Mixed conducting catalyst support materials for the direct methanol fuel cell

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Abstract

Finely dispersed Pt- and Pt/Ru-particles have been deposited on high surface-area ruthenium dioxide (RuO_2) using the Petrow and Allen method [U.S. Patent No. 4,044,193 (23 August 1977)]. RuO_2 has been synthesized according to different preparation methods. It turned out that the product showing the highest surface area could be produced by a simple fast precipitation method. The electrocatalytic activities of catalysts on different ruthenium oxide supports have been investigated in half-cell experiments by stationary current voltage measurements. Pt/Ru-catalysts deposited on a Vulcan XC-72 carbon black have been used for comparison.

X-ray analysis methods (XRD, EDX) have been used to characterize the composition and crystallinity of the materials and their geometric surface areas have been determined by the BET method.

It turned out that the electric conductivity of the RuO_2 materials was comparable to that observed for Vulcan XC-72. Furthermore, RuO_2 materials having a BET surface area above 125 m^2/g could be synthesized. (Vulcan XC-71: $\sim$250 m^2/g).

Surprisingly, no significant electrochemical activity was found when Pt/Ru was deposited on freshly precipitated hydrous RuO_2. Deposition of noble metals on calcined RuO_2 resulted in electrochemical activities comparable to the ones obtained for the Vulcan XC-72 support. Thus, no extraordinary enhancement of catalytic activity for the methanol has been observed when RuO_2 oxide was used as a mixed conducting catalyst support. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the main problems of the direct methanol fuel cell (DMFC) is the still insufficient activity of the anode catalysts [1]. Pure platinum is poisoned by reaction intermediates such as CO_{ads} [2,3]. In order to improve the catalyst performance, platinum alloys (typically Pt-Ru) are used in DMFCs. Pt accomplishes the dissociative chemisorption of methanol and Ru forms a surface oxy-hydroxide which is then used to oxidize the carbonaceous residues to CO_2 [4,5].

A large number of investigations have been reported on the electro-oxidation of methanol using metal oxides [6,7] in order to improve the catalytic activity of platinum, but so far Pt-Ru alloys remain the most active catalysts for methanol oxidation.

A further approach to increase the anode performance is to use "active support materials". Based on the mechanism of methanol oxidation proposed by McNicol [8], it can be expected that ruthenium-oxide-phases at the catalyst surface might play a crucial role in oxidizing adsorbed CO-species on Pt-catalysts. It has been reported recently that mixed conducting compounds such as ruthenium oxides [9] enhance the catalytic activity of Pt-type catalysts. In this work, the influence of mixed conducting catalyst supports on the electro-oxidation of methanol is reported.

2. Experimental

2.1. Catalyst preparation and characterization

The RuO_2 support materials were prepared using a sol–gel process [10]. Sodium hydroxide solution was slowly added to an aqueous solution of ruthenium chloride. In this process, sodium hydroxide was employed primarily for adjusting the pH to a value of $\sim$7, the point at which a controlled precipitation occurs. The residue was washed with water

and freeze-dried at $-80\,^\circ$C with a substrate temperature of $+5\,^\circ$C. A part of the materials has been annealed in air at $370\,^\circ$C for 1 h. Commercial $RuO_2 \cdot xH_2O$ obtained by Merck was used as comparison to the synthesized materials.

Finely dispersed Pt- and Pt-Ru-particles have been deposited on different carrier materials (ruthenium oxides and Vulcan XC-72) using the Petrow and Allen method [11,12]. Powdered sodium bisulfate was added to an aqueous solution of chloroplatinic acid followed by the addition of hydrogen peroxide at an adjusted pH of 5. To obtain Pt-Ru-catalysts, an aqueous solution containing appropriate concentrations of ruthenium chloride was added dropwise resulting in a brown colloidal product. The support material was then admixed to the colloidal solution of noble metal oxides and stirred for an hour. Finally, the supported catalyst was washed thoroughly with water to remove chloride, and the resulting aqueous suspension of mixed oxides was reduced at room temperature with bubbling hydrogen [12].

X-ray analysis methods (XRD, EDX) have been used to characterize the composition, the crystallinity and the particle size of the materials. Spectral contributions of the Cu $K\alpha_2$ line were substracted by a Rachinger algorithm correction. To assess the particle size, the $RuO_2(1\,1\,0)$ reflection was fitted to a Gaussian lineshape on a linear background.

The surface areas of the materials have been determined by the BET method. The specific resistance of the support materials has been measured using the four-point method.

2.2. Electrochemical measurements

The preparation of the thin film electrodes followed the method described by Schmidt et al. [13]. Glassy carbon electrodes (12 mm diameter, $1131\,cm^2$) 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 noble metal loading of $\sim$56 μg/cm^2. After evaporation of the water in a nitrogen stream, the resulting thin catalyst film was covered with 80 μl of a 0.1% Nafion$^®$ 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 [14,15].

The catalysts were characterized by stationary current–voltage curves at room temperature in a three-electrode cell. One molar methanol solution in 0.5 m H_2SO_4 was used as the electrolyte. Potentials were measured using a Hg_2SO_4/SO_4^{2-} electrode but are referenced to the reversible hydrogen electrode (RHE).

3. Results and discussion

3.1. Catalyst composition

The results of EDX, BET surface area measurements and specific resistance of the support and catalyst materials are summarized in Table 1. The quantitative EDX analysis shows that the composition of the materials is within the desired range (20% noble metal), taking into account the errors resulting from surface roughness. As far as catalysts on ruthenium oxide supports are concerned, the accuracy is very limited since the positions of the strongest Pt- and Ru-line (PtM and RuL) are very close and become hard to distinguish for quantitative analysis when a large excess of ruthenium is involved.

The electric conductivity of the RuO_2 materials in any case is comparable to the one observed for Vulcan XC-72. Furthermore, RuO_2 materials having a BET surface area above 125 m^2/g could be synthesized.

3.2. Crystalline structure

Fig. 1 shows XRD powder patterns of ruthenium oxide supports before and after annealing. No peak could be detected for uncalcined ruthenium oxide materials. When the temperature was raised to $370\,^\circ$C, diffraction peaks corresponding to anhydrous RuO_2 were observed thus showing that the uncalcined powder consists of amorphous phases. On raising the temperature, more powder becomes crystalline and the crystallite size increases. The average

Table 1
Properties of support- and catalyst-materials

| Material	Expected composition (at.%)	Composition (EDX) (at.%)	BET surface area (m^2/g)	Specific resistance ($\times 10^{-4}\ \Omega$ m)
Vulcan XC-72		–	212	2.3
Pt-Ru on Vulcan XC-72	50% Pt, 50% Ru	46% Pt, 54% Ru	167	2.3
Merck $RuO_2 \cdot xH_2O$		–	193	1.2
Pt-Ru on Merck $RuO_2 \cdot xH_2O$	11% Pt, 89% Ru	10% Pt, 90% Ru	189	1.7
Merck RuO_2 calcined		–	95	0.8
Pt on Merck RuO_2 calcined	10% Pt, 90% Ru	9% Pt, 91% Ru	81	1.2
$RuO_2 \cdot xH_2O$		–	126	2.2
Pt-Ru on $RuO_2 \cdot xH_2O$	11% Pt, 89% Ru	12% Pt, 88% Ru	91	2.2
RuO_2 calcined		–	135	1.4
Pt-Ru on RuO_2 calcined	9% Pt, 91% Ru	15% Pt, 85% Ru	151	1.4
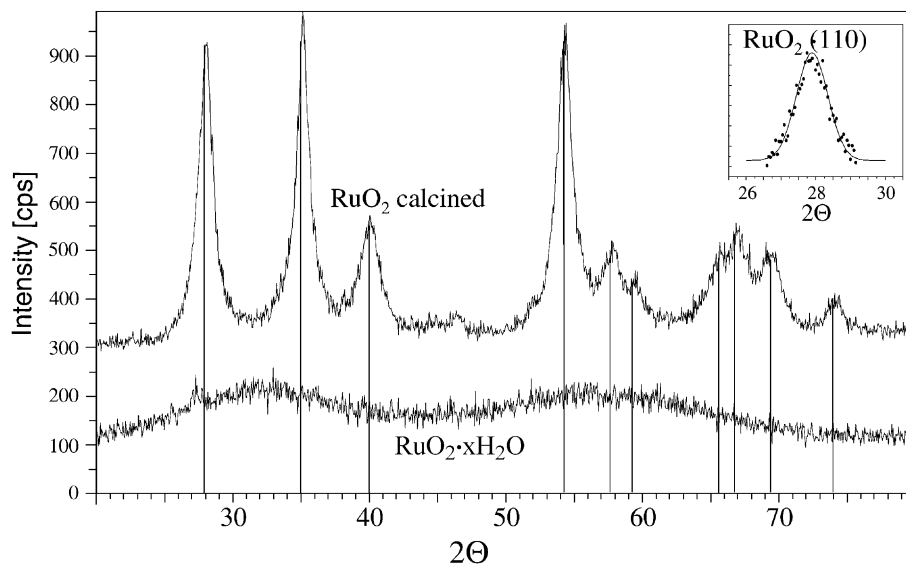
Fig. 1. XRD spectra of ruthenium oxides before and after annealing.

crystallite size can be calculated from the Scherrer formula [16]:

$$L = \frac{0.9\lambda_{K\alpha_1}}{B_{2\Theta}\cos\Theta_{max}},$$

where $\lambda_{K\alpha_1}$ is the X-ray wavelength (1.54056 Å for Cu $K\alpha_1$ radiation), $B_{2\Theta}$ the width of the diffraction peak at half-height (rad), and Θ_{max} is the angle at the position of the peak maximum. Hence, the calculation gives an average particle size of 130–140 Å for the annealed materials.

Fig. 2 shows XRD diagrams of Pt deposited on freshly precipitated and calcined RuO_2 after reduction. It is evident that the uncalcined material consists mainly of amorphous Ru-oxide and Pt phases. Furthermore, it contains a non negligible content of metallic Ru. As the main objective of this work is to examine the influence of mixed conducting ruthenium oxides,

larger amounts of Ru-metal are not desirable. Therefore, the materials were annealed in air at 370 °C, even though there are indications, that the catalytic active ruthenium-oxide phase changes into a dehydrated phase at temperatures over 150 °C and finally into anhydrous RuO_2 at about 300 °C [9], both being very poor proton conductors [17].

The same effect can be observed in Fig. 3. XRD spectra of Pt-Ru on hydrous $RuO_2 \cdot xH_2O$ and $RuO_2 \cdot xH_2O$ (Merck) as well as Pt-Ru on annealed RuO_2 are shown. Again it becomes obvious that for the uncalcined material large amounts of the ruthenium oxide are reduced to metallic ruthenium accompanied by a 28% decrease of the BET surface area (see Table 1). Therefore, the formation of a metallic Ru phase might be a possible explanation for the loss in BET surface area as such loss is not found after the reduction of annealed RuO_2 materials.
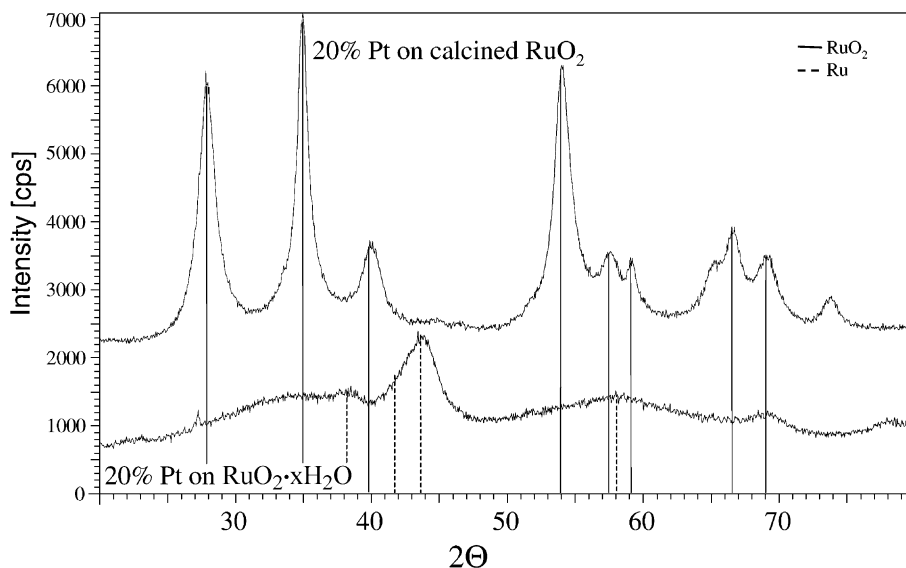

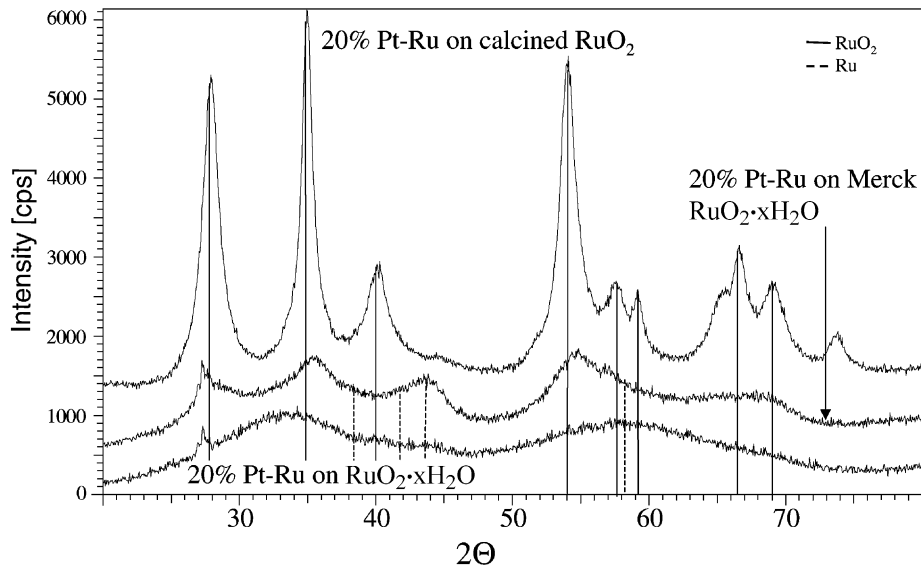Fig. 2. XRD spectra of 20% Pt on ruthenium oxide supports after reduction.

Fig. 3. XRD spectra of 20% Pt-Ru on ruthenium oxide supports after reduction.

3.3. Electrochemical measurements

Fig. 4 shows a comparison of pure Pt-catalysts supported on carbon (Vulcan XC-72), calcined RuO_2 and freshly precipitated RuO_2 with respect to the oxidation of methanol. The commercially available material from E-Tek is given as a reference. The activity decreases in the sequence: E-Tek,

Vulcan XC-72, RuO_2 calc., RuO_2 (Merck) calc., $RuO_2 \cdot xH_2O$, $RuO_2 \cdot xH_2O$ (Merck). Surprisingly, it is observed that catalysts supported on calcined RuO_2 show a dramatic potential jump when the polarization exceeds $\sim$800 mV. This can be attributed to the formation of a catalytic inactive surface oxide [18]. Normally, this behavior is observed for Pt/Ru-containing catalysts (Fig. 5).
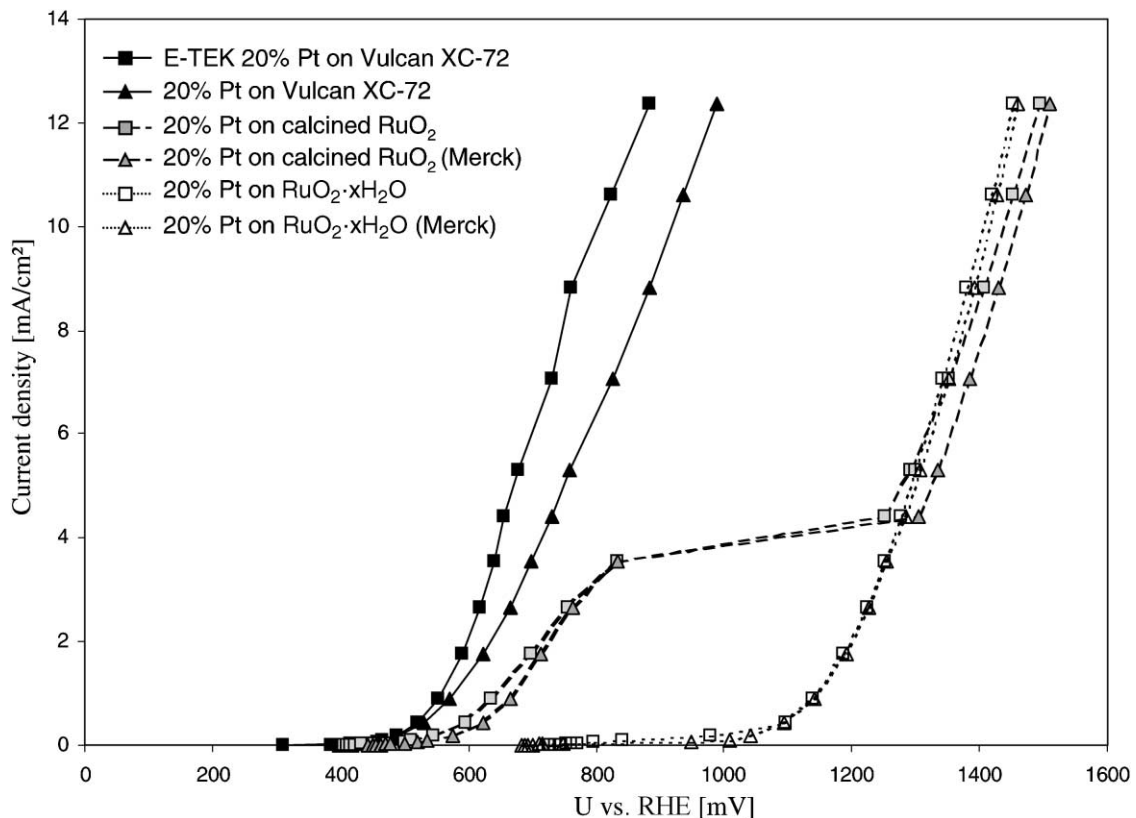

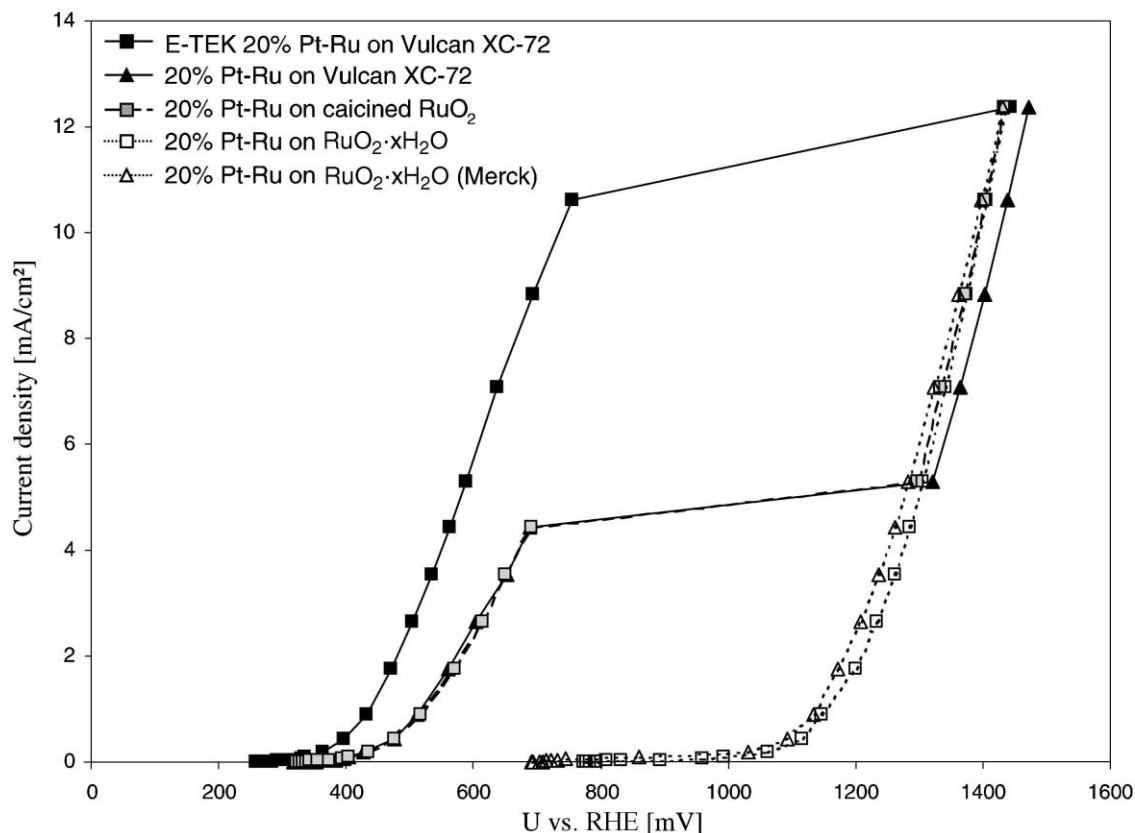Fig. 4. 20% Pt on ruthenium oxides compared to 20% Pt on Vulcan XC-72.

Fig. 5. 20% Pt-Ru on ruthenium oxides compared to 20% Pt-Ru on Vulcan XC-72.

A comparison of supported Pt/Ru-catalysts is shown in Fig. 5. As expected, Pt/Ru catalysts are more active at lower potentials than catalysts containing pure Pt. The activity decreases in the sequence: E-Tek, Vulcan, RuO_2 calc., $RuO_2 \cdot xH_2O$, $RuO_2 \cdot xH_2O$ (Merck). The catalytic performance of Pt-Ru on Vulcan XC-72 and of Pt-Ru on annealed RuO_2 does not show any striking difference. No enhancement can be found when ruthenium oxide is applied as support material. A possible reason for this behavior is the fact that the predominant phase after annealing is anhydrous RuO_2 which is a very bad proton conductor and therefore no good water dissociator. Dissociation of water is one of the mechanisms for proton transfer into a proton conducting material [19].

As the dissociation of water and the provision of OH-surface species for the oxidation of CO_{ads} is the important cocatalytic contribution of Ru-species, anhydrous RuO_2 does not meet the requirements to be an "active support material". Neither does the uncalcined material fulfill these qualifications. Figs. 4 and 5 show that catalysts supported on uncalcined RuO_2 are completely inactive. The formation of a metallic ruthenium phase either reduces drastically the proton transfer to the support material or it blocks the catalytic activity of the deposited Pt-particles. It is well know that the ideal Ru-content for electrochemical methanol oxidation should not be larger than 50% [20,21] which in this case is exceeded by far.

4. Conclusions

High surface area ruthenium oxides ($\geq 120 \, m^2/g$) were used as catalyst supports for Pt- and Pt-Ru-catalysts. The electric conductivity of these materials is comparable to that observed for Vulcan XC-72. X-ray diffraction shows that hydrous $RuO_2 \cdot xH_2O$ consists of amorphous phases which are partly reduced to metallic ruthenium in the course of the catalyst preparation. For that reason, a part of the material was annealed at 370 °C in oxygen. From the XRD spectra, it becomes obvious that the calcined material consists of crystalline anhydrous RuO_2 before and after reduction. No Ru-metal phases are observed. However, anhydrous RuO_2 is a very bad proton conductor and therefore does not show any contribution as an "active support material".

Deposition of noble metal catalysts on calcined RuO_2 results in electrochemical activities comparable to those obtained for the Vulcan XC-72 support. Thus, no extraordinary enhancement of catalytic activity for the methanol oxidation has been observed when RuO_2 was used as catalyst support.

Catalysts supported on uncalcined RuO_2 are completely inactive. It seems as if the presence of large amounts of metallic ruthenium decreases or even inhibits the catalytic activity.

Further work on the influence of ruthenium oxide supports on the electro-oxidation of methanol is in progress.

Acknowledgements

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