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Active Form of Ru for the CH$_3$OH Electro-oxidation Reaction

Introduction of a Simple Electrochemical In Situ Method

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In this work, unsupported Pt/Ru catalysts are used to address the issue of Ru oxide involvement during the methanol oxidation reaction, from the point of view of both Ru "oxidation state" (metal vs oxide) and amount of Ru oxide. It is shown that a simple electrochemical method is useful as in situ probe for the Ru oxidation state. The method also yields insight into the Pt to Ru site distribution of the catalyst surface. The results indicate that the electrochemical formation of reversibly reducible Ru oxides is effectively suppressed in CH$_3$OH solutions, most probably because of its involvement in the anodic oxidation reaction to CO$_2$. In the case of PtRu alloys that consist of surfaces of well-distributed Pt to Ru sites, Ru oxides are not detected on this surface for CH$_3$OH concentrations greater than 0.1 M. It is also shown that the electrochemical formation of Ru oxides at the potential of interest prior to the CH$_3$OH oxidation reaction deenhances the catalyst activity for CH$_3$OH oxidation. However, the experiments suggest the deenhancement is low (<5% at 0.6 and <15% at 0.8 V vs the reversible hydrogen electrode) and only observed at potentials equal to or more positive than 0.6 V.

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Pt and binary Pt/Ru catalysts have attracted much attention as anode catalysts for low-temperature fuel cells. Until now, Pt/Ru systems are the state-of-the-art catalysts, particularly for direct methanol fuel cells. The beneficial catalytic effect of Pt/Ru catalysts is largely assigned to a bi-functional mechanism, as demonstrated in the following scheme\(^1\)–\(^3\):

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} &\rightarrow \text{Pt} - (\text{CH}_3\text{OH})_{\text{ads}} + \text{H}_2\text{O} + 4\text{e}^- + 4\text{H}^+ \quad [1] \\
\text{Pt} - (\text{CH}_3\text{OH})_{\text{ads}} &\rightarrow \text{Pt} - (\text{CO})_{\text{ads}} + 4\text{H}^+ + 4\text{e}^- \quad [2] \\
\text{Ru} + \text{H}_2\text{O} &\rightarrow \text{RuO} - \text{OH} + \text{H}^+ + \text{1e}^- \quad [3] \\
\text{Pt} - (\text{CO})_{\text{ads}} + \text{RuO} - \text{OH} &\rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + \text{1e}^- \quad [4]
\end{align*}
\]

As a result of the adsorption/dehydrogenation reaction of CH$_3$OH that takes place on Pt sites, an intermediate "CO"-type species is formed. This species is believed to be oxidized to CO$_2$ with the assistance of –OH species that are viewed to be formed by the partial oxidation of H$_2$O on Ru surface sites. Based on this reaction scheme, it is clear that the distribution of Pt to Ru surface sites on the atomic level influences the CH$_3$OH and CO oxidation reactions.\(^4\),\(^6\) The nature of the most active form of Ru assisting in the CH$_3$OH electro-oxidation reaction to CO$_2$ has attracted a certain amount of discussion in the literature.\(^7\)–\(^10\) It has been suggested that catalysts consisting of two phases, namely, Pt and hydrous Ru oxide (RuO$_x$H$_y$), are more active than PtRu alloy catalysts, i.e., Pt$^x$Ru$^y$.\(^5\)

Kim et al.\(^8\) carried out X-ray photoelectron spectroscopy (XPS) experiments involving immediate transfer of the electrodes that consisted of Ru and RuO$_x$ nanoparticles deposited on Pt(111) surfaces to an ultrahigh-vacuum chamber. They showed that Ru oxides can be electrochemically reduced to Ru metal. Their data also suggest that even the RuO$_2$ nanoparticles can at least partially be reduced to Ru metal in the electrochemical environment. Based on their results the authors concluded that under fuel cell operating conditions, the presence of a metallic Ru phase, which is covered by a weakly bonded Ru oxide state precursor, e.g., a–Ru–OH species, is a prerequisite for an effective CH$_3$OH electro-oxidation catalysis. This is in agreement with reports by Frelink et al.\(^9\),\(^10\) who employed in situ electrochemical ellipsometry and quartz crystal microbalance measurements to study the influence of methanol on the Ru oxide formation reaction. Other work has involved a more demanding technique, namely X-ray adsorption near-edge structure (XANES) spectroscopy.\(^11\) Viswanathan et al. set up a cell that allows XANES measurements under real fuel cell operating conditions to be carried out. The experiments were carried out using H$_2$ and H$_2$ + CO anode fuels and unsupported PtRu alloy catalysts. They showed that under fuel cell operating conditions both Pt and Ru are present in the metallic state.

In this work, a simple electrochemical method is introduced that allows the in situ estimation of the Ru "oxidation" state (metal vs oxide) during the CH$_3$OH electro-oxidation reaction. The method also yields an estimate of the Pt to Ru site distribution of the catalyst surfaces. The influence of electrochemically preformed Ru oxides on the CH$_3$OH oxidation activity is also discussed.

Experimental

Catalyst powder preparation.— Unsupported Pt/Ru catalyst powders are used in this study. The powders are prepared and well characterized as discussed elsewhere.\(^1\)–\(^2\) All Pt/Ru catalysts consist of Pt to Ru ratios of 70 to 30 atom %. A PtRu alloy powder catalyst was prepared via a very rapid chemical reduction method and is referred to as PtRu (chemically reduced catalyst). A second catalyst was prepared by ball milling Pt and RuO$_x$ powders and is referred to as Pt/RuO$_x$ (ball-mill) catalyst. A third catalyst was prepared by thermal decomposition of RuCl$_3$ that was dispersed on Pt powder using a mortar. Part of the latter catalyst powder that is referred to as Pt/RuO$_2$ (thermal) catalyst was reduced in an H$_2$ atmosphere at 100°C and is referred to as Pt/Ru (H$_2$ reduced) catalyst.

Summary of catalyst powder properties.— The catalysts prepared in this work have been characterized previously.\(^1\)–\(^2\) hence, their as-prepared properties are only briefly summarized in this section. The PtRu (chemically reduced) catalyst is viewed to consist of a bulk PtRu alloy with a surface made of randomly distributed Pt to Ru sites of 70 to 30 atom % composition. This preparation method has been shown to result in high-surface-area catalysts consisting of particles in the nanoscale range.\(^12\) The Pt/Ru (H$_2$ reduced) catalyst is viewed to consist of nonalloyed Pt particles that are covered with Ru islands of unknown size. The surface is enriched in Ru, and the Ru islands consist of mainly Ru metal and easily reducible Ru oxides. The Pt/RuO$_2$ (thermal) catalyst is viewed to be similar to the Pt/Ru (H$_2$ reduced) catalyst. However, the Ru islands of the former mainly consist of RuO$_2$ and RuO. Metallic Ru is not present in the as-prepared catalyst according to XPS data.\(^12\) The Pt/RuO$_2$ (ballmill) catalyst also consists of a bulk PtRu alloy of the same composition as the PtRu (chemically reduced catalyst). Its surface, however, is enriched with Ru and possibly consists of randomly distributed Pt to Ru sites as well as some Ru islands. XPS data
suggest that the surface Ru of both the chemically reduced and the ballmill catalyst is mainly present as Ru and RuO.

**Working electrode preparation.**—The catalyst powders were formed into electrodes by sonicating 13 mg of a particular powder dispersed in solutions consisting of 300 μL of a Nafion 117 solution (5 wt % Nafion dissolved in lower alcohols, Fluka) and 2 mL H2O for 30 min. Appropriate amounts (1–20 μL) of the suspensions were pipetted onto ca. 0.35 cm2 geometrical area Au foil electrodes (99.9% Au, 0.1 mm thick, Goodfellow), forming thin catalyst layers. The electrodes were dried in air and room temperature. The Au foils were firmly attached to Au wire electrodes, and Au not covered with the catalyst powder was carefully wrapped with Teflon tape.

**Cells and electrodes.**—Three compartment cells, in which the reference electrode was separated from the working and counter electrode compartment by a Luggin capillary, were employed for the electrochemical studies. All potentials reported in this paper are vs the reversible hydrogen electrode (RHE) for 0.5 M H2SO4 solution, even though either a mercury sulfate electrode (MSE, MSE = 0.68 V vs RHE) or a saturated calomel electrode (SCE, SCE = −0.24 V vs RHE) was used for the actual experiments. A large-surface-area Pt gauze served as counter electrode.

**Techniques and instrumentations.**—Electrochemical experiments were carried out using a Solartron SI 1287 electrochemical interface (Solartronics Group, Ltd.) driven by a Corware software program (Scribner, Assoc.). Measured currents are normalized using the electroactive Pt area (Ap) or the adsorbed CO (COads) stripping charge, unless otherwise stated. The Ap and COads values were determined as described in the following paragraph. Furthermore, COads stripping voltammograms were recorded before and after a particular set of experiments were carried out. The characteristics of the COads stripping voltammograms were essentially the same before and after a set of experiments were carried out for all the data discussed in this work.

**COads to Pt surface area conversion factors: Electroactive Pt surface area estimation.**—CO was adsorbed onto the Pt-based powder electrodes at 0.15 V by bubbling CO gas (Matheson purity, Matheson gas) through the 0.5 M H2SO4 solution for 10 min. Solution CO was subsequently removed by bubbling high-purity argon gas (Air products) for 30 min, holding the potential at 0.15 V. The potential was then cycled at 10 mV s−1 starting at 0.15 V for two complete oxidation/reduction cycles. The electroactive Pt surface area was determined using the combined COads stripping and (COOH) oxidation current method, as described previously. The following conversion factors, which were determined in the previous work, were used to convert the COads stripping charge (QCOads) to the electroactive Pt area: PtRu (chemically reduced) powder 0.7; Pt/RuO2 (ballmill) 0.5; Pt/RuO2 (thermal) 0.55, and Pt/Ru (H2 reduced) 0.45.

**Solutions.**—All CH3OH oxidation studies were carried out using 0.5 M CH3OH + 0.5 M H2SO4 solutions. Prior to the electrochemical studies, the solutions were deoxygenized using high-purity Argon gas. ACS-grade chemicals and high-resistivity 18 MΩ water were used. All experiments were carried out at room temperature.

**Results and Discussion**

**Description of the in situ determination of Ru “oxidation” state (metal vs oxide) method.**—Figure 1 shows a schematic describing the experimental sequence utilized in this work that allows the in situ testing of the Ru oxide involvement in the methanol oxidation reaction. The experiments are carried out in 0.5 M H2SO4, i.e., background solutions, and 0.5 M H2SO4 solutions containing up to 5 M CH3OH. In all cases, a potential (E−) of 0.1 V is applied for 30 s to condition the electrodes. This period is referred to as P1. Subsequently, during the second period (P2), the potential is stepped to an E+ value of 0.3, 0.4, or 0.5 V and current–time transients are recorded. P2 lasts 5 min, as further discussed below. For Pt/Ru catalysts studied in the H2SO4 background solutions, the current measured during P2 results from double-layer charging, desorption of H, and the electro-oxidation of Ru surface sites. Pt is not oxidized within the practical potential range studied in this work, while the so-called “reversibly reducible” Ru oxides are formed on Ru metal electrodes within a potential range of ca. 0.3−0.9 V. In the H2SO4 solutions that contain CH3OH, the CH3OH electro-oxidation reaction also contributes to the current measured during P2. During a third period (P3), a cathodic current of 50 μA is applied and the potential–time transients are recorded. The reduction reactions taking place during P3 are the reduction of the Ru oxides formed during the preceding potentiostatic experiment, i.e., during P2, and double-layer charging. If the potential drops to values of less than 0.3 V, the adsorption of H (Hads) on the catalyst sites and eventually the H2 evolution reaction (HER), respectively, also take place. In this work, 0.3 V is generally taken as the lower limit to study the reduction of the Ru oxides formed during P2. The Ru oxides formed during P2 may not be completely reduced to Ru metal at 0.3 V; hence, care needs to be taken when the potential–time transients are used to obtain the amounts of Ru oxides formed, as discussed below. Furthermore, all experiments are terminated before a potential of 0 V is reached. This precaution avoids the production of H2 that may be oxidized during subsequent experiments and also ensuring the potential to reach <0.1 V, however, ensures that all the Ru oxides formed during P2 are reduced and reproducible current and potential–time transients are obtained. Reduction charges passed between the beginning of galvanostatic reduction and 0.3 V yield a measurement of the amount of Ru oxides formed and still residing on the surface at the end of the 5 min at P2, for both the H2SO4 background and the H2SO4 + CH3OH solutions. Careful comparisons of potential–time transients in these different solutions are predicted to yield information about the influence of the CH3OH oxidation reaction on the amount of Ru oxide remaining on the surface during P2, i.e., not participating in the CH3OH oxidation reaction that is assumed to take place according to a bi-functional mechanism (Eq. 1–4).
Probing the reliability of the experimental test procedure.—Probing for experimental interferences, impurities, etc., using the \( \text{H}_2\text{SO}_4 \) background solution.—The first task in this work is to test the reliability of the above-described experimental procedure. In this section, oxidation and reduction charge values measured in the \( \text{H}_2\text{SO}_4 \) background solutions are compared for P2 and P3. The data are discussed using the PtRu (chemically reduced) catalyst powder. As discussed in previous work, the PtRu (chemically reduced) catalyst powder used in this work consists of a single PtRu bulk alloy phase.\(^\text{11}\) A lattice parameter for the face centered cubic (fcc) Pt phase of 0.3886 (\( \pm 1.6 \times 10^{-4} \)) nm was estimated from experimental X-ray diffraction (XRD) data. This lattice parameter value indicates that the Ru is entirely dissolved in the Pt fcc lattice using a previously established Vegard’s law relationship based on theoretical as well as experimental data.\(^\text{3}\) The surface of this catalyst is viewed to be made of randomly distributed Pt to Ru sites of 70–30 atom % composition and to have the same bulk and surface composition. The latter conclusions are based on experimental CO adsorption and reduction charge values measured in the work,\(^\text{49}\) chemically reduced PtRu catalyst.\(^\text{49}\) It is seen that the Ru oxide formation and reduction reactions for sufficiently low potentials involve the HER. There may be contributions from hydrogen adsorption on Pt using a lower limit of 0.085 V; however, this should not play a role in the interpretation of the data of this particular experiment. It is seen that the \( Q_{\text{O-CV}} \) and \( Q_{\text{R-CV}} \) values are independent of the sweep rate tested between 10 and 100 mV s\(^{-1}\). Reduction charge values (\( Q_{\text{R-trans}} \)), extracted from potential–time transients recorded during P3 for the same catalyst electrode as used in Fig. 2b, are also shown in Table I. The potential–time transients obtained after 5 min of potentiostatic holding at each potential are shown in Fig. 2c and were recorded in the 0.5 M \( \text{H}_2\text{SO}_4 \) background solution using a constant cathodic current of 50 \( \mu \text{A} \). The \( Q_{\text{R-trans}} \) values are the product of the current (50 \( \mu \text{A} \)) multiplied by the time needed for the potential to decay to a value of 0.085 V (chosen as this value so as to be consistent with the limits used for the CVs). The lower potential integration limit of 0.085 V used for these particular experiments were chosen because the Ru oxides formed during P2 are reduced at this potential,\(^\text{13}\) while more negative potentials involve the HER. There may be contributions from hydrogen adsorption on Pt using a lower limit of 0.085 V; however, this could also be used for the purpose of the experiments discussed in this work.

![Figure 2](http://www.ecsdl.org/terms_use.jsp)
were integrated using the CV data for the 0.3
formation/reduction reaction. Oxidation and reduction charge values
quantitative information about the reversibility of the Ru oxide
sients recorded during P3 are used to extract exact values for the
P2. Therefore, care needs to be taken when the potential–time tran-
different
↔
0.3
/H20849
charges in percentage
A2294 Ru oxide
i.e., up to 0.5 V, is of interest here, the oxidation of Ru metal to
cause the potential range relevant for practical fuel cell applications,
reversibility of the Ru oxide formation and reduction reaction. Be-


\[
\begin{array}{cccccc}
\text{Upper integration} & Q_{R-trans} & Q_{O-CV} & Q_{O-CV} \times 100 & Q_{E-CV} & Q_{R-trans} \times 100 \\
\text{limit vs} & \text{(mC)} & \text{(mC)} & \text{(%)} & \text{(mC)} & \text{(%)} \\
\text{RHE}^\text{a} & \text{V} & & & & \\
0.3 & 2.6 & 2.8 & 93 & 2.3 & 113 \\
0.4 & 3.1 & 3.2 & 97 & 2.7 & 87 \\
0.5 & 3.7 & 3.6 & 103 & 3.1 & 84 \\
\end{array}
\]

^a Charge integration between 0.085 V and an upper potential limit
^b Integration limit (V)
m and the corresponding
E
Q
R-RH

\[\text{Reversibility of Ru oxide formation and reduction reaction (extent of error in the estimation of the amount of Ru oxides formed using 0.3 V as integration limit).—A critical point for the method used in this work, if applied to estimate the amount of Ru oxide formed, is the reversibility of the Ru oxide formation and reduction reaction. Because the potential range relevant for practical fuel cell applications, i.e., up to 0.5 V, of interest here, the oxidation of Ru metal to Ru oxide (suggested to be RuO}^2\text{) plays a critical role. Information about the reversibility of the Ru oxide formation/reduction reaction can be extracted from CV data by integrating the oxidation and reduction charge within the potential range of interest. Therefore, for all catalysts, multiple CVs (obtained in the same manner as done for the data shown in Fig. 2b) were used to gain quantitative information about the reversibility of the Ru oxide formation/reduction reaction. Oxidation and reduction charge values were integrated using the CV data for the 0.3 to 0.5 V and the 0.3 to 0.5 V range, and the ratio of the reduction vs the oxidation charges in percentage (% Q/O) for a particular potential range were calculated. The data are summarized in Table II. It is seen that for all catalyst powders studied in this work, the % Q/O value is less than 100%, i.e., the reduction charge is smaller than the oxidation charge value. This indicates that more negative potentials than 0.3 V are needed to completely reduce the Ru oxides formed during P2. Therefore, care needs to be taken when the potential–time transients recorded during P2 are used to extract exact values for the amount of Ru oxides reduced. However, the method should still be valid to obtain information about the influence of the CH\text{OH oxidation reaction on the extent of suppression of Ru oxide formation (due to its involvement in the reaction), as further discussed below. In addition, limitations of this method due to a possible influence of a CH\text{OH oxidation current on the net cathodic current applied during P3 are tested and discussed later in this paper.}

\[\text{In situ Ru oxide estimation experiments using the PtRu (chemically reduced) catalyst and different CH}_4\text{OH concentrations. —Figure 3 shows typical potential–time transients for the PtRu (chemically reduced) catalyst recorded after P2 using an E+ value of 0.5 V. These in situ Ru “oxidation” state estimation experiments were carried out in 0.5 M H}_2\text{SO}_4 solutions containing different concentrations, 0–5 M, of CH\text{OH. For all concentrations of CH}_4\text{OH, it is seen that less time, i.e., less charge is needed to reach a potential of 0.3 V during P3 than found for the background solution. Less charge is equivalent to less Ru oxide, thus indicating that the presence of CH}_4\text{OH results in a decrease in the amount of Ru oxide available to be reduced in P3. For all solutions containing CH}_4\text{OH concentrations exceeding 0.1 M, the starting potential of these transients is less than 0.3 V. This indicates that the amount of Ru oxides left on the surface during P2 is very small for solutions containing CH}_4\text{OH concentrations larger than 0.1 M. The influence of the CH}_4\text{OH concentration on the degree of suppression of the available Ru oxide, remaining on the surface and not involved with the CH}_4\text{OH oxidation, is shown in a more quantitative manner in Table III for two E+ limits applied during P2, namely, 0.4 and 0.5 V. The last column indicates the relative amount in percentage of Ru oxide formed. This amount is calculated relative to the approximate amount of Ru oxide formed in the methanol-free H}_2\text{SO}_4 solution estimated at either 0.4 or 0.5 V. Details of the calculation and limitations are discussed above. For simplicity, the contribution of double-layer charging is ignored in this calculation. It is seen that for both the E+ limits of 0.4 and 0.5 V used during P2, the amount of Ru oxide available to be cathodically reduced rapidly decreases with increasing CH}_4\text{OH concentration. The suppression of the amount of available Ru oxide in the presence of CH}_4\text{OH during P2 appears to be consistent with the bi-functional mechanism proposed}

\[\text{Table II. Averaged percentage values of the reduction vs oxidation charge ratios (% }Q/Q\text{) for PtRu catalysts.}

\[
\begin{array}{cccc}
\text{Catalyst} & \text{ }Q/O\text{ (0.3 }\rightarrow\text{ 0.4 V)} & \text{ }Q/O\text{ (0.3 }\rightarrow\text{ 0.5 V)} \\
\text{PtRu (chemically reduced)} & 41 \pm 5 & 45 \pm 5 \\
\text{Pt/RuO}^2\text{ (ballmill)} & 40 \pm 5 & 47 \pm 5 \\
\text{Pt/RuO}^2\text{ (thermal)} & 51 \pm 5 & 47 \pm 5 \\
\text{Pt/Ru (H}_2\text{O}_2\text{-reduced)} & 55 \pm 5 & 70 \pm 5 \\
\end{array}
\]

^a Extracted from background CV data recorded at 10 mV s\text{ in 0.5 M H}_2\text{SO}_4 between 0.3 V and E+ limits of 0.4 and 0.5 V, as indicated in column 2 and 3, respectively.

\[\text{Figure 3. Potential–time transients recorded for a PtRu (chemically reduced) catalyst electrode in 0.5 M H}_2\text{SO}_4 + \text{different CH}_4\text{OH concentrations, as follows: (a) 5 M CH}_3\text{OH, (b) 0.5 M CH}_3\text{OH, (c) 0.1 M CH}_3\text{OH, (d) 0.01 M CH}_3\text{OH, and (e) 0 M CH}_3\text{OH. The transients were recorded after 5 min at 0.5 V vs RHE. The CO}_2\text{ charge of this particular electrode was 11.4 mC, suggesting an electroactive Pt surface area of 19.4 cm}^2\text{.}

\[\text{Table III. Averaged percentage values of the reduction vs oxidation charge ratios (% }Q/Q\text{) for PtRu catalysts.}

\[
\begin{array}{cccc}
\text{Catalyst} & \text{ }Q/O\text{ (0.3 }\rightarrow\text{ 0.4 V)} & \text{ }Q/O\text{ (0.3 }\rightarrow\text{ 0.5 V)} \\
\text{PtRu (chemically reduced)} & 41 \pm 5 & 45 \pm 5 \\
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\text{Pt/Ru (H}_2\text{O}_2\text{-reduced)} & 55 \pm 5 & 70 \pm 5 \\
\end{array}
\]
Eq. 3 with increasing CH₃ species neighboring Pt sites, thus freeing the Ru surface sites from the oxy-
3 that water adsorbs on Ru sites, forming a Ru–OH type species used for the complete oxidation of adsorbed "CH₃ is shown in Fig. 4, suggesting a correlation between the amount of measured after 5 min during P2 for the same PtRu catalyst electrode used for the data shown in Fig. 3. The following solutions.

<table>
<thead>
<tr>
<th>$E^+$ (V) vs RHE</th>
<th>$C_{\text{CH}_3\text{OH}}$/M</th>
<th>$\tilde{t}$ (s)</th>
<th>$Q^d$ (mC)</th>
<th>Relative amount of Ru oxide formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0</td>
<td>10</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>0.01</td>
<td>4</td>
<td>0.2</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>$5 \times 10^{-3}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>8</td>
<td>0.4</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>$2.5 \times 10^{-2}$</td>
<td>2.5</td>
<td></td>
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<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

a Tested for PtRu (chemically reduced) catalyst. A PtRu electrode of 11.4 μC CO₂ads charge, i.e., 19 cm² Pt surface area is used for the estimation. A 0.5 M H₂SO₄ electrolyte solution + different CH₃OH concentrations, as indicated in column 2, are used as electrolyte solutions.

b Potential applied during period P2.

c Time needed to reach a potential of 0.3 V vs RHE applying a −50 μA cathodic current during P3.

d Charge passed to reach a potential of 0.3 V vs RHE applying a −50 μA cathodic current during P3, i.e., the time values reported in column 3 are used for the calculation of the $Q$ values.

e Relative amount (%) of Ru oxide formed in 0.5 M H₂SO₄ + (concentration indicated in column 2) CH₃OH solutions. The charge ($Q$) in the CH₃OH-free background H₂SO₄ solution is taken as 100%. Double-layer charging contributions are ignored in this calculation.

Figure 4. Dependence of oxidation current on the CH₃OH concentration measured after 5 min during P2 for the same PtRu (chemically reduced) catalyst electrode used for the data shown in Fig. 3. The following $E^+$ values were used: (○) 0.3, (□) 0.4, and (△) 0.5 V.

Table III. Influence of the CH₃OH concentration on the Ru-oxide formation reaction.

Figure 5. Potential–time transients recorded during P3 in 0.5 M H₂SO₄ for a PtRu (chemically reduced) electrode after 5 min at 0.5 V. A range of cathodic currents (10–2000 μA) were applied as indicated in the figure. The electroactive Pt area for this electrode was estimated to be 22 cm².

Limitation of the method due to high CH₃OH oxidation currents.—The possibility exists that methanol oxidation can interfere with the charging results obtained in P3. This arises because CH₃OH can continue to be oxidized after the initiation of P3, provided the potential is still in the range where this reaction occurs to a significant extent. This anodic current will necessitate the effective passage of a cathodic current which is higher than the applied 50 μA, in order that the “net” cathodic current still be 50 μA. The contribution of methanol oxidation will obviously diminish rapidly as the potential falls from say 0.5 V to lower anodic values; the concentration of methanol in solution will also play a considerable role (see Fig. 4). The obvious question is: To what extent does this situation contribute to the decreased P3 Ru oxide charge observed in the presence of methanol, if at all? Referring to Fig. 3, the question is how much of the change in the cathodic charging curves, in the presence of methanol, is due to an effectively higher cathodic current (which will indeed be changing throughout the transient). To answer this question, cathodic galvanostatic charging curves were obtained for the background H₂SO₄ solution over a range of applied currents thought to be comparable to the maximum contributions that the methanol oxidation reaction could make using Fig. 4 and assuming the unrealistically “worst-case-scenario” where the anodic methanol current does not diminish from the 0.5 V values. The results are shown in Fig. 5 for applied cathodic currents in the range of 10–2000 μA, the higher values representing methanol contributions up to 0.5 M at 0.5 V, and certainly a worst case scenario. (The CH₃OH oxidation current for the 22 cm² electroactive Pt area PtRu catalyst electrode used to collect the data shown in Fig. 5 was measured to be 1 mA at 0.5 V and 0.5 M CH₃OH.) It is immediately
apparent that the galvanostatic charging profiles are quite different from those observed in Fig. 3, where the effect was associated with the presence of methanol during the polarization in P2/H2O as well as its possible influence during P3 itself. The profiles in Fig. 5 show what is expected for an oxide-reduction process being conducted over a wide range of cathodic charging currents, i.e., the time for the reduction process diminishes in direct relation to the applied current. There is some variation in the initial potential observed upon application of the cathodic current, amounting to about 60 mV over the 200 times range of applied currents. Such a change would certainly not be out of the question for an electrochemical process over this range of applied currents. In contrast, the profiles in Fig. 3 show an approximately 250-mV potential drop in going from a zero methanol concentration to 0.5 M. That this could be associated with additional cathodic charging currents, i.e., by way of the bi-functional mechanism, and the decreased amount of Ru oxides results in a more cathodic starting potential upon initiation of P3. In the case of 0.5 M CH3OH and higher, there is so little Ru oxide not being utilized for methanol oxidation during P2 that the initial P3 potential is around 0.22 V. This is the potential where hydrogen deposition begins to occur, and it is this cathodic process that is handling at least part of the charging current. For 0.1 M CH3OH, the initial P3 potential is about 0.32 V, indicating that some Ru oxide is still available for cathodic galvanostatic reduction; however, the amount is less than with 0.01 M or obviously no methanol.

Application of in situ estimation test procedure to the different Pt/Ru catalysts.—Figure 6a-d shows the potential–time transients recorded during P3 for all four Pt/Ru catalysts studied in this work. The gray and the black lines show the transients recorded in the 0.5 M H2SO4 background and in the 0.5 M H2SO4 + 0.5 M CH3OH solutions, respectively. Similar to the graphs shown in Fig. 3, the potential is seen to start to decay from the same value as applied during P2 for the potential–time transients recorded in the 0.5 M H2SO4 solutions, while the potential starts to decay at

**Figure 6.** Potential–time transients recorded during P3 in 0.5 M H2SO4 (gray lines) and 0.5 M H2SO4 + 0.5 M CH3OH (black lines) solutions for different Pt/Ru catalysts, as follows: (a) PtRu (chemically reduced) catalyst, (b) Pt/RuO2 (ballmill) catalyst, (c) Pt/RuO2 (thermal) catalyst, and (d) Pt/Ru (H2 reduced) catalyst. The potential used during the preceding period P2 is indicated in the figures on the left hand side y-scale. The following COads charge and electroactive Pt areas were found: (a) 12.3 mC, 20.5 cm²; (b) 18 mC, 21.5 cm²; (c) 9.9 mC, 12.9 cm²; and (d) 40 mC, 42.8 cm².
more negative values and much smaller charge values are obtained for the integration between the start of the potential–time transients and the time needed to reach 0.3 V for the 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solutions. Therefore, the data suggest that for all four catalysts studied in this work, CH$_3$OH appears to consume the Ru oxides being generated during P$_2$, thereby lowering the amount of oxide to be reduced during P$_3$. For the PtRu (chemically reduced) and the Pt/RuO$_2$ (ballmill) catalysts, all potential–time transients recorded in the 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solutions start to decay below 0.3 V. This indicates that the H$_2$ads reaction takes place immediately, and hence very little (or no) Ru oxide remains from the preceding experiment in the 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solution. (The results in, e.g., Fig. 6a, offer further support to the above argument that continued methanol oxidation is not interfering significantly with the P3 results, based on the fact that the gray curve starting from 0.3 V is so different from the dark curves also starting at 0.3 V.) Both the ballmill and chemically reduced catalysts are viewed to have surfaces made of uniformly and well-dispersed Pt and Ru sites. Therefore, the absence of (with this method) detectable Ru oxides suggests that these catalysts consist of well-distributed Pt-to-Ru surface sites. For the case of the H$_2$-reduced and the thermal catalysts, the potential–time transients suggest that a smaller amount of Ru oxide remains in the 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH vs the 0.5 M H$_2$SO$_4$ solution; however, more oxide is observed during P3 than was the case with the other two catalyst types. The relative amounts (%) of Ru oxide (observed during P3) in the 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solutions vs the 0.5 M H$_2$SO$_4$ solutions, for the H$_2$-reduced and thermal catalysts at 0.4 and 0.5 V, were calculated as discussed for the data shown in Table II. The relative amounts of Ru oxides formed are ca. 11 and 28% for the Pt/Ru (H$_2$-reduced) catalyst and ca. 34 and 10% for the Pt/RuO$_2$ (thermal) catalyst at 0.4 and 0.5 V, respectively. The fact that the amount of detected Ru oxides is not as strongly suppressed for these two catalysts (as seems to be the case for the chemically reduced and ballmill catalysts) is believed to reflect the fact that these two Pt/Ru catalysts consist of surfaces made of poorly distributed Pt to Ru sites. This, in turn, suggests that the Ru oxide detected is formed on sites not in direct contact with Pt sites available for the CH$_3$OH adsorption/dehydrogenation reaction.

It is noteworthy that numerous potential–time transients for a particular electrode were obtained by sweeping repetitively between the 0.5 M H$_2$SO$_4$ and the 0.5 M H$_2$SO$_4$ + CH$_3$OH containing solutions. For the same experimental conditions, essentially the same potential–time transients were obtained. This indicates that the catalyst properties are not measurably influenced during the experiments and that the observed formation of Ru oxides is reversible. The former was also confirmed by CO$_{th}$ stripping voltammograms carried out before and after the in-situ oxidation state estimation experiments. It was found that the CO$_{th}$ stripping voltammograms were essentially the same for all catalysts.

**Influence of electrochemically preformed Ru oxides on the CH$_3$OH electro-oxidation activity for the PtRu (chemically reduced) catalyst.—** Estimation of extent of Ru oxide formation in background solutions.— On the basis of the studies carried out in this work, it can be said that a smaller amount of Ru oxide remains to be detected during the CH$_3$OH electro-oxidation reaction in comparison with the H$_2$SO$_4$ background case. Furthermore, the experimental data suggest that Ru in its metallic state is the required form for the H$_2$O adsorption reaction needed for the bi-functional CH$_3$OH to CO$_2$ oxidation reaction to take place rather than Ru oxides. This result is consistent with the conclusion of Frelink et al. and Kim et al. The latter further proposed that the presence of Ru oxides decreases the activity for the CH$_3$OH oxidation reaction acting as catalytic de-enhancers. This conclusion was based on the experimental observation that shows a decrease in the relative CH$_3$OH oxidation activity for Pt/Ru as compared to the Pt-only catalysts with increasing potential. In order for this to be the case, a reasonable amount of Ru oxide needs to be formed within the potential window used for the CH$_3$OH electro-oxidation reaction. This proposed catalytic de-enhancing effect of Ru oxides on the CH$_3$OH oxidation reaction is examined in more detail in the following sections. The PtRu (chemically reduced) catalyst is used here. This catalyst is used as it has been shown to display superior CH$_3$OH oxidation activities as compared to the Pt/RuO$_2$ (thermal) and Pt/Ru (H$_2$-reduced) catalysts.

Furthermore, it has been suggested in previous work that the Ru surface area can be calculated from the CO$_{th}$ charge for this alloy catalyst using a CO$_{th}$ charge to Ru surface area conversion factor of 0.3. This Ru surface area estimated in this manner may only be an estimate. Therefore, one needs to be cautious in using the absolute numbers calculated from the Ru surface area data. Nevertheless, the main conclusions made below hold even if the Ru areas calculated in this manner are not exact.

Figure 7a shows background CV's recorded in 0.5 M H$_2$SO$_4$ solutions for the PtRu (chemically reduced) catalyst. The potential is cycled at 10 mV s$^{-1}$ between 0.025 V and different $E_+$ limits. As discussed above, previous studies have shown that at low potentials ($<$0.1 V), the Ru is in its metallic state for this alloy catalyst. At potentials below 0.3 V, the H adsorption/desorption reaction takes place on Pt as well as Ru sites. For the case of Ru metal, it has been shown that a reversibly reducible Ru oxide (involving a proposed 2 e$^-$ per Ru surface site reaction, i.e., RuO$^+$) is formed. It has been suggested that one monolayer of this oxide is formed by cycling to ca. 0.9 V. Potential cycling to more positive potentials results in the formation of higher and irreversibly reducible Ru oxides. Therefore, less than one monolayer of Ru oxide is formed within the practical fuel cell potential range, i.e., below 0.5 V. An estimation of the amount of Ru oxide formed as a function of potential is shown in more quantitative manners in Fig. 7b and c. Figure 7b shows the charge ($Q_a$), extracted from the CV shown in Fig. 7a. The charge is integrated over 30-mV potential intervals and is corrected for the double-layer charging contributions of Pt sites (2.5 μC cm$^{-2}$ Pt for a 30-mV potential interval). In fact, the contribution of Pt double-layer charging is small (<10%). The $Q_a$ values shown in Fig. 7b are then further divided by a theoretical charge ($Q_{th}$) value of 420 μC cm$^{-2}$. This theoretical charge value is equivalent to the charge needed assuming that one monolayer of RuO is formed from Ru metal sites. The percentage value of the $Q_a$ to $Q_{th}$ ratio ($\% Q_a/Q_{th}$) is similar to a coverage value of the Ru surface with oxide. The data shown in Fig. 7c suggest that at potentials below 0.4 V, less than 15% of the Ru surface is covered with RuO. Based on these data, a strong influence of electrochemically formed Ru oxide on the CH$_3$OH oxidation reaction is only expected to be observable at more positive potentials (>0.5 V), i.e., within a potential range not of interest for real fuel cell applications, as further discussed in the following section.

**Estimation of the degree of the influence of electrochemically preformed Ru oxides on the CH$_3$OH oxidation reaction.—** In this section the possibility of a de-enhancing effect of Ru oxide preformed at different constant potentials on the CH$_3$OH oxidation activity is discussed. The PtRu (chemically reduced) catalyst is used for this purpose. The CH$_3$OH oxidation current is measured after 250 s at a constant potential of 0.4, 0.6, and 0.8 V. At each potential, two sets of experiments are carried out. In one set, the potential is stepped to the value of interest using 150 mL of a 0.5 M H$_2$SO$_4$ electrolyte solution. After 30 s, the well-stirred solution is spiked with 2.025 mL CH$_3$OH, thus resulting in a 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solution, and the current is measured after a total of 250 s at the potential of interest. These experiments are referred to as “spiked.” In the second type of experiments, referred to as “not spiked,” the potential is stepped to the value of interest in 150 mL of 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solution. Prior to all potential step experiments, the potential is held at 0.1 V for 30 s to condition the electrodes. In the case of the first set of experiments, Ru oxides are formed electrochemically (at the potential at which the CH$_3$OH oxidation activity is measured) before
CH$_3$OH is added, while in the second type of experiment, the formation of Ru oxides occurs from the start of the potential step in the presence of CH$_3$OH. Typical examples of current density–time transients recorded at 0.8 V in this manner are shown in Fig. 8. In these plots, the current scale is normalized using the Pt surface area of the corresponding electrodes. It is seen that the electrochemical preformation of Ru oxides, at the potential where the CH$_3$OH oxidation reaction is studied, results in a decrease in CH$_3$OH oxidation activity, i.e., exhibiting a de-enhancing effect on the CH$_3$OH oxidation reaction. Table IV shows the averaged values of the experimentally observed CH$_3$OH oxidation current densities found for the “spiked” and “not spiked” solutions for all three potentials studied. The increase in the CH$_3$OH oxidation current with increasing potential (>0.6 V) is very small. This is consistent with previously reported data.

The last column in Table IV shows the ratio of the current density of the spiked vs the not-spiked solution ($j_{spiked}/j_{not-spiked}$) as a percentage. Smaller CH$_3$OH oxidation currents for the spiked vs the not-spiked solutions are observed for 0.6 and 0.8 V, while the CH$_3$OH oxidation currents are essentially the same for both proce-

Table IV. Influence of electrochemically preformed Ru oxide on the CH$_3$OH electro-oxidation activity.

<table>
<thead>
<tr>
<th>$E$ vs RHE (V)</th>
<th>Solution$^b$</th>
<th>$j_{spiked}$ (A cm$^{-2}$)</th>
<th>$j_{not-spiked}$ (A cm$^{-2}$)</th>
<th>$j_{spiked}/j_{not-spiked}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>Spiked</td>
<td>$9 \times 10^{-6} \pm 4 \times 10^{-7}$</td>
<td>$100 \pm 5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not spiked</td>
<td>$8.9 \times 10^{-6} \pm 4 \times 10^{-7}$</td>
<td>$95 \pm 3$</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>Spiked</td>
<td>$1.6 \times 10^{-4} \pm 4 \times 10^{-6}$</td>
<td>$80 \pm 5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not spiked</td>
<td>$1.7 \times 10^{-4} \pm 4 \times 10^{-6}$</td>
<td>$95 \pm 3$</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>Spiked</td>
<td>$1.6 \times 10^{-4} \pm 1 \times 10^{-4}$</td>
<td>$80 \pm 5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not spiked</td>
<td>$2 \times 10^{-4} \pm 1 \times 10^{-4}$</td>
<td>$95 \pm 3$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ru oxides are electrochemically preformed at the potential indicated in column one for 30 s in 150 mL of 0.5 M H$_2$SO$_4$ solutions, i.e., prior to spiking the solution with 2.025 mL CH$_3$OH.

$^b$ In all cases 150 mL of 0.5 M H$_2$SO$_4$ solutions are used. In some cases, the H$_2$SO$_4$ solution is spiked with 2.025 mL CH$_3$OH (equivalent to 0.5 M) after 30 s at 0.4, 0.6, or 0.8 V (referred to as spiked solution), while a CH$_3$OH of 0.5 M concentration is present throughout the other experiments referred to as not spiked.

$^c$ Currents are measured after 250 s at 0.4, 0.6, or 0.8 V and are normalized for the electroactive Pt surface area. The Pt surface area is determined using the combined CO$_{ads}$ and COOH$_2$ method, as described in the Experimental section.

$^d$ Percentage of the ratio of the CH$_3$OH oxidation current experimentally observed in the spiked vs the not-spiked solution ($j_{spiked}/j_{not-spiked}$).
duries at 0.4 V. The decrease becomes more pronounced with increasing potential. At more positive potentials, the oxide coverage of the Ru surface sites is larger. The results found in this work tend to support Kim et al.’s view of the catalytic de-enhancing effect of electrochemically formed Ru oxides on the CH$_3$OH oxidation reaction. However, it is seen that the decrease in CH$_3$OH oxidation activity due to the prior formation of Ru oxides is small. The high $j_{on}$ values of ca. 80–100% indicate that the suppression of the CH$_3$OH oxidation current is only in the range of ca. 0–20% between 0.4 and 0.8 V. In fact, within the practical potential range for fuel cell operations (i.e., 0.4 V), the electrochemical preformation of Ru oxides appears not to influence the CH$_3$OH oxidation activity. It should also be noted that it is possible that at more positive potentials (>0.6 V), different types of Ru oxides may form in the presence of CH$_3$OH and influence the results. Furthermore, at more positive potentials the formation of Pt oxides becomes more pronounced, which is equivalent to a decrease in active surface sites for the CH$_3$OH adsorption reaction (i.e., lower surface area). These are all factors that could be responsible for the experimentally observed decreasing influence of potential on CH$_3$OH oxidation currents at potentials larger than 0.6 V. These issues have not been further investigated in this work, as this positive potential range (>0.6 V) is not of interest for practical fuel cell operations.

Conclusions

In this work, a simple electrochemical method has been introduced that allows the in situ estimation of the involvement of Ru oxides during the oxidation of organics such as methanol. The method has been applied to different unsupported Pt/Ru catalysts. The results indicate that the electrochemical formation of Ru oxides is effectively suppressed during the CH$_3$OH oxidation reaction and very little or no sustainable Ru oxides are formed in solutions containing CH$_3$OH concentrations larger than 0.1 M. The results are believed to be in agreement with a bi-functional mechanism for the CH$_3$OH oxidation reaction, i.e., suggesting that water is adsorbed on the Ru surface, forming a Ru–OH type species that is used up in the complete oxidation reaction of CH$_3$OH to CO$_2$. Furthermore, the results suggest that Ru in its metallic form is the active precursor state to form –OH species needed for the complete oxidation of CH$_3$OH to CO$_2$ at low potentials. These results are in agreement with previous reports.

It also appears that the method introduced in this work is an indicator for the distribution of Pt vs Ru catalyst surface sites. For Pt/Ru catalysts that are viewed to consist of well-distributed Pt to Ru surface sites, the Ru oxide formation appears to be largely suppressed during the CH$_3$OH oxidation reaction, while Ru oxides are found to remain on the surface (although, to a smaller extent than in CH$_3$OH free solutions) for Pt/Ru catalysts consisting of poorly distributed Pt to Ru surface sites.

The method introduced in this work is simple and involves instrumentation (a potentiostat) generally available in an electrochemistry laboratory. The interpretation of the data is straightforward and not influenced by changes in the double-layer structure, such as potential-dependent anion adsorption. Such influences complicate the interpretation of in situ electrochemical ellipsometric and quartz crystal microbalance measurements. This method can likely also be applied to other fuel cell catalyst systems to test for a bi-functional mechanism, the potential of ad-metal components to form oxygen surface species (–OH adsorbed species) needed for the complete CH$_3$OH to CO$_2$ oxidation reaction, and to obtain a rough estimate of the distribution of Pt to ad-metal surface sites.

The results found in this work support the view that Ru in its metallic state (in the fuel cell environment) is the most active form to assist in the complete oxidation of CH$_3$OH to CO$_2$ at low potentials, via the –OH or –O formation mechanism. Additional electrochemical experiments have also been carried out in this work that indicate that Ru oxides formed electrochemically at the potential of interest likely act as a de-enhancer for the CH$_3$OH oxidation reaction. However, the amount of Ru oxides formed within the potential range of interest for fuel cell applications is very small, and the de-enhancing effect is only clearly observed at potentials larger than 0.6 V.

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