ELLIPSOMETRY AND DEMS STUDY OF THE ELECTROOXIDATION OF METHANOL AT Pt AND Ru- AND Sn- PROMOTED Pt

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Abstract—The oxidation of submonolayers of Ru and Sn on Pt in sulfuric acid was monitored with ellipsometry. In the presence of methanol the oxides on Ru and Sn disappear but the Pt-oxide is not affected by methanol. This signifies that Ru and Sn are present in their zero valent state during the methanol oxidation.

DEMS measurements showed that both metals enhance methanol oxidation. The promoting role of these metals is explained with the bifunctional mechanism.

Key words: ellipsometry, DEMS, methanol, Pt, Ru, Sn promotion.

INTRODUCTION

The investigation of methanol oxidation is of importance because of its possible application in the direct methanol fuel cell. Because of the necessity of an acid electrolyte the choice of the catalyst is confined to noble metals of which Pt has the highest activity. This metal, however, has a high overpotential for this reaction and deactivates rapidly. Therefore several efforts have been made to modify its electrocatalytic behaviour[1, 2]. The oxidation of methanol at Pt is generally accepted to proceed via two major steps:

(i) dissociative adsorption of methanol:

\[ \text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-} \text{COH}_{\text{ads}} + 3\text{H}^+ + 3\text{e} \quad (1) \]

in which the adsorbate can be (COH)_{ads} or CO_{ads} [3].

(ii) oxidation of the adsorbate with an oxygen species that is present on Pt:

\[ \text{Pt-COH} + \text{Pt-} \text{OH} \rightarrow \text{CO}_2 + 2\text{Pt} + 2\text{H}^+ + 2\text{e} \quad (2) \]

Here the oxygen supplying species is represented as Pt-OH. It is still a moot question whether the oxygen originates from an adsorbed hydroxy species or from activated water. The main reason for the low activity of Pt for the methanol oxidation is its inability to provide an oxygen species at low potential; Pt-OH is formed at relatively high potentials. It is well known[4, 5, 6] that the activity of Pt can be improved by addition of metals like Sn or Ru. Since neither Ru [7] nor Sn [8] are active for the methanol oxidation, the promoting metal should only partially cover the Pt surface. If the coverage with the promoting metal is too high, the number of methanol adsorption sites becomes too small and thus the oxidation activity decreases. The promoting effect of these metals is usually attributed to either a bifunctional[9] or to a ligand[10] effect. The bifunctional effect involves the forming of an oxygenated species at the promoting metal at less anodic potential than at Pt, with the result that the methanol adsorbate can be oxidised at a lower potential. According to the ligand theory the promoting metal changes the electronic state of the Pt, thus influencing the reactivity of the Pt. Other explanations, which are sometimes mentioned in the literature[10] for the electrocatalytic action of adatoms, viz. a geometric (third-body) effect and a redox effect are not likely: the geometric effect would imply that other (geometrically similar) metals are also active as promoters which has not been observed for methanol oxidation. If the promoting action were due to a redox effect[11], a redox couple should be observed in the cyclic voltammetric measurements. The promoting metal can be electrochemically deposited as an adatom or applied via immersion[12] onto Pt; in both cases a submonolayer is formed. Another method is to prepare a Pt/M (M = Sn or Ru) alloy via electrocodeposition[3]. The electrocatalytic behaviour of an adatom layer was found to be similar to that of the codeposited alloy, both for Ru and for Sn[6, 9, 13].

The adsorbed methanolic intermediates have been extensively investigated with a large variety of surface detection methods. Ellipsometry is an optical method for the characterization of the metal/electrolyte interface[14] and is often applied to monitor the formation of thin films at a metal surface. The technique is based on the changes in the polarization state of monochromatic light upon reflection at the surface; the measuring parameters are \( \Delta \) and \( \Psi \) which are related to phase retardation and relative amplitude. Since ellipsometry is an \textit{in situ} technique we applied this method in com-
bination with Differential Electrochemical Mass Spectroscopy (DEMS) to get more insight into the role of Ru and Sn promoters on the methanol oxidation at Pt. The results will be discussed in the view of a bifunctional or ligand effect of the promoting metal.

EXPERIMENTAL

Combined cyclic voltammetry and ellipsometry experiments were carried out at a smooth Pt disc electrode (area 0.5 cm²) using a Wenking potentiocell POS 73 with Philips PM 8043 recorder and an automated ellipsometer Rudolph RR 2200 with tungsten iodine light source and monochromatic filter resulting in light with a wavelength of 546.1 nm. The optical cell is cylindrical and supplied with windows arranged for an angle of incidence of 70° at the substrate.

Combined voltammetric and DEMS experiments were performed at a platinized gauze electrode (real area 60 cm²) using a mass spectrometer system (Leybold PGA 100) and computer controlled AutoLab potentiostat (Eco Chemie) which is arranged for simultaneous recording of current- and mass response. The setup is similar to that of Vielstich et al.[15].

In both electrochemical cells the counter electrode is a Pt foil and the reference electrode a Hg/Hg₂SO₄ electrode (MSE); E = + 0.68 V vs. RHE.

The experiments were carried out in 0.5 M H₂SO₄ (or 1 M HClO₄) with or without CH₃OH (Merck) (up to 0.33 M); monolayers of Ru or Sn were deposited by potential cycling in solutions containing low concentrations of ruthenium(III)-nitrosyl nitrate (Johnson Matthey) or SnSO₄ (Janssen Chimica) in 0.5 M H₂SO₄. All chemicals are p.a. grade. All solutions were prepared with Ecostat water (18.2 MR). Argon (99.99%) was used to provide oxygen free electrolyte. The Pt disc was polished with 0.05 µm alumina paste.

RESULTS AND DISCUSSION

Methanol adsorption

Figure 1 gives the voltammogram of Pt in 0.5 M H₂SO₄ in the presence and absence of methanol. Comparison of both the anodic scans shows that methanol oxidation starts at a potential at which no oxide formation on Pt is yet found. This fact, often noted in the literature, makes it plausible that an activated water molecule takes part in the electro-oxidation of methanol (cf. eq.2) and not a Pt-oxide or -hydroxide. Furthermore the peak potential of methanol oxidation is seen to coincide with the onset of Pt-oxide formation, which shows that Pt-oxides are inactive for the oxidation of methanol. In the anodic scan methanol oxidation restarts at a potential at which the Pt-oxide is partially reduced. Figure 2 shows the corresponding optical Δ-E curves in 0.5 M H₂SO₄; the Ψ-E curves show similar behaviour and are therefore not given. Without methanol a steep decrease of Δ is seen during the anodic scan at potentials higher than +0.1 V vs. MSE, this is indicative of the growth of Pt-oxide and coincides with the potential region where Pt oxidation is observed in the cyclic voltammogram (cf. fig 1). Furthermore, a slight decrease in Δ is found in the potential region from −0.6 V to +0.1 V; in the presence of methanol however, Δ remains virtually constant in the same potential region.

The decrease of Δ in the double layer region was also observed by Hyde et al.[16] and attributed to a restructuring of the water layer causing a higher density. If the optical curve is measured in 1 M HClO₄, a similar behaviour is found, only the decrease of Δ in the double layer region is smaller. This small difference between sulfate and perchlorate electrolyte is probably due to the stronger adsorption of sulfate ions. According to Horanyi[17], the adsorption of bisulfate increases with potential and reaches a maximum at −0.05 V vs. MSE.

The fact that in the presence of methanol Δ becomes virtually constant indicates that the adsorbed water layer on the electrode is modified. It is known[18, 19, 20, 21] that methanol (depending on the concentration) adsorbs in the potential range −0.60 V to +0.1 V vs. MSE. The flattening of the Δ-E curve must therefore be due to the presence of adsorbed methanolic species, which have (partially)
replaced both the adsorbed electrolyte anions and adsorbed water molecules. The replacement of the adsorbed sulfate anions is in agreement with the data of Horanyi[17] which show that less sulfate is detected in the presence of methanol.

Figure 2 provides only indirect evidence for the presence of an adsorbed methanolic species; no direct evidence for this adsorbate is found with ellipsometry. This however offers us a great advantage; now we are able to detect possible changes in the Pt surface oxidation in the presence of methanol. The potential at which the oxide coverage begins is seen to shift to a slightly higher potential in the presence of methanol; however the total A and \( \Psi \) changes up to the potential of reversal (+0.65 V vs. MSE) are virtually the same with and without methanol. One might state that the onset of Pt-oxide formation is only slightly retarded by the presence of methanolic species. This is in agreement with the quatz-microwave balance results of Wilde et al.[21]. The fact that the total changes in A and \( \Psi \) are not affected by the presence of methanol implies that Pt-oxides do not take part in the oxidation of methanol and that at higher potentials no more methanolic adsorbates are present.

**Pt-Ru system**

Figure 3 shows the cyclic voltammogram for Pt in the presence of \( 1.35 \times 10^{-5} \) M Ru ions in the electrolyte. The current in the hydrogen adsorption region has decreased compared with the voltammogram in the absence of Ru and an anodic hump at ca. +0.05 V vs. MSE is observed which points to the presence of a Ru species. In the cathodic scan the current in the double layer region has increased due to Ru deposition. Calculation of the Ru coverage by measuring the change in the hydrogen adsorption region is not fully reliable since Ru itself is known to adsorb hydrogen[22]. We therefore calculated the Ru coverage from the anodic Ru peak following the method of Watanabe and Motoo[9]. This gave \( \Theta_{Ru} = 0.50 \) on the basis of one electron transfer. Figure 4 gives the corresponding A-E curves before and after Ru addition. A rather drastic change in the A-E curve is seen. In the presence of Ru A already starts to decrease at ca. -0.3 V in the anodic scan; furthermore in the cathodic scan the change in A is extended over a wider potential range. This potential range is extended even further at higher Ru concentrations as shown by the full line in Fig. 5 for 2.7 \( 10^{-5} \) M. The \( \Psi-E \) curves show similar changes.

For comparison both the voltammetric and ellipsometric responses of a Ru electrode were measured. The optical curve is given in Fig. 6 and shows that A starts to decrease in the anodic scan at ca. -0.3 V. It
is known that the Ru surface is oxidized\[22, 23\] at 
\( E > -0.3 \text{ V} \), hence the \( \Delta E \) change in Fig. 6 indicates 
oxide growth. It is noted that the Pt/Ru electrode 
behaviour (Fig. 4 or 5) closely resembles the \( \Delta E \) 
curve for Ru and thus shows predominantly the Ru 
features. One can therefore confirm that the peak at 
\(+0.05 \text{ V} \) in the anodic voltammogram is due to 
the oxidation of Ru atoms on the Pt surface which are 
reduced in the cathodic scan.

With the pure Ru electrode it is found that Ru 
dissolves with repeated scanning to potentials higher 
than +0.2 \text{ V}; this confirms the work of Beden \textit{et al.}[13] on Pt-Ru.

In the presence of methanol (0.167 M) the ellipsometric 
curve of the Pt/Ru system (2.7 \( \times \) 10\(^{-5} \) M Ru 
ions) changes significantly (Fig. 5 dashed line); the Ru 
features have become less distinct. At higher methanol concentration (0.33 M) they are totally 
absent and the \( \Delta E \) curve is now virtually identical 
to the ellipsometric curve of Pt without Ru; the only 
difference is the shift in \( \Delta \) by 0.25 over the whole 
potential region. Though the observed change in \( \Delta \) 
seems now only due to oxidation and reduction of Pt, there is still Ru present at the surface as can be 
deduced from the \( \Delta \) shift with respect to that of the 
Ru-free Pt (cf. Fig. 5). We further demonstrated this 
by an experiment in which after methanol oxidation 
the electrolyte was replaced by fresh sulfuric acid 
without Ru-salt and methanol. The optical diagram 
still showed the characteristic Ru features.

In another experiment a Pt-Ru electrode was pre-
pared by potential scanning in a Ru containing 
electrolyte outside the optical cell. Optical measure-
ments in a Ru-free electrolyte showed the character-
istic Ru features. After addition of methanol again 
similar optical changes were observed as for the Ru 
containing electrolyte.

The ellipsometric curve of Ru itself does not alter 
in the presence of methanol. This is in accordance 
with Franaszczuk \textit{et al.}[24] who did not find meth-
anol adsorption on Ru. The voltammmogram of the 
Pt-Ru-methanol system in 0.5 M H\(_2\)SO\(_4\) + 0.33 M 
CH\(_3\)OH is given in Fig. 7(A) for different Ru 
concentrations. These data show that in the anodic scan the 
mechanism is enhanced in the presence of Ru-
ions in the potential region up to 0 \text{ V} vs. MSE, while at higher potentials the activity decreases. To 
verify that the increase in oxidation current is indeed 
due to methanol oxidation, simultaneous DEMS 
measurements were carried out. The results are given 
in Fig. 7(B) and demonstrate that in the potential 
region -0.3 to 0 \text{ V} vs. MSE the CO\(_2\) production 
increases with higher Ru concentration.

The results of the Pt-Ru system may be sum-
marized as follows: Ru, which is present in sub-
monolayer form on Pt, is oxidized at potentials 
\( \geq -0.3 \text{ V} \) vs. MSE. This Ru oxide growth can be followed 
with ellipsometry and appears to be virtually 
the same as that found on Ru metal. The Ru-oxides 
are found to disappear in the presence of methanol 
wheras those on a Ru electrode do not. In the same 
potential region where the oxides are formed, an 
enhancement in the methanol oxidation activity is 
observed.

We may thus conclude that the disappearance of the 
Ru-oxide is caused by the reaction with an

\[
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru(OH)} + \text{H}^+ + \text{e} \quad (3)
\]

\[
\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-COH} + 3\text{H}^+ + 3\text{e} \quad (4)
\]

\[
\text{Pt-COH} + \text{Ru(OH)} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + 2\text{H}^+ + 2\text{e} \quad (5)
\]

This mechanism was first proposed by Watanabe 
and Motoo[9] and represents the bifunctional 
model. They assume that monovalent Ru(OH) is the 
active Ru species, this is also supposed by Herrero \textit{et al.}[25]. With ellipsometry the exact nature of the 
Ru-oxide species cannot be established, RuO\(_2\) 
howerver may be excluded because this was 
found[26] to be inactive for the methanol oxidation.

The ellipsometric data indicate that Ru is present 
in the metallic state during the methanol oxidation, 
which implies that the reactions (equation 3-5) are 
rapid. The conclusion that Ru is zero-valent was also 
postulated by Janssen and Moolhuysen[6] but con-
tradicts the XPS and Mössbauer measurements of 
Hamnett and Kennedy[27, 28] which show that all 
Ru is present as Ru(III). They concluded that the
actual processes must take place at Pt via a Ru-Pt oxide species. These measurements were however carried out ex-situ and are thus not fully relevant for the actual situation at the surface during methanol oxidation.

**Pt-Sn system**

Figure 8 gives the cyclic voltammograms for Pt in the presence of difference SnSO₄ concentrations. It shows the same characteristics as the voltammogram for Pt-Ru (Fig. 3). The hydrogen region is partially suppressed and the current increase around $-0.2\,\text{V}$ in the cathodic scan indicates the reduction of a Sn species. The anodic peak at $+0.05\,\text{V}$ indicates the oxidation of a Sn species. At higher anodic potentials Sn is found to dissolve from the surface. The Sn coverage was calculated from the difference between the hydrogen adsorption area ($Q_n$) in the absence and presence of Sn; $\Theta_{\text{Sn}} = (Q_n - Q_{\text{Sn}})/Q_n$. For the three presented curves of Fig. 8 these coverages are respectively $\Theta_{\text{Sn}} = 0.20$; $\Theta_{\text{Sn}} = 0.52$ and $\Theta_{\text{Sn}} = 0.72$. The corresponding $\Delta-E$ curves are shown in Fig. 9 for Sn coverages of $\Theta_{\text{Sn}} = 0.20$ and $\Theta_{\text{Sn}} = 0.72$. Compared to the $\Delta-E$ curve of Pt (cf. Fig. 2) a change in $\Delta$ is seen in the low potential region during the cathodic scan, this indicates the upd of Sn; with increasing Sn coverage the changes in $\Delta$ are more pronounced. During the anodic scan $\Delta$ decreases only slightly with potential in the low potential region. The larger decrease of $\Delta$ at $E > ca. 0.3\,\text{V}$ indicates the growth of a layer which is most likely oxidation of Pt that is not covered with Sn. The $\Psi-E$ curves gave a different pattern. This is demonstrated by Fig. 10 which represents the change of $\Psi$ vs. $\Delta$ during a full scan for the Pt Sn system with $\Theta_{\text{Sn}} = 0.20$. It follows from the theory of ellipsometry[14] that the growth of a very thin film with constant refractive index is represented by a linear $\Psi-\Delta$ curve. For the cathodic scan the $\Psi$ vs. $\Delta$ curve is linear in the potential range from 0.6V to ca. 0V; this line signifies the decrease in oxide coverage during reduction, while around $-0.05\,\text{V}$ the slope of the line changes indicating the onset of another process via. Sn upd. After scan reversal at $-0.6\,\text{V}$ it is noted that the curve turns around until at $ca. 0.1\,\text{V}$ $\Psi$ reaches a maximum. In the potential range 0.2 to 0.6V the curve is again linear and virtually retraces the oxide reduction line. This behaviour can be explained as follows: Pt is oxidized and reduced in the potential region 0.2 to 0.6V and Sn that is deposited on Pt is oxidized in the potential region $-0.2$ to $0.2\,\text{V}$. Hence the anodic peak at 0.05V in the voltammogram of Fig. 9 represents the surface oxidation of Sn.

It was observed that with repeated scanning in the Sn-containing electrolyte the optical behaviour of the Pt electrode changed. This was established by taking optical measurements at the Pt electrode in a Sn-free electrolyte. The $\Delta$, $\Psi$ data differ from the values obtained at Pt before Sn addition. This change of the Pt substrate indicates that some Sn dissolves into platinum as was also noted by others[29, 30, 31]. With prolonged oxidation at high potential $\Delta$ and $\Psi$ return slowly to the original values.

In the presence of 0.16M methanol the ellipsometric curve for the Pt-Sn ($\Theta = 0.72$) electrode changes as shown in Fig. 11. The Sn features have become less dominant in the potential range $-0.5$ to ca. $0.3\,\text{V}$; with 0.33M methanol the original $\Delta-E$ plot for Pt is obtained. It was concluded above that Sn-oxides are formed in the potential region up to $0.2\,\text{V}$ vs. MSE. The optical change of Fig. 11 then implies that the Sn-oxide disappears due to reaction with methanol. It is possible that also some removal
of Sn species from the surface is involved. It is known that at higher potentials some dissolution of Sn-oxide occurs\[6, 31\], which could be enhanced by methanol. Vassiliev et al.[29] concluded from radiotracer experiments that the Sn coverage is lower in the presence of methanol; they found that Sn already disappears at \(-0.35\) V. We however found that after methanol oxidation there is still Sn present on the electrode surface.

Voltammetry and DEMS measurements of methanol oxidation at Pt with different Sn concentrations are presented in Figs. 12(A) and 12(B). The results, as with Ru, show a simultaneous increase of current and CO\(_2\) in the presence of Sn at potentials \(-0.15\) to \(0\) V, signifying an enhanced methanol oxidation. Thus the Sn surface species enhances the methanol oxidation in the same potential region as where it is oxidized in the absence of methanol.

The behaviour of the Pt-Sn system is thus similar to the Pt-Ru system. The bifunctional mechanism as was discussed for Ru, will therefore also apply for Sn.

\[
\begin{align*}
\text{Sn} + \text{H}_2\text{O} &\rightarrow \text{Sn(OH)} + \text{H}^+ + e^- \\
\text{Pt} + \text{CH}_3\text{OH} &\rightarrow \text{Pt-COH} + 3\text{H}^+ + 3e^- \\
\text{Pt-COH} + \text{Sn(OH)} &\rightarrow \text{Pt} + \text{Sn} + \text{CO}_2 + 2\text{H}^+ + 2e^- 
\end{align*}
\]

Sn(OH) is used here as a formal notation. According to Iwasita\[2]\ Sn is present in different redox states depending on the potential; Janssen and Mooilhuysen\[32\] favor a zero-valent state and Sobkowski et al.[31] concluded to an adsorbed divalent hydroxy- or sulfate tin complex. The ellipsometric results presented here seem to indicate that Sn is zero valent during the methanol oxidation, which again implies that all reactions (equations 6–8) must be very rapid.

CONCLUSIONS

—The amount of Pt-oxide formed during a potential scan is not affected by the presence of methanal, but the onset potential of Pt oxidation is shifted to slightly higher potentials in the presence of methanal.

—The oxidation of Ru and Sn, deposited on the Pt surface in submonolayer coverage, can be followed with ellipsometry.

—In the presence of methanal the oxide coverage of Ru and Sn disappears. Therefore both metals must be present in the zero-valent state at Pt during the methanal oxidation.

—DEMS and voltammetric measurements show that Ru and Sn enhance the methanal oxidation in the same potential region where these metals are covered with an oxide layer in the absence of methanal.

—A bifunctional mechanism is proposed for the effect of both Sn and Ru, although an additional ligand effect can not be excluded on the basis of these measurements.

REFERENCES

Ellipsometry and DEMS study of the electrooxidation of methanol