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CH₃OH oxidation activities of an unsupported Pt_xRu_y powder catalyst before and after different electrochemical treatments

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An unsupported Pt₇₅Ru₂₅ powder was synthesized by co-reducing the corresponding precursor salts rapidly. An alloy powder of Pt₇₅Ru₂₅ composition was formed in this manner. The catalyst powders were subjected to various electrochemical treatments in either 0.5 M H₂SO₄ or 0.5 M CH₃OH + 0.5 M H₂SO₄ solutions. Applying specific electrochemical treatments in respect to time (e.g., the potential cycling number) relative to the E⁺ value result in either a decrease or increase in the CH₃OH oxidation activity of this catalyst. The differently treated catalyst powders were further studied using EDX, XPS and CO adsorbed (CO_{ads}) stripping voltamograms and transients. The results suggest that removal of surface Ru-oxides result in an increase in CH₃OH electro-oxidation activity, while extensive loss of Ru from the catalyst surface results in a decrease in CH₃OH oxidation activity. Refluxing this as-prepared catalyst powder in an excess of boiling 0.5 M H₂SO₄ did neither result in the removal of the surface Ru-oxides nor improve the CH₃OH oxidation activity.

Introduction

Direct methanol fuel cells (DMFCs) have attracted a lot of attention due to their potential use as power sources for portable and micro-electronic devices [1]. Pt-Ru systems are the best performing catalysts for the CH₃OH oxidation reaction [2]. Their catalytic benefit is largely due to a bi-functional mechanism. According to the bi-functional mechanism, Ru is capable of adsorbing H₂O at low potentials, thus generating –OH_{ads} species on the catalyst surface that are needed to completely oxidize CH₃OH to CO₂ [3]. Despite advances in FC technologies, the DMFC performance still needs to be improved, namely, (i) the kinetics of both the anode and cathode reactions need to be increased, (ii) cross-over of CH₃OH from the anode to the cathode needs to be reduced, and (iii) the stability of the Pt-Ru anode catalysts needs to be enhanced. The latter results in cross-over of Ru from the anode to the cathode compartment during FC operation [4-6]. The Ru is deposited in the cathode compartment, possibly blocking Pt cathode catalysts sites that are needed for the reduction of the cathode fuel, i.e., O₂ [6]. Furthermore, oxidation of CH₃OH fuel, that crossed-over, can then take place in the cathode compartment. As a result the overall cathode potential, and hence, also the cell voltage are reduced [4].

Some studies using commercially available unsupported Pt-Ru catalyst powders have been carried out to study the Ru dissolution issues in DMFCs. It has been established that a separate, likely hydrous Ru-oxide phase dissolves from the Pt-Ru catalysts even at the open-circuit potential (ocp) [4]. It has further been shown that the separate Ru phase can be dissolved in boiling H_2SO_4 , thus reducing the dissolution and cross-over of Ru in the FC. Furthermore, FC experiments have shown that the anode performance is not altered when the separate Ru phase is dissolved from the Pt-Ru catalysts, and that the observed loss of the DMFC performance is solely due to a lower cathode performance [4, 5]. Based on these results it is concluded that fully alloyed Pt-Ru catalysts should be used to reduce Ru dissolution issues. However, commercially available Pt-Ru catalysts often consist of a mixture of phases, namely Pt_xRu_y alloys as well as separate Ru/Ru-oxide phases. The amount of Ru in the separate phase can be large, e.g., approaching 30-40 % of the total amount of Ru in the catalyst [7]. It should be noted that during DMFC operation parts of the anode may experience very positive potentials favoring loss of Ru even from Pt_xRu_y alloys. Therefore, the use of fully alloyed Pt-Ru catalysts may not solve the Ru dissolution problem; however, the cross-over of Ru is likely less extensive when fully alloyed catalysts are used.

In this work an unsupported Pt_xRu_y catalyst is used due to its ease of characterization compared to supported nano-sized (< 5 nm) Pt-Ru catalysts. Further studies will need to be carried out to show if the findings for this catalyst powder also apply to nano-sized carbon supported Pt-Ru catalysts. A synthesis method is used that is expected to result in a Pt_xRu_y alloy of the same alloy and overall Pt to Ru ratios, i.e., not forming large amounts of separate Ru and/or Ru-oxide phases. The Pt_xRu_y catalyst powder is subjected to different electrochemical treatments as well as to refluxing in boiling 0.5 M H_2SO_4 . The variously treated catalysts are characterized for their activity to electro-oxidize CH_3OH . They are further characterized using XRD, XPS, EDX and electro-oxidation studies of adsorbed CO (CO_{ads}).

Experimental

Catalyst synthesis

An unsupported Pt_xRu_y catalyst powder was synthesized utilizing a rapid chemical reduction method. An aqueous solution consisting of 0.707 g PtCl_4 (99.9 % purity, Alfa Aesar) and 0.158 g $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$ (Alfa Aesar, Metal basis assay 44.64 %) was reduced at room temperature by adding a 100 % excess of NaBH_4 (J. T. Baker, ACS grade) at once. The reaction mixture was stirred for an additional hour, subsequently filtered and the formed powder was then washed with an excessive amount of H_2O . The powder was dried in air oven at 80°C . The powder prepared in this manner is referred to as as-prepared catalyst. 0.05 g of the as-prepared catalyst powder was also refluxed in boiling 0.5 M H_2SO_4 for 24 h. The refluxed powder was subsequently filtered and washed with excessive amounts of H_2O . This powder is referred to as refluxed powder.

Electrodes and electrochemical cells

9 mg of the catalyst powder was dispersed in 1 ml of H₂O by sonication. Immediately after sonication, 20 μ l's of the ink were deposited on a Au foil electrode and left to dry at room temperature. 20 μ l's of a 0.025 wt.% Nafion solution in lower alcohols were then spread over the catalyst powder to form a thin layer of Nafion. These electrodes were studied in a two compartment glass cell, in which the reference electrode is separated from the working and counter electrode compartment by a Lugging capillary. All potentials are reported vs. the reversible hydrogen electrode (RHE). However, either a standard calomel electrode (SCE) or a mercury sulfate electrode (MSE) was used as reference electrode. Electrochemical experiments involving the SCE were limited to one hour to avoid possible interferences of chloride. The electrochemical experiments were carried out at room temperature and either 0.5 M H₂SO₄ or 0.5 M H₂SO₄ + 0.5 M CH₃OH solutions were used. The solutions were deoxygenated by bubbling argon gas for 30 min. prior to the electrochemical experiments.

Instrumentation

Electrochemical experiments were carried out using a Solartron 1285 (Solartron Group, Ltd.) electrochemical interface driven by Corrware software (Scribner Assoc.). Powder X-ray diffraction (XRD) of the as-prepared and refluxed catalysts powders were recorded using a Philips XRD machine with Cu K α source. A JEOL 840A scanning electron microscope equipped with an Oxford Instruments 6560 INCAX-sight light element energy dispersive X-ray (EDX) spectrometer was used to obtain the Pt and Ru composition of the catalyst powders. The EDX analyses were carried out using an accelerating voltage of 20 kV and a working distance of 15 mm. At total live count time of 60 s was used. A Kratos Axis Ultra X-ray photoelectron spectroscope (XPS) equipped with a monochromated Al X-ray source was also used. On each sample, at least three areas were analyzed. The XPS analyses were carried out using an accelerating voltage of 14 kV, a current of 10 mA and an aperture size of 300 μ m x 700 μ m. The Au 4f peak at 84 eV was used to compensate for possible charging effects. On each sample, a survey spectra was collected, before high resolution spectra were acquired. Peak assignments were based on the NIST database (http://srdata.nist.gov/xps/Bind_E.asp), and deconvolution of the XPS spectra were performed using CasaXPS (ver. 2.2.107) data processing software. A Shirley background correction was used. A Gaussian-Lorentzian, 70:30 % mix, function was used to deconvolute the spectra. All XPS and EDX samples were analyzed on the Au foil electrode prepared as described above in electrodes and electrochemical cells.

Electrochemical experiments

Each electrode was conditioned by completing 50 cycles at 20 mV s⁻¹ between 0 and 0.4 V in 0.5 M H₂SO₄. The conditioned electrodes were then subjected to different treatments by potential cycling at 10 mV s⁻¹ between 0 V and a specific upper potential value (E⁺). The influence of E⁺ values between 0.6 and 1.2 V were studied. In some cases electrodes were also subjected to potential holding experiments at a constant E⁺ value.

The catalysts were also characterized using CO adsorbed (CO_{ads}) stripping experiments. For the CO_{ads} stripping experiments, CO was adsorbed onto the electrode at 0.15 V by bubbling ultra

high purity CO gas through the 0.5 M H₂SO₄ solution for 30 min. Solution CO was subsequently removed by bubbling argon gas through the solution for 10 min., while the potential was maintained at 0.15 V. In case of the CO_{ads} stripping experiments, the potential was then cycled at 10 mV s⁻¹ starting into the positive direction at 0.15 V for two complete oxidation/reduction cycles between 0 and 0.8 V. CO_{ads} stripping current-transients were also recorded at 0.418 V. CH₃OH oxidation activities of the electrodes were obtained from cyclic voltammograms (CVs) as well as from current time transients recorded at a constant potential. 0.5 M CH₃OH + 0.5 M H₂SO₄ solutions were utilized for these studies and all electrochemical measurements were carried out at room temperature unless otherwise noted.

Results and Discussions

Characteristics of the as-prepared and refluxed powders

Fig. 1 shows XRD patterns of the as-prepared and refluxed catalyst powders. It is seen that the spectra of the two powders are essentially the same. Both patterns are typical for a face centered cubic (fcc) Pt structure. A lattice parameter (*a*) of 3.89 Å is extracted from these spectra using the Pt(111) diffraction peak. This lattice parameter in combination with the quasi Vegard's law relationship, that applies to Pt_{*x*}Ru_{*y*} alloys [2, 8], suggests an alloy composition of 75 to 25 at.% Pt to Ru. Therefore, this Pt_{*x*}Ru_{*y*} alloy powder is further referred to as Pt₇₅Ru₂₅. EDX analyses suggest an overall Pt to Ru at. % composition of 75 to 25 for both powders. This is the same Pt:Ru ratio as suggested for the alloy composition by the XRD data. Therefore, these results suggest that the Ru is largely dissolved in the Pt fcc lattice for both the as-prepared and refluxed powders, i.e., the presence of large amounts of separate Ru/Ru-oxide phases can be excluded. The latter is further consistent with the fact that the EDX and XRD results are identical for the as-prepared and refluxed powders. According to literature results [4, 7], separate Ru phases can be leached from Pt-Ru catalyst powders by a reflux treatment in 0.5 M H₂SO₄ at 100 °C. Therefore, the fact that the same compositions are obtained for the two powders continues to suggest that the Ru is mainly dissolved in the Pt fcc lattice.

CH₃OH oxidation studies were also carried out for the as-prepared and the refluxed catalysts. Fig. 2 shows examples of CH₃OH oxidation CVs for the CH₃OH oxidation of a refluxed and an as-prepared catalyst powder. It seen that the CVs are very similar within the variation of the experiments. CO_{ads} stripping and background CVs recorded in 0.5 M H₂SO₄ were also found to be the same for the as-prepared and refluxed catalysts. This further indicates that the as-prepared and refluxed catalysts are essentially the same. Therefore, the results presented in the reminder of this work are for the refluxed catalyst powder unless otherwise stated. Furthermore, it is known that Pt-Ru alloy powder catalysts of 75:25 at.% Pt to Ru alloy ratio yield high electro-catalytic CH₃OH oxidation activities. In fact, their CH₃OH oxidation currents measured per Pt + Ru surface area and at specific potentials have been reported to be close (within 10 % of the CH₃OH activity) to the most active form for unsupported Pt-Ru alloy powder catalysts [2].

Fig. 1 Powder X-ray diffraction pattern of refluxed and as prepared $\text{Pt}_{75}\text{Ru}_{25}$ catalysts

Fig.2 CH_3OH oxidation CVs (5th cycle) recorded for as prepared and refluxed catalysts in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution at 10 mV s^{-1}

The influence of the electrochemical treatments on the CH_3OH oxidation activity

The influence of potential cycling experiments to different E^+ values on the CH_3OH oxidation characteristics are discussed in the following sections. The results shown are for electrochemical cycling experiments carried out in 0.5 M CH_3OH + 0.5 M H_2SO_4 solutions. It

should be noted that similar results were found using CH₃OH free, i.e., 0.5 M H₂SO₄ solutions. The catalysts are also characterized by XPS and EDX before and after electrochemical treatments. It is noteworthy that essentially the same experiments were carried out that involved holding the potential at, rather than potential cycling to different E⁺ limits. The results were essentially the same with the exception that the potential holding experiments needed to be carried out over longer periods of time to achieve the same changes in the electrochemical characteristics of the catalyst powder. Furthermore, the discussion of the influence of the E⁺ value mainly focuses on the region of 0.8 V and more positive values. This region appears to be in agreement with Ru dissolution studies of Ru metal electrodes carried out by electrochemical quartz crystal microbalance (EQCMB) measurements [9]. The latter showed that electrochemical Ru dissolution takes place within the potential window of 0.6 and 0.8 V; however, at a “small” rate. The electrochemical dissolution rate becomes rapid (increases in an exponential manner) at potentials more positive than 0.8 V [9]. It is known that within the range of E⁺ values up to 0.5 V, RuOH and RuO are formed on the surface of the Ru electrode [10]. The electrochemical oxidation of Ru metal to RuOH species starts in the 0 to 0.2 V range [10]. At potentials of 0.6 V and more positive the formation of tri- and tetravalent Ru-species can take place. The tri- and tetravalent species of Ru are generally not very stable even in acidic solutions [9], hence, explaining the observed increase in Ru dissolution rate above 0.8 V. The exact mechanism of losing Ru from Pt-Ru electrodes in acid solutions is not known with certainty. It seems to be generally viewed as an electrochemical step, followed by dissolution of Ru in the form of Ru(+III)- and Ru(+IV)-complex species. However, it has also been suggested that the Ru may be lost as nano-particles such as e.g., Ru₂O₃ and/or RuO₂ [4].

Fig. 3a shows a series of forward cycles for the CH₃OH oxidation reaction for Pt₇₅Ru₂₅ electrodes that are cycled to different E⁺ values. The 50th cycles are shown and a new electrode is used for each case. For the case of the E⁺ value of 0.6 V, the CH₃OH oxidation activity is very similar to the conditioned only electrode, i.e., the CH₃OH oxidation activity of the catalyst is not detectably altered by the potential cycling experiment up to 0.6 V. However, clear changes in the CH₃OH oxidation activity are observed for the more positive E⁺ values. In case of the E⁺ values of 0.8 and 1 V, an increase in the CH₃OH oxidation peak current as well as a shift in the CH₃OH oxidation potential to more negative potentials are observed. In the case of the 1.2 V value, the CH₃OH oxidation current at peak maxima is large, however, the onset potential of the CH₃OH oxidation reaction is shifted to positive values. The latter indicates a poorer electro-catalytic performance. The influence of the individual E⁺ values was studied as a function of the potential cycling number. It was found that in case of the 0.8 V E⁺ value a “steady-state” CH₃OH oxidation activity was achieved within 50 cycles. The term “steady-state” is used here based on the observation that the CH₃OH oxidation CVs are the same for the 50th to the 300th potential cycles tested. This is shown in Fig. 3b for the case of the 2nd, 50th and 300th cycle. In case of the E⁺ values of 1 and 1.2 V, such a “steady-state” behavior was not observed. Furthermore, the CH₃OH oxidation activity decreased with increasing potential cycling number after 250 and 30 cycles for the E⁺ values of 1 and 1.2 V, respectively. It should be noted that a decrease in the CH₃OH oxidation activity refers to experimentally observed shifts in the CH₃OH onset potential to more positive values.

Similar changes in the CH₃OH oxidation activity are also observed in current-time transient graphs recorded at constant potentials of 0.44 V. This is shown in Fig. 3c for a conditioned

electrode and an electrode 50 times cycled to the E^+ value of 0.8 V. An increase in the CH_3OH oxidation current of 30 % is observed for the cycled electrode. This is similar to the increase in current observed in the CV experiments for this electrode shown in Fig. 3b.

Fig.3 (a) 50th forward cycle for Pt₇₅Ru₂₅ catalyst electrodes cycled to various E^+ values. Fig.3 (b) shows the same, but for the 2nd, 50th and 300th forward cycles using the E^+ value of 0.8 V. All CVs are recorded in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution at 10 mV s⁻¹. Fig. 3 (c) shows current-time transients recorded in 0.5 M CH_3OH + 0.5 M H_2SO_4 solutions at 0.44 V for the Pt₇₅Ru₂₅ catalyst after conditioning and after 50 cycles to E^+ of 0.8 V.

It is noteworthy that the CH_3OH oxidation activity was also studied at 60 °C as a function of E -cycling of the catalyst powder. CV and current-time transients measured at 60 °C in 0.5 M

CH₃OH + 0.5 M H₂SO₄ solutions show an increase in CH₃OH activity of 26 % after 50 cycles to an E+ value of 0.8 V in 0.5 M H₂SO₄ and at room temperature.

CO_{ads} oxidation studies

CO_{ads} oxidation experiments were carried out to gain insight into the changes taking place on the catalyst surface during the E-cycling experiments. Fig. 4 shows a series of CO_{ads} stripping voltamograms for Pt₇₅Ru₂₅ electrodes cycled 50 times to different E+ limits. The CO_{ads} stripping voltamogram for the conditioned only electrode is also shown. The current scale in each CO_{ads} stripping voltamogram is normalized using the Q_{COads} value of the corresponding electrode measured after conditioning. The CO_{ads} stripping voltamogram for the conditioned electrode and the electrode cycled 50 times to 0.6 V are the same. This continues to indicate that the electro-catalytic activity of the catalyst powder is not measurably altered by the potential cycling experiments up to 0.6 V. In case of the E+ values of 0.8 and 1 V, the onset potential for the CO_{ads} stripping reaction is shifted to more negative potentials and the CO_{ads} stripping reaction is completed at lower potentials than for the conditioned only catalyst electrode. This indicates that the CO_{ads} stripping kinetics are more rapid for these two E-cycled catalyst electrodes. Decreases in the CO_{ads} stripping charge (Q_{COads}) values of 17 and 31 % are observed upon the E-cycling experiment to 0.8 and 1 V, respectively. The Q_{COads} values yield an approximate measurement of the electrochemical surface area (ECSA) of these catalysts. Therefore, the fact that the Q_{COads}, and hence, the ECSA value, decrease with E-cycling suggests that the experimentally observed increases of more than 30 % in the CH₃OH oxidation activity (Fig. 3a) cannot be assigned to an increase in the ECSA value. Therefore, it is concluded that the observed increases in the CH₃OH oxidation activity are related to true improvements in electro-catalytic activity of these catalyst powders. The loss in the Q_{COads} value is more pronounced, 47 %, for the catalyst powder cycled to 1.2 V. Furthermore, the onset potential for the CO_{ads} stripping reaction is shifted to more positive and two peaks are observed for the latter. Examination of the H_{ads/des} region of this electrode reveals the “butterfly” characteristics that are typically observed for polycrystalline Pt electrodes. These results suggest that the surface of this electrode has become enriched in Pt, i.e., a significant amount of Ru must have been lost from the surface. Consequently, the CO_{ads} stripping reaction kinetics are also reduced.

Current-time transients for the CO_{ads} stripping reaction were recorded at a constant potential as described in the experimental section for the differently treated electrodes. Important characteristics of the catalyst surface, as the induction time for the -OH_{ads} formation reaction (t_i) and the distribution of active Pt and Ru sites, can be extracted from these transients as shown in previous work [8, 11]. Similar to the CH₃OH oxidation, the CO_{ads} stripping reaction to CO₂ also takes place according to a bi-functional mechanism, as summarized in eqs. 1+2:

Fig. 4 CO_{ads} stripping voltammograms recorded at 10 mV s^{-1} for $\text{Pt}_{75}\text{Ru}_{25}$ electrodes cycled 50 times to different E^+ values. The stripping voltammogram of a conditioned electrode is also shown in each graph for comparison.

The CO_{ads} stripping transients discussed in this work are recorded at 0.418 V. Therefore, it can be assumed that the $-\text{OH}_{\text{ads}}$ formation reaction, i.e., eq. 1, takes place exclusively on Ru sites.

Furthermore, M in reaction 2 stands for Pt and Ru sites that are in the metallic form at 0.15 V, where the CO is adsorbed. Fig. 5 shows examples of CO_{ads} current-time transients recorded for Pt₇₅Ru₂₅ electrodes before and after 50 cycles to different E+ values. As for the CO_{ads} stripping voltamograms, the current scale of the transients is normalized using the Q_{CO_{ads}} value of the corresponding conditioned electrode. Consistent with the CO_{ads} stripping CVs shown in Fig. 4, the CO_{ads} to CO₂ oxidation reaction is seen to be faster for the Pt₇₅Ru₂₅ catalysts “activated” by cycling 50 times to either 0.8 or 1 V than for the conditioned catalyst. The CO_{ads} stripping transients can be divided into different regions, as discussed in this paragraph. The decaying current at very short time periods reflects the double layer charging current. Subsequently, an increase in the current is observed. The time needed for the current to increase, t_i, reflects the time needed for the recombination reaction of M-CO_{ads} + Ru-OH_{ads}, i.e., eq. 2 to be initiated. The increase in current observed after t_i results from the recombination reaction of -CO_{ads} located near an active Ru-OH_{ads} site. This recombination reaction takes place between t_i and t_o. It is also possible that more Ru-OH_{ads} sites are formed during this period, thus further contributing to the current increase and assisting in the oxidation of the -CO_{ads} molecules. The percentage fraction of the Q_{CO_{ads}} value passed during the time t_i to t_o vs. the total Q_{CO_{ads}} value of the electrode (% Q_o) presents a measurement of the number of -CO_{ads} molecules located near an active Ru-OH_{ads} site plus the number of Ru-OH_{ads} formed. A good CO_{ads} oxidation catalyst achieves a high % Q_o value in a short time. Therefore, the % Q_o vs. the t_o value (% Q_o/t_o) represents a measurement of the number of neighbouring M-CO_{ads} and active Ru-OH_{ads} sites [8]. After t_o, the current decays and eventually approaches zero values. During this time CO_{ads} molecules located further away from active Ru-OH_{ads} sites are oxidized. It is known that the CO_{ads} molecule can move across Pt catalyst surfaces utilizing CO_{ads} free metallic catalyst sites (M*), as indicated in eq. (3) [11].

In the period after t_o, the rate of the recombination reaction shown in eq. 2 is determined by the time needed for CO_{ads} molecules to move across the catalyst surface to an active Ru-OH_{ads} site.

The characteristic values of the CO_{ads} stripping time transients shown in Fig. 5 are summarized in Table 1. It is seen from Fig. 5 that the CO_{ads} stripping reaction is completed faster as the E+ value increases. The transient for the E+ value of 1.2 V is not shown. In the latter case, only a small fraction of the total CO_{ads} molecules was oxidized during a period of 300 s, and the characteristic features, namely t_i and t_o, were not clearly defined. Therefore, this transient is not shown. Overall, the CO_{ads} stripping transient results are consistent with the CO_{ads} stripping voltamograms and follow the same trend observed for the increase in the CH₃OH oxidation reaction with the E+ value (Fig. 3a). Analyses of the transients also show that the t_i values are lower as the E+ value increases suggesting that the recombination reaction (eq. 2) is initiated faster. The latter may be due to a faster formation of active Ru-OH_{ads} for these two E-cycled catalysts. Furthermore, the t_o values decrease as the E+ value increases. This results in an increase in the %Q_o/t_o values, thus suggesting that the number of neighbouring (nearby) CO_{ads} molecules to active Ru-OH_{ads} sites has increased.

Fig. 5 CO_{ads} stripping transients recorded at 0.418 V for $\text{Pt}_{75}\text{Ru}_{25}$ conditioned electrodes and $\text{Pt}_{75}\text{Ru}_{25}$ electrodes cycled 50 times to either 0.8 or 1 V.

Table I. Characteristic numbers for the CO_{ads} stripping reaction extracted for current-time transients recorded at 0.418 V

Samples	t_i (s)	Q_o (%)	t_o (s)	Q_o/t_o (% s^{-1})
Conditioned $\text{Pt}_{75}\text{Ru}_{25}$	3.8	27.1	38.6	0.6
$\text{Pt}_{75}\text{Ru}_{25}$ subjected to E^+ of 0.8 V	2.6	26.3	16.8	1.6
$\text{Pt}_{75}\text{Ru}_{25}$ subjected to E^+ of 1 V	2	17.7	6.4	2.8
$\text{Pt}_{75}\text{Ru}_{25}$ subjected to E^+ of 1.2 V	N/A	N/A	N/A	N/A

XPS and EDX analyses for as-prepared, refluxed and E^+ cycled electrodes

Fig. 6 shows the Ru 3p core level XPS spectra for a conditioned and a $\text{Pt}_{75}\text{Ru}_{25}$ catalyst electrode cycled to 0.8 V. It is noteworthy that the electrodes are emmersed off the electrolyte

solution after the negative potential scan to 0.15 V is completed. The spectra for the as-prepared and refluxed Pt₇₅Ru₂₅ catalyst powders not subjected to any electrochemical treatment were found to be the same as the spectra for the conditioned electrode. The results for the deconvolution of the spectra are summarized in Table II. Table II also shows the Pt to Ru ratio for the electrodes. The Pt to Ru ratio is seen to be the same for all electrodes, i.e., 75:25 at.%. Column 2 shows the ratios determined from XPS spectra. The Pt 4f core level spectra (highest intensity peak for Pt), and the Ru 3p core level spectra (C 1s free peak for Ru) are used for the XPS analyses shown in this section. The mean free path length depth of X-rays for Pt and Ru are in the 1.5-1.7 nm range [2], hence, the XPS ratios shown in Table II present an indication of the Pt to Ru surface ratios. Column 3 shows the same, but, for EDX measurements, which reflect the total Pt to Ru ratio of the catalysts and electrodes. It is seen that the EDX ratio is the same for all samples investigated, namely 75:25 at.% of Pt to Ru. This indicates that the electrochemical treatments did not affect the bulk of the catalyst powders. It is likely that changes that result in the different CH₃OH oxidation activities take place at the catalyst surface. The latter is confirmed by the XPS data. The XPS data suggest the same Pt to Ru at. % ratio of 47:53 (± 5 %) for the as-prepared, refluxed catalysts, and conditioned catalyst electrodes. The fact that the Pt to Ru surface ratios are the same for the as-prepared, refluxed and conditioned electrodes suggests that the catalyst surface is not altered by the conditioning of the electrode, i.e., cycling up to 0.4 V. Furthermore, the combined results for the Pt:Ru ratios obtained from XPS and EDX suggest a higher Ru content on the surface than in the bulk of the catalyst. For example, 100 potential cycles to an E+ value of 0.8 V results in a decrease of the amount of surface Ru, i.e., a larger Pt to Ru at. % ratio of 75 to 25 (Table II). These results, in combination with the fact that the CH₃OH oxidation activity is enhanced upon the potential cycling treatment using at least 50 cycles to 0.8 V, suggest that an excess amount of Ru on the catalyst surface reduces the optimal number of neighbouring Pt to Ru catalyst surface sites for the CH₃OH oxidation reaction. (According to the literature, an ideal CH₃OH oxidation catalyst consists of 3 Pt and 1 neighboring Ru catalyst surface site [2].) Deconvolution of the XPS spectra for the Ru 3p region are shown in Fig. 6. The results suggest that Ru, in the form of Ru-oxides, is lost from the catalyst surface during the E-cycling experiment to the E+ value of 0.8 V.

Fig.6 XPS of Ru 3p core level region of (a) the conditioned Pt₇₅Ru₂₅ electrode and (b) a Pt₇₅Ru₂₅ electrode cycled 100 times to an E+ value of 0.8 V.

Table II. Summary of XPS and EDX data for as-prepared, refluxed and E-cycled Pt₂₅Ru₇₅ catalyst powders

Sample	X _{Pt} /X _{Ru} (at.%)		I _{Ru} /I _{Ru_xO_y} (%)
	From XPS	From EDX	
As prepared Pt ₇₅ Ru ₂₅	45/55	76/24	30/70
Refluxed Pt ₇₅ Ru ₂₅	47/53	73/27	31/69
Conditioned Pt ₇₅ Ru ₂₅	47/53	73/27	31/69
Pt ₇₅ Ru ₂₅ 100 times E-cycled to 0.8 V	76/24	75/25	44/56

Summary and Conclusions

An unsupported Pt_xRu_y alloy catalyst powder of 75:25 at.% Pt to Ru composition has been made. Most of the Ru is dissolved in the Pt fcc lattice and the alloy and bulk composition of the powder are the same according to XRD and EDX measurements. XPS measurements reveal that an excess amount (not detectable by EDX) of Ru, likely in the form of Ru-oxide, is present on the

catalyst surface. Surface Ru is removable by electrochemical treatment of the catalyst powder. The electro-catalytic activity of the catalyst powder for the oxidation of CH₃OH and stripping of CO_{ads} is influenced by the electrochemical treatment. The resulting activity depends on the electrochemical treatment (number of cycles in combination with the E⁺ value). At potentials below 0.6 V, changes in the catalyst activity are not detected. However, changes in the catalytic activity of the alloy catalyst powders are clearly observed for E⁺ values of 0.8 V and higher. The latter also appears to be consistent with previous work that has shown that the Ru dissolution rate of Ru metal electrodes increases rapidly at potentials more positive than 0.8 V [9]. The potential cycling treatment to 0.8 V appears beneficial, as it results in an increase in the CH₃OH and CO_{ads} stripping kinetics. The increase is observed after 50 potential cycles, and further cycling (up to 300 cycles) does not significantly alter the electro-catalytic activity of the catalyst surface. At more positive potentials, the changes are more rapid and the catalyst surface appears to become enriched in Pt. This is for example observed for the alloy catalyst powder cycled 50 times to 1.2 V. A refluxing treatment of the as-prepared Pt_xRu_y catalyst powder in boiling 0.5 M H₂SO₄ did not result in a removal of the excess Ru. The electrochemical treatment was found to be essential to achieve the higher CH₃OH and CO_{ads} stripping kinetics for this catalyst powder. Additional studies are needed to test whether these treatments also apply for nano-sized and carbon supported Pt-Ru catalysts.

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