minutes.

## **2.4. Electrochemical testing of the PtW/C.**

A standard three-electrode electrochemical cell was used for the testing of PtW/C electrodes in sulfuric acid electrolytes. Platinised platinum was used as a counter electrode and reversible hydrogen electrode as a reference electrode. 0.5 M solution of  $\text{H}_2\text{SO}_4$  were prepared from concentrated  $\text{H}_2\text{SO}_4$  (pro analysi, Merck) and high purity MilliQ (Millipore) water. The solutions were deoxygenated prior to each experiment.

To evaluate the CO-tolerance of the prepared PtW catalyst carbon monoxide (10% CO in Ar, Scott Specialty Gases, 5.0) was bubbled through the electrolyte for at least 40 minutes, while the potential of the working electrode was kept at 0.05 V. Then a cyclic voltammogram of the oxidation of the adsorbed as well as dissolved CO was recorded. To de-couple the oxidation of the adsorbed CO layer from the so-called “continuous” CO oxidation cyclic voltammograms of the oxidation of the CO adlayer were also recorded. In this case the saturation of the electrolyte with CO was followed by its purging with nitrogen.

To measure the activity of the PtW/C catalyst towards CO<sub>2</sub> reduction the working electrode was exposed to a CO<sub>2</sub>-saturated electrolyte for various time intervals, while its potential was kept at 0.1 V. Then a cyclic voltammogram was recorded to detect a possible formation of the adsorbates.

All electrochemical experiments were performed using a computer-controlled Autolab PGSTAT 20 potentiostat.

### ***3. Results and discussion.***

#### ***3.1. Preparation and characterisation of the PtW/C catalysts.***

The results of the elemental analysis of the bulk and surface composition of the synthesized PtW/C catalyst are summarized in Table 1. The XPS spectra of the catalyst for W 4f and 5p and Pt 4f regions are shown in Figs. 1a and 1b, respectively.

As can be seen from Table 1 bulk composition of the prepared catalyst deviates from the target suggesting that some loss of W occurs in the synthesis (see Table 1). XPS peaks at 35.3 and 37.4 eV indicate that in as-prepared catalyst W is present in the form of its trioxide, WO<sub>3</sub>, [19]. In the Pt 4f region of the XPS spectra two peaks at 71.4 and 74.7 eV, characteristic to metallic Pt, are observed (see Fig. 1b) [19]. The latter finding appears somewhat surprising given the well-known fact that the Pt nano-particles are often covered with the surface oxide layer. Reduction of the surface Pt oxide under the XPS measurement conditions can be one of the possible explanations for this observation [20]. The XPS analysis also shows that the surface of the PtW/C catalyst is enriched with W compared to the bulk (Table 1) [21].

Similar effects – some loss of transition metal component and enrichment of the catalyst surface with transition metal component – were previously observed by us for the case of PtMo/C materials [14]. As we have suggested in Ref.14 the reason for lowered Mo content in the PtMo/C materials was twofold: i) dissolution of the hydrated MoO<sub>3</sub> at pH of the synthesis medium below 0 and ii) partial, non-quantitative, precipitation of the Mo species in the form of the hydrated MoO<sub>3</sub> during the synthesis. Only the latter remains true in the case of W as it is well known that WO<sub>3</sub> is not soluble even in very strong acids [15,22]. Significant

loss of W – up to 50% - in the preparation of PtW/C and PtRuW/C catalysts was also reported by Yang et al [23]. They related the problem to the dissolution of the precipitated  $WO_x$  during the washing of the catalyst with water as the use of an acidified washing solution entirely prevented the loss of tungsten [23]. In our opinion, washing-out of the unreacted precursor salt is a more likely explanation for the loss of tungsten during the synthesis as it is known that the precipitation of the  $WO_3$  as well as  $MoO_3$  is a slow and non-quantitative process. Therefore, use of an acidified washing solution can extend the precipitation time leading to reduced transition metal losses. This supposition is further supported by the results of Shukla et al, who did not observe any loss of tungsten during the preparation of the PtW/C materials, while applying copious washing of the catalyst with hot distilled water [24].

Apart from insolubility of  $WO_3$  at pH lower than 0, the red-ox chemistry of tungsten is similar to that of molybdenum. Not surprisingly XPS analysis shows that, similarly to Mo in PtMo/C materials, W is present in the form of  $WO_3$  in as-prepared catalyst, indicating that no reduction of the  $W^{6+}$  precursor cation takes place under the conditions of the synthesis. This result is also supported by the majority of the previous studies [5,6,8,23,24,25], where tungsten was found in the form of its trioxide in the as-prepared PtW/C catalysts regardless of the synthesis method used. However, in addition to  $WO_3$ , some authors have also detected the presence of the more reduced species such as  $WO_2$  [24] and non-stoichiometric mixed oxide of  $W^{5+}/W^{6+}$  [23].

As for the surface enrichment with the transition metal oxide, we have suggested in our previous paper on the preparation and properties of the PtMo/C catalysts [14] that surface enrichment with Mo occurs due to a mismatch of the rates of the platinum reduction and the  $MoO_3 \cdot xH_2O$  precipitation. This effect is also likely to be present in the case of PtW/C catalyst resulting in somewhat higher content of W on the surface of the catalyst compared to its bulk. Literature data suggests that surface composition of the catalyst is totally determined by the synthesis procedure employed [6,23,24]. References 6 and 23 illustrate that sequential precipitation of the components usually leads to the higher surface concentration of the component that precipitates as last. Simultaneous deposition of the components via the impregnation of the carbon support with the metal precursor solutions followed by the reduction of the platinum precursor and precipitation of the tungsten oxide was employed by Shukla et al [24], potentially leading to a material with well-mixed components. Unfortunately, no data on the surface composition of the catalyst was reported [24].

### ***3.2. Electrochemical properties of PtW/C catalyst.***

#### ***3.2.1. Blank electrolyte.***

The cyclic voltammogram of the PtW/C catalyst in 0.5 M H<sub>2</sub>SO<sub>4</sub> is shown in Figure 2. At the potentials below 0.3 V two pairs of peaks are clearly visible. On the positive-going scan at potentials between 0.3 and 0.45 V a broad feature with no apparent counter-part on the negative-going scan is observed. At yet more positive potentials between 0.45 and 0.75 V there is a pair of broad peaks corresponding to a surface red-ox reactions of the carbon support [26]. Finally, at the potentials above 0.8 V on the positive-going scan an incipient oxidation of the surface of Pt particles takes place.

It has been convincingly shown previously that the voltammetric features at the potentials below 0.45 V result from the overlap of hydrogen adsorption/desorption on Pt and reoxidation of hydrogen tungsten bronze formed through a spillover of the adsorbed hydrogen from platinum to tungsten oxide [6,27,28,29,30,31]:



Other electrochemical processes such as oxidation of W<sup>0</sup> to higher oxidation states [25]:



and oxidation of the sub-stoichiometric tungsten oxides into tungsten trioxide [6,27,29,31]:



have also been suggested to account for the faradaic current at the potentials below 0.45 V.

It appears difficult to unambiguously determine the origin of these peaks based only on the cyclic voltammetry. However, taking into account that W is present in the form of its trioxide in as-prepared catalyst (see XPS results in the previous section) and that this peak appears also on the first positive-going voltammetric scan, we consider a combination of the bronze route (equation 3) and the usual reactions on Pt (equation 1) to be a more likely option for the system.

Due to a significant overlap between reoxidation of hydrogen tungsten bronze and desorption of hydrogen on Pt, it appears difficult to estimate the active surface area of Pt using a traditional approach of calculating the charge transferred in the latter process. Therefore, an alternative approach such as estimation of the charge transferred in the oxidation of an adlayer of CO must be used.

The stability of the PtW/C catalyst was evaluated by keeping it for prolonged time (ca. 2 months) in the 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at open circuit potential as well as by prolonged cycling (at least 300 cycles) between 0.05 and 0.9 V. No changes in the blank voltammetric profile were noticed in either case, suggesting that the PtW/C, contrary to PtMo/C materials, is perfectly stable under our experimental conditions. Stable performance of the PtW/C catalysts under the fuel cell conditions as well as upon cycling in the membrane-electrode assembly set-up was reported by Shim et al [6]. Chen and Tseung investigated the stability of

the bimetallic PtW electrodes at elevated temperatures and found  $\text{WO}_3$  to be slightly soluble at 60° C in sulfuric acid media [32]. Coating of the Pt/ $\text{WO}_3$  electrodes with Nafion was shown to reduce the solubility of tungsten oxide significantly [32], suggesting that degradation of the fuel cell performance due to tungsten oxide dissolution would be unlikely to occur.

### 3.2.2. CO oxidation.

A cyclic voltammogram of the PtW/C electrode in CO-saturated 0.5 M  $\text{H}_2\text{SO}_4$  is shown in Fig. 3. It is clear that voltammetric peaks at potentials below 0.45 V related to the reactions on Pt and W in supporting electrolyte (equation 1 and 3) are strongly suppressed. It is well known that CO adsorbs strongly on Pt totally inhibiting electroadsorption/desorption of hydrogen at high CO coverage. The disappearance of the voltammetric features assigned to the reactions involving tungsten suggests again that these features originate from the oxidation of hydrogen tungsten bronze, which is suppressed due to the absence of hydrogen spillover from the Pt sites blocked by CO, and not from the reactions of tungsten oxide(s) as it is widely believed that CO does not adsorb on tungsten [25] or tungsten oxide(s) [23].

Judging from the cyclic voltammogram oxidation of CO on PtW/C catalyst begins at the potentials as low as ca. 0.3 V (see Fig. 3). Two features are observed: a broad pre-wave between ca. 0.3 V and ca 0.7 V and a peak at around 0.8 V. Our results are in good agreement with the previously published data [23,25], where similar profiles for CO oxidation on PtW/C materials have been reported. Using in situ mass spectroscopy Nagel et al have shown that on W-modified Pt the oxidation of the dissolved CO occurs at the potentials as low as 0.12 V, although no obvious oxidation of CO below 0.3 V could be inferred from the cyclic voltammogram [25]. The main peak for CO oxidation was observed at ca. 0.65 V [25]. The amount of CO oxidised in the pre-wave at low overpotential does not exceed 2 % of the total adsorbed layer as estimated from the in situ mass spectroscopy data [25]. Yang et al reported that the oxidation of the CO adlayer also commences at ca. 0.3 V followed by the main peak at ca. 0.65 V [23]. In the present work the main oxidation peak is observed at slightly higher overpotentials, at ca. 0.8 V, presumably due to a higher scan rate employed by the authors (100 mV/s in the present study instead of 10 mV/s in both Refs. 23,25). However, influence of the catalyst surface composition and structure cannot be excluded.

A decrease of the current of the pre-wave between 0.3 and 0.7 V was observed upon purging of the electrolyte with nitrogen to remove dissolved CO (not shown), indicating that the reaction order with respect to CO is positive. A similar observation was previously made



for pure Pt catalysts and was attributed to the oxidation of weakly-bound CO adlayer formed at high CO coverage [33]. The main oxidation peak at ca. 0.8 V remained unaffected.

Our data agrees well with previously reported results on CO tolerance of Pt-WO<sub>3</sub> catalysts for PEMFC [2], where Pt-WO<sub>3</sub> was categorised as a catalysts that operates via the promoted mechanism, i.e. enables the oxidation of the CO adlayer at an increased rate at low overpotentials via, for example, the bifunctional mechanism. Contrary to intrinsically CO-tolerant catalysts such as PtRu, for example, it does not significantly affect the adsorption energy of CO [2]. However, since the amount of CO oxidised in the pre-wave on PtW/C materials is relatively small and most of the electrode surface still remains occupied with CO and, hence, is unavailable for the oxidation of hydrogen, we do not expect that PtW/C would demonstrate high CO-tolerance under fuel cell conditions.

### 3.2.3. CO<sub>2</sub> reduction.

Figure 4 shows a cyclic voltammogram of the PtW/C electrode after 1 hour exposure to CO<sub>2</sub>-saturated electrolyte at 0.1 V. As can be seen hydrogen adsorption/desorption on Pt is significantly suppressed by the formed adsorbate, making the peak of the hydrogen tungsten bronze reoxidation at ca. 0.3 V more clearly resolved (see Fig. 4). The oxidation of the formed adsorbate begins at around 0.6 V, followed by a double peak at around 0.8 V.

Similarity of the voltammetric profile shown in Fig.4 to that in Fig. 3 and the fact that the adsorbate blocks the adsorption/desorption of hydrogen on Pt sites of the PtW/C catalyst, while not significantly affecting the red-ox reactions involving W, suggests that the adsorbate is likely to be carbon monoxide adsorbed on Pt sites. This indicates that CO<sub>2</sub> reduction on our bimetallic PtW/C catalyst occurs similarly to that on pure Pt and the addition of tungsten oxide apparently does not change the selectivity of the reaction. The multiplicity of the peaks for CO adsorbate oxidation as well as incomplete suppression of the peak of the hydrogen tungsten bronze reoxidation is most likely related to the coverage effect, i.e. CO coverage formed on Pt surface in the reduction of CO<sub>2</sub> is lower compared to the direct adsorption of CO from the electrolyte.

CO<sub>2</sub> reduction on different metals has been extensively studied [see, for example, review 34], and it is now generally agreed that the main product of the carbon dioxide reduction on Pt is carbon monoxide. The reaction can schematically be represented by the following equation:



where hydrogen adsorbed on Pt reacts with carbon dioxide giving adsorbed carbon monoxide and water. Since carbon monoxide adsorbs strongly on Pt and blocks the adsorption sites for hydrogen, the reaction is self-limiting and stops when the Pt surface saturates with CO [34].

It is interesting to compare the kinetics of the CO<sub>2</sub> reduction on bimetallic PtW/C catalyst to that on pure Pt/C in order to evaluate the activity of the former material in this reaction. Figure 5 compares the rates of the relative CO coverage build-up for PtW/C and Pt/C at 0.1 V. Relative CO coverage was calculated as a ratio between the charge, transferred in the oxidation of an adlayer formed after an exposure of the PtW/C electrode to CO<sub>2</sub>-saturated solution for a given time, and the charge, transferred in the oxidation of a saturated CO adlayer prepared via direct dosing of CO, i.e. adsorption of CO from the CO-saturated solution. As can be seen, rate of the CO adsorbate accumulation and, hence, CO<sub>2</sub> reduction on PtW/C is much lower compared to that on Pt/C. One of the possible reasons for the difference might be that the surface concentration of hydrogen on PtW/C catalysts at a given potential is lower than that on Pt/C. Indeed, reactions 2 and 3 essentially provide a parallel route for the hydrogen ionisation, apparently making its equilibrium concentration at the surface of PtW/C lower than that of Pt/C at a given potential. As adsorbed hydrogen is one of the reactants (see eq. 6) this can substantially influence the reaction kinetics. However, other reasons such as electronic or structural effects due to the presence of WO<sub>3</sub> on the surface of Pt cannot be excluded.

Another important observation concerning CO<sub>2</sub> reduction on PtW/C electrodes is that no apparent levelling off of the curve in Fig.5 is observed at large times. This indicates that although the rate of CO build-up due to the reduction of CO<sub>2</sub> on PtW/C electrode is lower compared to that on Pt/C, it is likely that similarly to pure Pt/C materials the saturation of the Pt surface of PtW/C with CO will eventually occur leading to a complete poisoning of the anode at room temperature. However, at elevated temperature saturation with CO is not necessarily reached even for Pt/C due to the non-negligible desorption rate of CO [2]. This combined with the lower CO build-up rate on PtW/C might indicate that PtW/C would be a relatively CO<sub>2</sub>-tolerant catalyst under PEM fuel cell conditions.

Our results on CO<sub>2</sub> reduction on Pt/C electrode differ significantly from those recently reported by Smolinka et al [35], where the relative saturation coverage of the CO adlayer produced in the CO<sub>2</sub> reduction reaction at room temperature was claimed not to exceed 0.6. In our opinion, the latter value results from insufficiently long kinetic measurements.

#### ***4. Conclusions.***

Bimetallic carbon supported PtW catalyst was prepared using reductive co-precipitation with formic acid as reducing agent. The bulk as well as surface composition of the catalyst was investigated using energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS), respectively. The activity of the prepared PtW/C catalyst in CO

oxidation and CO<sub>2</sub> reduction was evaluated with the help of cyclic voltammetry in sulfuric acid solution.

Elemental analysis of the synthesized PtW/C material showed that the bulk as well as surface composition of the prepared catalysts deviate slightly from the targeted Pt<sub>0.6</sub>W<sub>0.4</sub>/C due to the loss of W. X-ray photoelectron spectroscopy showed that in as-prepared materials W is present in the form of its trioxide, WO<sub>3</sub>, while Pt is fully reduced to Pt<sup>0</sup>. XPS also revealed that the W concentration at the surface of the catalyst is higher than that in the bulk. Similarly to PtMo/C materials [14], the mismatch of the rates of Pt precursor reduction and that of hydrated WO<sub>3</sub> precipitation is likely to be the reason for the inhomogeneity of the prepared materials.

CO oxidation at PtW/C material was shown to commence at rather low overpotentials, ca. 0.3 V vs. RHE. However, it seems to involve only a minor fraction of the CO adlayer, the major part of the adsorbed CO layer being oxidised at the potentials as high as those for pure Pt catalysts – ca. 0.8 V vs. RHE. This suggests that PtW/C materials would not possess high CO-tolerance as they would not be able to provide sufficiently large amount of Pt free sites via the oxidation of adsorbed CO at low overpotentials to maintain the oxidation of hydrogen at a high rate.

The reduction of CO<sub>2</sub> on PtW/C leads to the formation of an adsorbate – presumably CO –on the Pt sites of the catalyst. The rate of the adsorbate build-up on PtW/C at 0.1 V is lower than that on pure Pt/C. However, our results indicate that upon a prolonged exposure of the PtW/C electrode to a CO<sub>2</sub>-saturated solution at the potentials below 0.3 V a complete poisoning of the Pt sites with the adsorbate is likely to occur at room temperature.

**Acknowledgement:** The authors would like to thank C.M. Roos (ECN, Petten) for EDX measurements and Ing. M.W.G.M. Verhoeven (Eindhoven University of Technology, Eindhoven) for XPS analysis of PtW/C samples.

Table 1. Elemental bulk and surface composition of the prepared PtW/C catalyst.

Target composition	$\text{Pt}_{0.60}\text{W}_{0.40}$
Bulk composition (EDX)	$\text{Pt}_{0.77}\text{W}_{0.23}$
Surface composition (XPS)	$\text{Pt}_{0.70}\text{W}_{0.30}$

**Figure captions:**

**Figure 1.** (a) W 4f and (b) Pt 4f regions of the X-ray photoelectron spectra of PtW/C electrocatalyst.

**Figure 2.** Cyclic voltammogram of the PtW/C electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, room temperature, scan rate 0.1 V/s.

**Figure 3.** Cyclic voltammogram of the PtW/C electrode in CO-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (thick line), blank profile of the PtW/C electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (thin line), room temperature, scan rate 0.1 V/s.

**Figure 4.** Cyclic voltammogram of the PtW/C electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, showing the oxidation of the adsorbate accumulated at the surface upon the exposure of the electrode to a CO<sub>2</sub>-saturated 0.5M H<sub>2</sub>SO<sub>4</sub> electrolyte for 3600 s. Room temperature, scan rate 0.1 V/s.

**Figure 5.** Dependence of the relative adsorbate coverage on time for PtW/C electrode (diamonds) and Pt/C electrode (triangles) upon exposure to a CO<sub>2</sub>-saturated 0.5M H<sub>2</sub>SO<sub>4</sub> electrolyte at 0.1 V and room temperature.

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22. The insolubility of (hydrated)  $\text{WO}_3$  in (strong as well as oxidising) acids makes it more difficult to analyse the bulk composition of the PtW/C materials using standard inductively-coupled plasma spectroscopy (ICP). Apart from “wet” chemical analysis [32], this leaves a few alternatives such as energy dispersive X-ray analysis (EDX) or neutron activation analysis (NAA). In this study both techniques have been used, however, it was our experience that NAA underestimates the total metal loading as well as W content. For this reason only results of EDX analysis are reported in the present work.
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