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The function of ruthenium oxides in Pt-Ru catalysts for methanol electro-oxidation at low temperatures

Abstract The electrocatalytic activities of different binary Pt-Ru(ox) catalysts have been investigated in half-cell experiments by cyclic voltammetry and stationary current–potential measurements. The materials have been prepared using a modification of the Adams method. X-ray analytical methods (X-ray diffraction, XRD, and energy dispersive X-ray spectroscopy, EDX) as well as thermogravimetric analysis (TGA) have been used to characterize the composition and the catalysts' content of the crystalline phases, and their surface areas have been determined by the BET method. It is found that the composition of the catalyst is strongly influenced by the synthesis temperature, which is varied between 400 and 600 °C. In contrast, the particle size of the metallic phases of the catalysts is not significantly affected for synthesis temperatures below 600 °C, as investigated by transmission electron microscopy. Synthesis temperatures of ≥500 °C favor the formation of crystalline RuO_2 phases, whereas at synthesis temperatures below 500 °C the presence of metallic alloy and of hydrous oxides was derived by the combined XRD and EDX measurements. The stationary current–potential curves show a correlation with the different synthesis temperatures. It can be concluded that both the presence of an alloyed metallic Pt-Ru phase as well as the presence of amorphous hydrated Ru oxides are favorable for the electrocatalytic oxidation of methanol.

Keywords Anode catalysts · Electro-oxidation · Hydrous ruthenium oxides · Methanol

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Introduction

It is widely accepted that a platinum-ruthenium catalyst demonstrates the best performance to date for the electrochemical oxidation of methanol in direct methanol fuel cells (DMFCs, e.g. [1, 2]). This improvement of catalytic activity compared to pure platinum can be attributed to a bifunctional mechanism: platinum accomplishes the dissociative chemisorption of methanol whereas ruthenium forms a surface oxy-hydroxide which subsequently oxidizes the carbonaceous adsorbate to CO_2 [3, 4]. Although the bifunctional mechanism is the most accepted mechanism, an alternative interpretation based on an electronic ligand effect is also supported by several groups [5, 6]. The ligand effect assumes that the alloy component changes the electronic properties of Pt atoms in its vicinity. Combining the electronic and bifunctional theories, it is postulated that the role of the second element is to increase oxy-hydroxide adsorption on the catalyst surface at lower potentials, and to decrease the adsorption strength of poisoning methanolic residues (e.g. CO).

Even within the supporters of the pure bifunctional mechanism, the actual state of the active ruthenium component is still a point of discussion. While some authors refer to the active ruthenium compound mainly as metallic Ru(0) in a bimetallic alloy [7, 8], other investigations suggest that, in Pt-Ru blacks commonly used as technical catalysts, hydrous oxides of ruthenium are the active components for oxidation of the carbonaceous intermediates adsorbed on the catalyst surface [9, 10]. Based on the mechanism of methanol oxidation proposed by McNicol [11], it can be expected that oxidized ruthenium phases originating from water adsorption at the catalyst surface play a crucial role in oxidizing adsorbed species. Furthermore, XPS spectroscopy of commercial Pt-Ru catalysts indicates the presence of hydrous ruthenium oxides, $RuO_X•XH_2O$ or RuO_XH_Y [12]. It is well known that hydrated ruthenium oxide phases (RuO_XH_Y) show mixed proton–electron

conductivity, thus rendering those materials as candidates for supercapacitors [13, 14], for example. The same properties could turn hydrous ruthenium oxide into an interesting co-catalyst for the electrochemical oxidation of methanol.

In this work, high surface area binary Pt-Ru black catalysts are investigated. The influence of crystalline and hydrous ruthenium oxide phases is compared to the effect of alloyed metallic ruthenium on the electro-oxidation of methanol.

Experimental

Catalyst preparation and characterization

The catalysts were prepared using a modification of the method described by Adams and Shriner [15]. Appropriate amounts of the noble metal halides and transition metal oxides were dissolved in water. After adding an excess of sodium nitrate to the solution, water was evaporated and the solid residue was melted in a furnace and kept at a constant temperature for 3 h. The reaction temperature was varied between 400 °C and 600 °C. After the reaction, the melt was cooled down to room temperature. The solidified product was subsequently washed thoroughly with water to remove residual chloride and nitrate. The resulting aqueous suspension of mixed noble metal oxides was reduced at room temperature with bubbling hydrogen [16].

The bulk composition of the catalyst materials was investigated by energy dispersive X-ray spectroscopy (EDX). The geometric surface areas of the catalyst were determined by the BET method using nitrogen as the adsorbate.

The catalyst particle size, the Ru content in the alloyed metallic particles as well as the content of the crystalline phases were determined by X-ray diffraction (XRD). Spectral contributions of the copper $K_{\alpha 2}$ line were subtracted by a Rachinger algorithm correction. To assess the particle size, the Pt(220) reflection was fitted to a Gaussian lineshape on a linear background.

The average particle size, L, was estimated from the Pt(220) diffraction peaks according to the Scherrer formula [17]:

$$L = \frac{0.9\lambda_{K\alpha 1}}{B_{(2\Theta)}\cos\Theta_{max}} \tag{1}$$

where $\lambda_{K\alpha 1}$ is the X-ray wavelength (1.54056 Å for Cu-$K_{\alpha 1}$ radiation), $B_{(2\Theta)}$ is the width of the diffraction peak at half-height (in radians), and Θ_{max} is the angle at the position of the peak maximum.

Additionally, an attempt was made to estimate the Ru content present in metallic Pt-Ru alloy particles from the shift of the Pt(111) peak to higher values of 2Θ. According to Vegard's law [18], the crystal lattice of a material contracts if it forms an alloy with elements displaying a smaller atomic radius, as is the case for

Ru dissolved in the fcc lattice of Pt. The determination of the lattice constants for Pt-Ru alloys has been based on lattice constant determinations from bulk alloys [19].

However, the particle sizes as well as the degree of alloying could not be determined with high accuracy, since the determination of line position and half width was severely disturbed by overlapping signals of different noble metal oxide phases.

Electrochemical measurements

Electrochemical measurements were carried out using the thin film method described by Schmidt et al. [20]. Glassy carbon disks of 12 mm diameter (1.13 cm^2) served as substrate for the catalyst materials. Aqueous suspensions of 2 mg$_{catalyst}$/mL were dispersed ultrasonically in water and a 160 μL aliqot was transferred onto the glassy carbon substrate, yielding a catalyst loading of 280 μg/cm^2. After evaporation of the water using a nitrogen stream, the resulting thin catalyst film was covered with 80 μL of an aqueous Nafion solution in order to fix the particles on the substrate. The resulting Nafion film had a thickness of about 0.2 μm. Therefore it was sufficiently thin (< 0.5 μm) so that film diffusion effects were negligible under these conditions [21, 22].

The catalysts were characterized by cyclic voltammetry (CV) and stationary current density versus potential curves at room temperature in a three-electrode cell. CV experiments were carried out at room temperature using 0.5 M H$_2$SO$_4$ as the electrolyte. CVs were typically recorded at a scan rate of 2 mV/s.

The stationary current–potential curves were measured galvanostatically at room temperature using 1 M methanol solution as a fuel in 0.5 M H$_2$SO$_4$ as the electrolyte. A minimum of 30 min was allowed for stabilization of the potential. Potentials were measured using a Hg/Hg$_2$SO$_4$/SO$_4^{2-}$ (0.5 M H$_2$SO$_4$) electrode, but are referenced to the reversible hydrogen electrode (RHE).
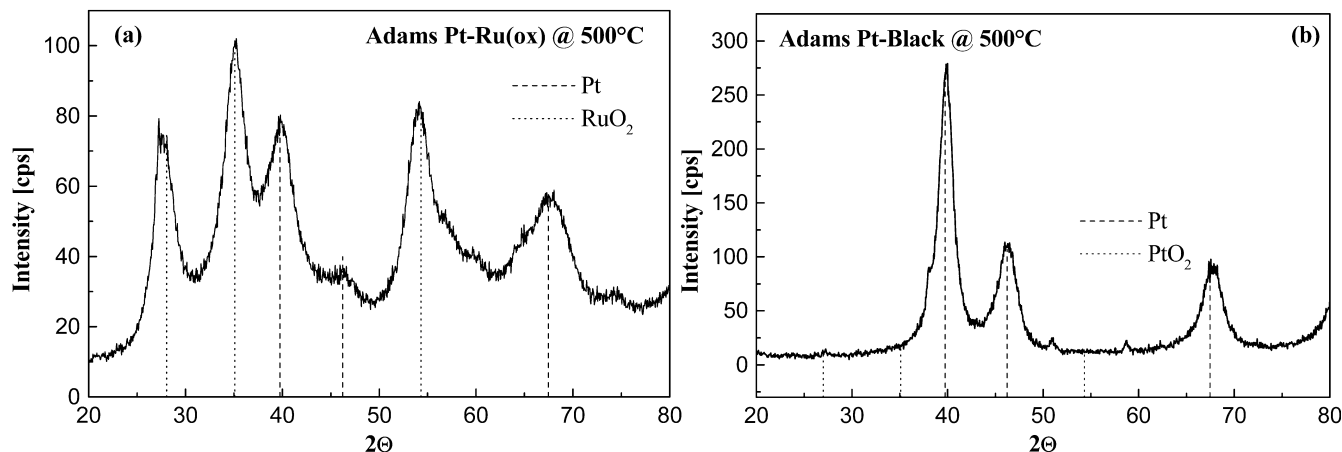
Results and discussion

Catalyst composition

Binary Pt-Ru catalyst materials of nominal atomic composition 1:1 were synthesized by different reaction temperatures according to the method described above. The results of EDX, BET surface area measurements and XRD analysis for these catalysts are summarized in Table 1.

Former XPS and EDX measurements [23] showed that the bulk and the surface compositions are almost identical, taking into account the errors of both methods resulting from surface roughness.

The results of the XRD analysis in Fig. 1 indicate that the Pt-Ru(ox) catalysts prepared by the Adams

Table 1 Characteristic properties of Pt-Ru(ox) catalysts prepared at different synthesis temperatures in the range 400–600 °C

Preparation temperature (°C)	Bulk composition (EDX) (at%)	BET surface area (m^2/g)	Average particle size of noble metals (XRD) (nm)	Ratio of Ru in alloy particles (at%)
400	54% Pt; 46% Ru	50	2–3	28
430	56% Pt; 44% Ru	52	3–4	26
470	55% Pt; 45% Ru	61	2–3	25
500	54% Pt; 46% Ru	82	2–3	18
530	55% Pt; 45% Ru	72	3–4	5
600	56% Pt; 44% Ru	50	–	0

Fig. 1 X-ray diffraction patterns of catalysts prepared by the Adams method [15]: (a) Adams Pt-Ru(ox) prepared at a temperature of 500 °C; (b) Adams Pt black prepared at a temperature of 500 °C

method at 500 °C contain varying amounts of crystalline noble metal oxides in addition to metal phases (Fig. 1a). As no oxide phases are present in the diffraction pattern of a pure Pt catalyst prepared by the same method (Fig. 1b), and pure RuO_2 prepared by the Adams method is not reduced to a metallic phase under the reduction conditions used, it can be concluded that the oxide phases consist mainly of RuO_2 and that Pt has been completely reduced to the metal.

Furthermore, no diffraction peaks indicating the presence of a pure metallic ruthenium phase are visible. This indicates that ruthenium is present either as an oxidized phase or as a metallic phase that is alloyed with fcc platinum. Considering the shift of the Pt(111) peak in the XRD pattern and earlier results from XPS analysis [23], where zerovalent ruthenium could be detected, it may be concluded that the catalysts are composed of Pt-Ru alloy particles next to ruthenium oxides.

Figure 2a shows a transmission electron micrograph (TEM) of a Pt-Ru(ox) catalyst prepared by the Adams method at 500 °C. The images indicate that the material consists of fine metal particles (higher contrast) supported on a larger grained oxide phase (lower contrast). No significant changes in particle morphology of the Pt-Ru(ox) catalysts were detected for synthesis tempera-

tures below 600 °C. At temperatures of 600 °C and above, large crystalline particles (Fig. 2b) can be seen by TEM. From the almost cubic shape in combination with XRD results, it is concluded that these are mainly crystalline oxide phases.

The nature of the oxidized ruthenium is still controversial. As the previously mentioned active $RuO_X \cdot XH_2O$ or $RuO_X H_Y$ is present as an amorphous structure [12], it cannot be detected by XRD measurements. In order to estimate the amount of amorphous oxidized Ru phase, thermogravimetric measurements (TGA) as well as CV have been carried out.

Different ruthenium oxides, commercial as well as Ru oxides synthesized in-house by the Adams method at two different temperatures, were investigated in order to determine the properties of the Ru oxide materials (Fig. 3). Both materials referred to as Adams RuO_2 have been prepared in exactly the same way as the Pt-Ru(ox) catalysts. The TGA in Fig. 3(a) shows a mass loss of 20% in the temperature range from 100 to 800 °C for the commercial hydrous ruthenium oxide. This is presumably due to the loss of water. In contrast, the Adams Ru oxide prepared at 500 °C exhibits no mass change up to a temperature of 1000 °C. It is therefore obvious that the H_2O content decreases with increasing preparation temperature, since the mass losses in the temperature range 100–800 °C are dramatically reduced for the commercial sample annealed at 370 °C and the Adams oxide synthesized at 450 °C. At high temperatures,

Fig. 2 TEM images of a Pt-Ru(ox) catalyst prepared by the Adams method at a synthesis temperature of (a) 500 °C and (b) 600 °C. Fine grained particles dominate at 500 °C, whereas formation of large cubically shaped crystallites is evident at 600 °C
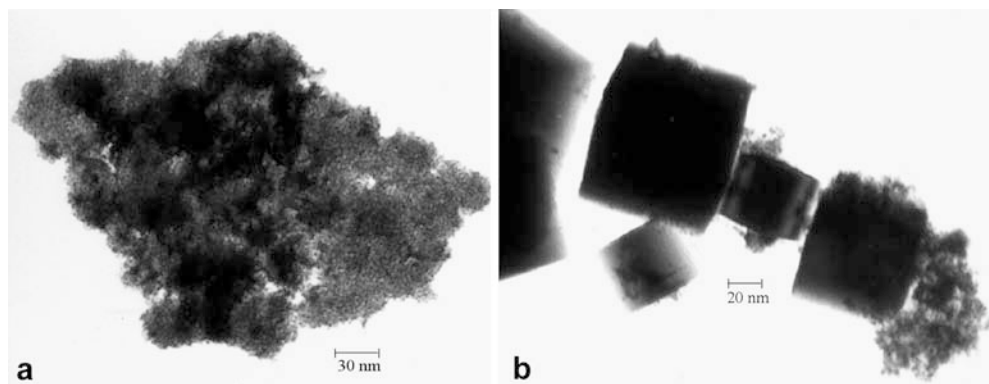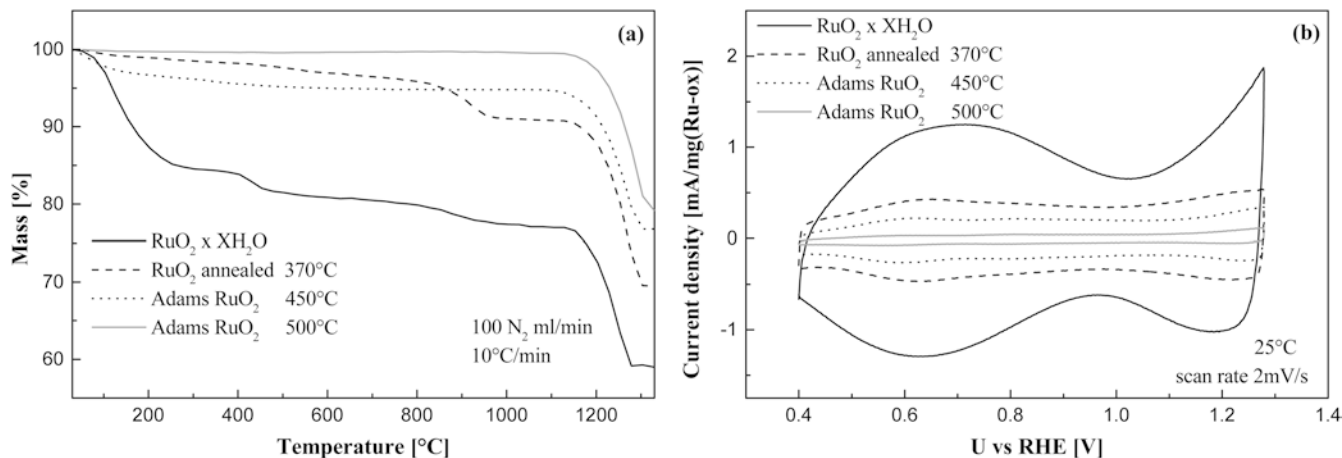
Fig. 3 Characterization of different Ru oxides: (a) thermogravimetric analysis; (b) cyclic voltammetry in 0.5 M H_2SO_4; scan rate 2 mV/s

however, all materials show a similar behavior: a large mass loss starting at about 1000 °C as a result of the well-documented decomposition of RuO_2 to Ru metal and O_2 [24].

The cyclic voltammetry (Fig. 3b) shows mainly featureless curves having broad peaks, indicating a capacitive behavior. It is apparent that the capacitance which is caused by the Ru redox processes and the proton conductivity of its hydrous oxides [25] decrease with preparation temperature, as similarly observed in Ru oxide materials investigated for applications in supercapacitors.

When comparing Ru oxides and Pt-Ru(ox) catalysts (Fig. 4), it can be seen from the 10% weight loss up to 600 °C that hydrous ruthenium oxides are present in the as-prepared Pt-Ru(ox) catalyst. (Note that the weight loss as a percentage of the Pt-Ru catalyst material is much lower than that of the pure Ru oxides, due to the presence of non-oxidized Pt in the catalyst). Obviously the ruthenium oxide prepared by the same method at the

same temperature as the Pt-Ru(ox) catalyst does not show any evidence of the presence of RuO_XH_Y. Hence platinum seems to play a crucial role to create hydrous phases during the catalyst synthesis.

The results are in good agreement with the CV measurements in Fig. 4(b). It is evident that the CV of the Pt-Ru catalyst bears similarities to the CV of the hydrous Ru oxide. As a general trend, the capacitance of Pt-Ru catalysts increases with decreasing preparation temperature, as can be seen in Fig. 5. Furthermore, from the comparison in Fig. 5 of Pt-Ru(ox) catalysts synthesized in the temperature range of 400–600 °C, it can be concluded that materials prepared at lower temperatures (below 500 °C) are reduced more easily to metallic phases. This is concluded from the TGA measurements, which show a weight increase at 200–800 °C for the materials prepared at temperatures below 500 °C. This mass increase is most likely caused by the oxidation of metallic ruthenium by oxygen impurities in the N_2 gas used for purging the thermal balance, as well as from back-diffusion of trace amounts of oxygen through the gas outlet [12]. Calibration tests using materials inert to oxygen carried out in advance did not show any indications of buoyancy effects. Comparing these measurements to the thermogravimetric analysis of the RuO_2 prepared by the Adams method at 450 °C, it seems that

Fig. 4 Different Ru oxides compared to a Pt-Ru(ox) catalyst: (a) thermogravimetric analysis; (b) cyclic voltammetry in 0.5 M H_2SO_4; scan rate 2 mV/s
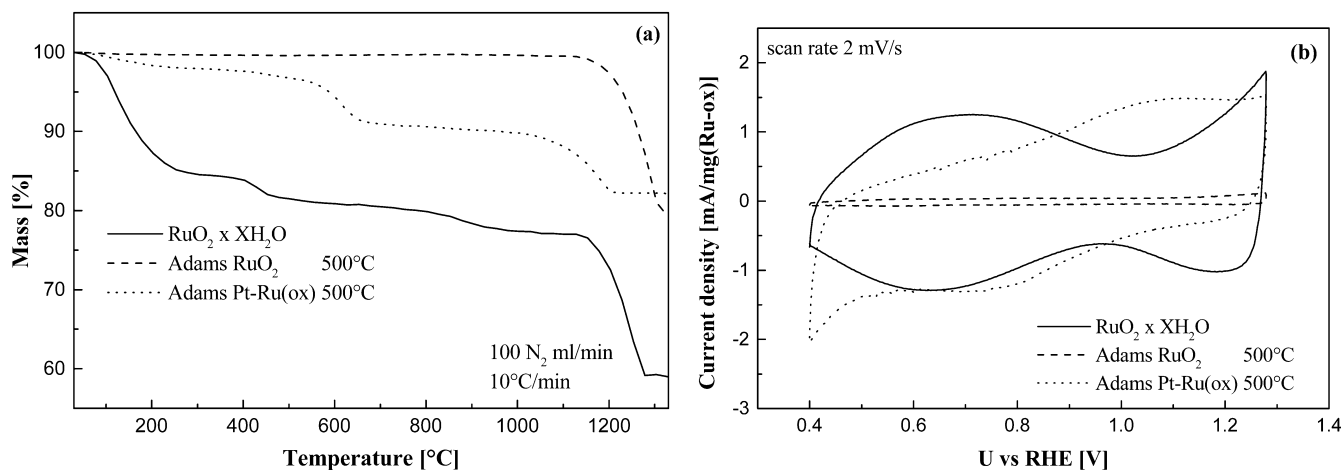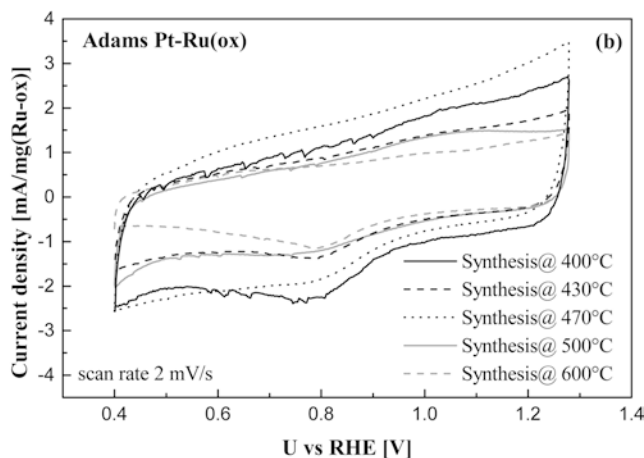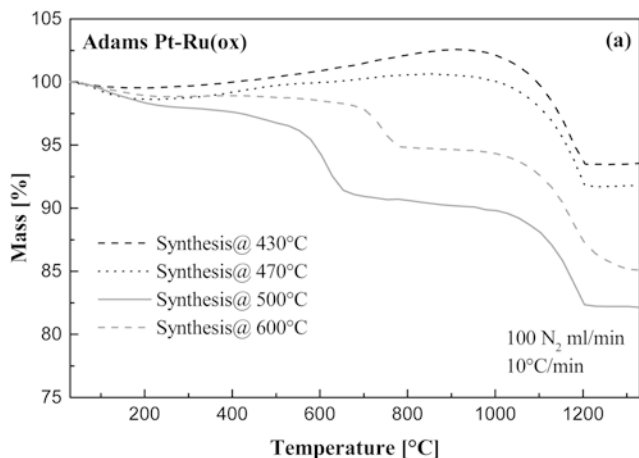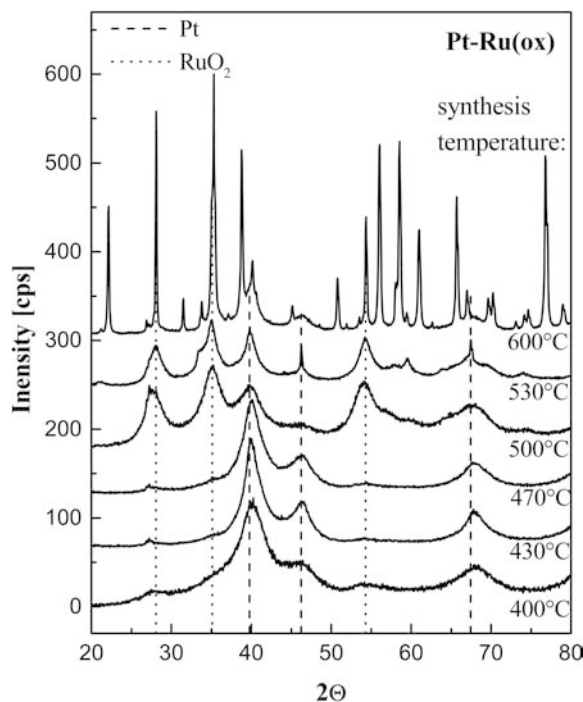
Fig. 5 Pt-Ru(ox) catalysts at different synthesis temperatures: (a) thermogravimetric analysis; (b) cyclic voltammetry in 0.5 M H₂SO₄; scan rate 2 mV/s

the presence of platinum not only assists in the formation of hydrous RuO_XH_Y phases but also facilitates the reduction of ruthenium oxides to metallic Ru. The cyclic voltammetry in Fig. 5(b) indicates a maximum capacitance for the Pt-Ru(ox) catalyst synthesized at 470 °C.

Figure 6 shows the XRD patterns of the Pt-Ru(ox) catalysts prepared at different temperatures. As mentioned earlier, hydrous ruthenium oxide exists in an amorphous structure and so does not appear in the XRD spectra. It can be observed that the intensity of the diffraction lines connected with Ru oxide increases with increasing preparation temperature, whereas the intensity of the lines indicating metallic Pt or Pt-Ru alloy phases decreases. Furthermore, the Pt(111) signal of catalysts prepared at temperatures below 530 °C is slightly shifted to higher values of 2Θ, thus indicating the formation of a bimetallic alloy (see also Table 1). No shift of the Pt(111) signal can be observed above a synthesis temperature of 530 °C.

Reactivity for methanol oxidation

All catalyst materials showed an open circuit potential of approximately 260 mV vs. RHE in 0.5 M H₂SO₄ + 1 M CH₃OH. Figure 7 shows a comparison of stationary current–potential characteristics of Pt-Ru(ox) catalysts synthesized at different temperatures. After application of a small current in the range of a few mA/mg, a large overpotential of over 200 mV is observed on all samples, which is followed by a region of diminished potential increase. The performance of the investigated catalyst samples can be clearly correlated with the synthesis temperatures. Catalysts synthesized at temperatures of 500 °C and above show higher overpotentials compared to the group of catalysts synthesized at temperatures below 500 °C. Apparently, a lower catalyst preparation temperature leads to a lower polarization of the electrode for methanol oxidation. A maximum in catalytic activity can be observed for Pt-Ru(ox)@470 °C, correlating with

Fig. 6 XRD patterns of Pt-Ru(ox) catalysts prepared at different synthesis temperatures

a maximum in capacitance (Fig. 5b). Furthermore, it is evident that a severe yet reversible deactivation of the catalyst materials occurs at potentials above 750 mV vs. RHE (Fig. 5a, insert). This can be attributed to the formation of a catalytically inactive surface oxide on Pt, which has been reported by several groups, e.g. [26, 27]. No fundamental changes can be observed in Fig. 7(b), taking the BET surface area into account.

To put the study in a broader context, comparisons of the Adams catalyst exhibiting the highest catalytic activity (Adams Pt-Ru(ox)@470 °C) to commercial catalysts by Johnson Matthey (JM) and E-TEK are shown in Fig. 8. Figure 8(a) shows that the so-prepared Adams catalyst is within the activity range of both commercial catalysts. According to the higher surface
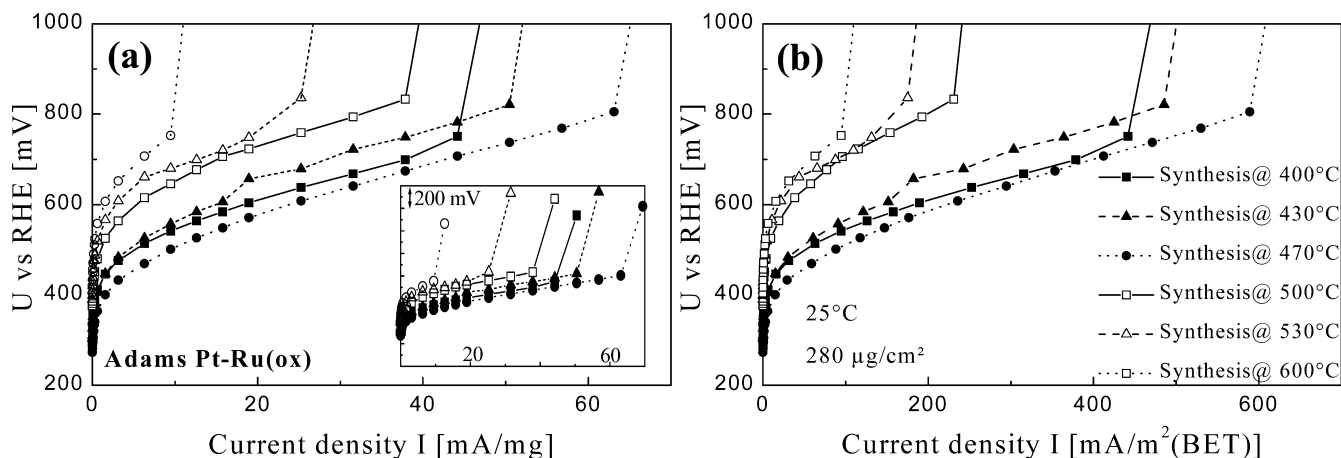
Fig. 7 Stationary current–potential measurements of Pt-Ru(ox) catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH prepared at different synthesis temperatures: (**a**) current density (mA/mg); (**b**) current density referring to the BET surface (mA/m^2)

areas of the commercial catalysts, Fig. 8(b) shows dramatic changes in activity when referring the current density to the BET surface area. In this plot a maximum in activity can be observed for the Adams Pt-Ru(ox)@470 °C catalyst.

Summary and conclusions

Binary Pt-Ru(ox) catalysts were prepared at different temperatures in the range of 400–600 °C according to the Adams method. The materials consisted of varying degrees of Pt-Ru binary alloys, crystalline RuO_2 phases and amorphous hydrated Ru oxides, as concluded from XPS and XRD measurements.

Formation of crystalline RuO_2 was favored by increasing preparation temperature, whereas a high degree of Pt-Ru alloy formation was favored by low

preparation temperatures. No significant influence of the synthesis temperature on the particle sizes of the metallic phase could be observed. When comparing the catalyst composition as analyzed by EDX with the nominal catalyst composition, a good agreement is observed considering the accuracy of the method. However, the degree of alloying (measured by the ratio of Ru in the alloy particles) is much lower compared to the EDX composition, decreasing from a value of 28% for a catalyst synthesized at 400 °C to 0% for a synthesis temperature of 600 °C. From the absence of crystalline RuO_2 signals in the XRD patterns of catalyst materials synthesized at low temperatures, it may be concluded that the remaining ruthenium is present as an amorphous hydrated Ru oxide phase. This is also supported by the capacitances observed in CV experiments. Obviously the presence of Pt during synthesis favors the formation of amorphous hydrated Ru oxide phases as well as the reduction of ruthenium oxides to Ru metal, forming a binary Pt-Ru alloy.

From the stationary current–potential curves measured at room temperature, it is evident that the catalytic activity with respect to the electrochemical oxidation of methanol is severely lowered by the presence of a crystalline RuO_2 phase. Optimum catalytic activity has been observed at a synthesis temperature of 470 °C. The

Fig. 8 Stationary current–potential measurements of the Adams Pt-Ru(ox) catalyst at 470 °C in 0.5 M H_2SO_4 + 1 M CH_3OH in comparison to commercial catalysts: (**a**) current density (mA/mg); (**b**) current density referring to the BET surface (mA/m^2)
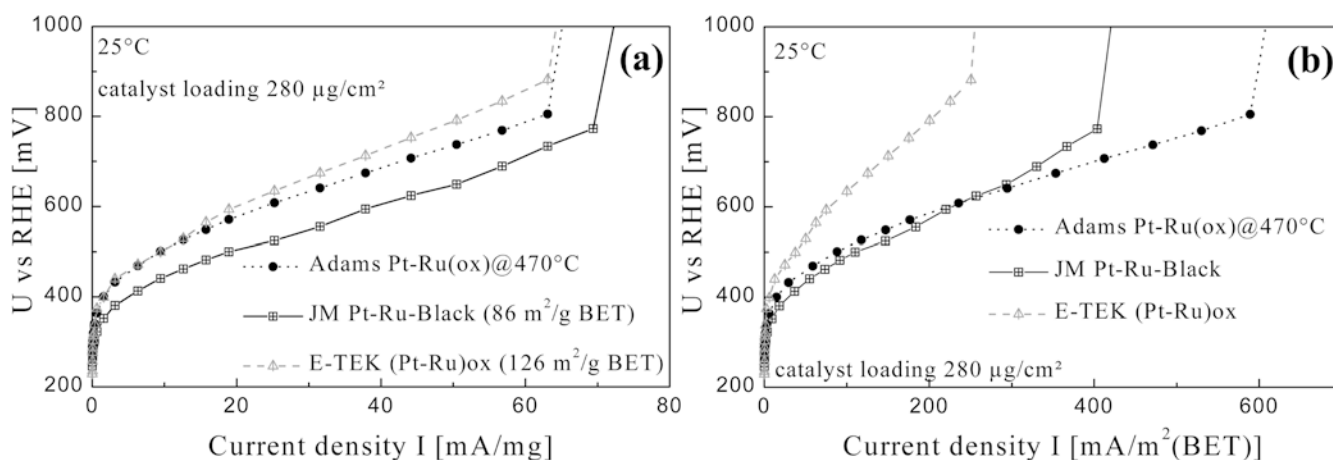
optimum catalytic activity correlates with an optimum in capacitance.

From the experimental results obtained so far, it can be concluded that both the presence of an alloyed metallic Pt-Ru phase as well as the presence of amorphous hydrated Ru oxides are favorable for catalysis of the electrochemical oxidation of methanol. An optimum in electrochemical performance at room temperature is apparently achieved here at an alloy composition of 25% Ru, corresponding to the Adams catalyst prepared at 470 °C (Table 1). However, the remaining amorphous hydrous Ru oxide phases are also involved in co-catalytic processes and therefore the separation of the influence of alloy formation and of hydrous oxides is difficult. Furthermore, since the analysis of the catalyst materials has been carried out using the materials as prepared, changes in composition and morphology during the electrochemical experiments (e.g. reduction of amorphous hydrous Ru oxides) cannot be ruled out. Therefore, further work is desirable to study the composition and structure of the catalysts under actual electrochemical operation.

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