DEMS AND SINGLE CELL MEASUREMENTS OF A DIRECT METHANOL FUEL CELL

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The adsorption and oxidation of CH$_3$OH were studied in 1 M HClO$_4$ on porous Pt and Pt$_x$Ru$_y$ electrodes by means of Differential Electrochemical Mass Spectrometry (DEMS). The electrodes were made by potentiostatic co-deposition on porous Au substrates. It was found that Pt$_{0.9}$Ru$_{0.1}$ shows the highest activity compared to pure Pt. For this composition the complete oxidation to CO$_2$ is favoured in contrast to other compositions which yield more amounts of formic acid. The oxidation of poisoning adsorbate species on Pt$_{0.9}$Ru$_{0.1}$ is shifted 0.15 V to negative potentials in comparison to Pt. First results on the oxidation of gaseous CH$_3$OH/H$_2$O mixtures in a Proton Exchange Membrane Fuel Cell at T = 100 °C are presented. The catalyst loading of gas diffusion electrodes for anode and cathode was 1 mg/cm$^2$. With a Pt$_{0.7}$Ru$_{0.3}$ anode catalyst and Pt as cathode catalyst current densities of > 0.1 A/cm$^2$ at 0.4 V were obtained.

INTRODUCTION

Methanol is considered a promising energy carrier for fuel cell systems in mobile and stationary applications. At present, the utilization of methanol in a Proton Exchange Membrane Fuel Cell (PEMFC) requires a reformer for hydrogen production and additional gas cleaning procedures for CO reduction of the fuel gas (1). In principle, the Direct Methanol Fuel Cell (DMFC) probably could avoid complicate fuel processing with its additional weight, volume and costs. Although the basic idea is known for many years the realization has only been demonstrated on a laboratory scale (2-4). The loading of the dispersed electrocatalyst supported on carbon in these demonstration systems was 4-5 mg/cm$^2$ and the power density achieved was 100 - 300 mW/cm$^2$. However, the amount of noble metal catalyst used for mobile application should be reduced to ≤ 1 mg/cm$^2$ whereas the power density should be further enhanced.

A basic concept of a complete DMFC system is illustrated in Fig. 1. Methanol and product water are mixed, evaporated and fed directly into the fuel cell. The heat necessary for methanol evaporation and cleaning of the anode exhaust gas can be provided by a catalytic converter. In such a way the advantage of a fuel cell system in terms of high efficiency and low emissions can be fulfilled. More focussed criteria for
the development of the main components of such a fuel cell system can be obtained by simulating a complete DMFC under various operating conditions (5).

The direct electrochemical oxidation of methanol in a PEMFC requires the development of optimized anode catalysts since the oxidation of CH$_3$OH on Pt that is presently the most active material leads to the formation of poisoning species such as CO, COH and CHO (6) on the electrode surface. In order to enhance the electrocatalytic activity of the anode towards the oxidation of CO and CH$_3$OH, PtRu alloys are being proposed as catalysts(7-9). The combination of cyclic voltammetry and Differential Electrochemical Mass Spectrometry (DEMS) (10) is a suitable method to study electrochemical reactions on porous electrodes. On-line mass spectrometry enables identification of volatile and gaseous reaction products formed during methanol oxidation in acid electrolytes. By varying the Pt to Ru ratio in the alloy the best composition for this reaction can be elucidated. In addition, single cell measurements with a PEMFC using carbon supported Pt and PtRu catalysts for the anode can give valuable information on the electrochemical activity of such alloys under practical conditions and can lead to a deeper insight into the process parameters of a complete fuel cell.

**EXPERIMENTAL**

DEMS measurements were carried out in an electrochemical flow cell attached directly to the vacuum chamber of the mass spectrometer. The electrolyte volume was approx. 2 ml. The working electrodes were prepared by sputtering first a gold substrate layer onto a hydrophobic ethylene-tetrafluoroethylene copolymer membrane (Scimat 200/40/60 from Scimat Ltd.; mean thickness 60 µm, mean pore size 0.17 µm, 50% porosity). Pt and/or Ru were then codeposited from solutions of RuCl$_3$ and H$_2$PtCl$_6$ in 1 M HClO$_4$ at a constant potential of 0.05 V vs. RHE during 30 min. The surface composition of the Pt$_x$Ru$_y$ layers were determined by XPS according to (11) while the composition of the bulk alloy was determined by EDAX. The analysis of each sample showed a good reproducibility of the preparation method. The comparison showed that the Pt concentration at the electrode surface was always higher than the corresponding solution composition. For the experiments described below PtRu alloys with Ru contents of <50 atomic % were investigated. To avoid possible surface segregation effects occurring during the experiments, always freshly prepared working electrodes were used.

For testing various Pt$_x$Ru$_y$ anode catalysts in a PEMFC, Membrane Electrode Assemblies (MEAs) were fabricated by hot-pressing gas diffusion electrodes (ETEK, Natick, MA) with a catalyst loading of 1 mg/cm$^2$ onto Nafion™ 117. MEAs were mounted in a laboratory PEM single cell with Ti current collectors and stainless steel end plates. The active electrode area in all experiments was 4 cm$^2$.

The test station for characterization of PEM single cells is shown in Fig. 2 enabling the utilization of various fuels such as pure H$_2$, reformate (H$_2$/CO$_2$/CO) and...
CH$_3$OH. Methanol/water mixtures with various volume ratios are fed into an evaporator and then introduced into the single cell. The cell temperature was 100 °C. Oxygen was used at 2 bar$_{atm}$, whereas gaseous CH$_3$OH/H$_2$O were used at atmospheric pressure. After activation of the MEA the performance of a PEM single cell was first evaluated using H$_2$/O$_2$. Then the fuel gas was switched from pure H$_2$ to CH$_3$OH/H$_2$O mixtures.

RESULTS AND DISCUSSION

In order to evaluate the electrocatalytic activity of porous Pt$_x$Ru$_y$ electrodes towards methanol, the electrooxidation of CH$_3$OH in perchloric acid, the adsorbate formation and the adsorbate oxidation in methanol free HClO$_4$ solution were studied by means of DEMS.

Fig. 3 shows CVs of 1 M CH$_3$OH in 1 M HClO$_4$ and simultaneously recorded MSCVs for m/z = 44 and 60 for porous Pt and Pt$_{0.9}$Ru$_{0.1}$. The potential dependent mass signal of m/z = 44 in the positive going potential scan is due to CO$_2$ formation during methanol oxidation whereas the signal at m/z = 60 is assigned to the radical cation of HCOOCH$_3$ indicating the formation of formic acid as partial oxidation product of methanol. The ester formation is explained by a chemical reaction of HCOOH with excess CH$_3$OH in the solution (6). The onset potential for methanol oxidation at the Pt$_{0.9}$Ru$_{0.1}$ electrode was observed to be about 0.15 V more negative as with pure Pt. This is the highest negative shift observed for all Pt$_x$Ru$_y$ electrodes studied. It should be mentioned that on a pure Ru electrode no faradaic current due to methanol oxidation neither ion currents of possible reaction products could be observed. Therefore, Ru in acid electrolytes shows no reactivity for methanol oxidation. In a first approximation the relative distribution for CO$_2$ and HCOOH formation during oxidation can be determined by integrating the ion current for m/z = 44 and 60 for a complete potential cycle. Fig. 4 shows such relative amounts as a function of the Pt content in Pt$_x$Ru$_y$. It can be seen that the ratio $Q(m/z = 44)$ to $Q(m/z = 60)$ has its maximum when the alloy contains about 90 % Pt. This indicates that the complete oxidation of CH$_3$OH to CO$_2$ is favoured on this alloy composition with respect to the formation of the partial oxidation product.

Considering the thermodynamics of the electrochemical methanol oxidation according to

$$\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta U = 1.21 \text{ V (at 25 °C)} \quad [1]$$

cell performance comparable to the H$_2$/O$_2$ fuel cell should be possible. However, a significantly lower activity of methanol oxidation on Pt electrodes is obtained which is explained by the formation of strongly adsorbed intermediates. To study the influence of the Ru content in Pt$_x$Ru$_y$ alloys on the formation of these species, cyclic voltammetric...
curves of CH₃OH in HClO₄ on adsorbate free electrode surfaces were monitored. For this purpose, a complete potential scan in methanol free solution was recorded for checking the cleanness of the electrode. A potential of $U_{ad} = 0.05$ V vs. RHE was adjusted and 1 M CH₃OH solution was introduced into the flow cell followed by starting a positive going potential scan. Fig. 5 shows the CVs and the simultaneously recorded MSCVs for $m/z = 44$ on pure Pt and Pt₀.₉Ru₀.₁. In the potential range between 0.05 and 0.3 V anodic peaks were observed at 0.2 V for Pt and at 0.18 V for Pt₀.₉Ru₀.₁ occurring only in the first potential scan. In this potential range no mass signals due to CO₂ were observed. CO₂ production on Pt and Pt₀.₉Ru₀.₁ commences at $U > 0.35$ V parallel to the increase of the faradaic currents in the CV. The anodic current in the range 0.05 - 0.3 V is explained by the formation an adsorbate layer having a higher oxidation state than methanol. On pure Pt, in-situ infrared spectroscopy has shown that the adsorbate layer formed consists of species such as linear bonded CO, COH and CHO (3). The highest anodic charge determined during the first positive going scan as seen in Fig. 5 was found for pure Pt. This adsorption charge decreases with increasing Ru content in PtₓRu₀₋ₓ. On pure Ru no adsorbate formation was observed. Thus methanol adsorption occurs only on Pt sites agree with results reported in literature (9,13).

In the next series of experiments the oxidation of the methanol adsorbate in CH₃OH free solutions was studied. After adsorption of methanol at $U_{ad} = 0.20$ V vs. RHE for 5 min. the methanol containing electrolyte was replaced completely by pure HClO₄ solution and the adsorbate was stripped in the first positive going potential scan. Fig. 6 shows the CVs and corresponding mass signals for CO₂ formation during oxidation of adsorbed methanol on pure Pt and Pt₀.₉Ru₀.₁. On Pt₀.₉Ru₀.₁ the peak potential observed for the complete oxidation of the adsorbate to CO₂ is shifted by 0.15 V negative compared to Pt. This is the same shift as observed for the oxidation of dissolved CH₃OH as discussed above. This observation gives evidence that Ru promotes the oxidation of the poisoning intermediate during oxidation of methanol.

The mechanism of the electrochemical CH₃OH oxidation on Pt electrodes is regarded to consist of two parallel reaction pathways (12,14). This is first the direct oxidation of a weakly adsorbed CH₃OH molecule to CO₂ and partially oxidized products such as HCOOH. Using DEMS this product can be identified as HCOOCH₃ as illustrated in Figs. 3 and 4. The second pathway is the oxidation of methanol via a strongly adsorbed intermediate partially blocking active site of the Pt surface. The adsorption is assumed to take place by dehydrogenation reactions forming different adsorbate species according to the following reactions

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\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt-CH}_2\text{OH} + \text{H}^+ + \text{e}^- \quad [2] \\
\text{Pt} + \text{Pt-CH}_2\text{OH} & \rightarrow \text{Pt}_2\text{-CHOH} + \text{H}^+ + \text{e}^- \quad [3] \\
\text{Pt} + \text{Pt}_2\text{-CHOH} & \rightarrow \text{Pt}_3\text{-COH} + \text{H}^+ + \text{e}^- \quad [4] \\
\text{Pt}_3\text{-COH} & \rightarrow \text{Pt-CO} + 2 \text{Pt} + \text{H}^+ + \text{e}^- \quad [5]
\end{align*}
\]
The experimental findings obtained on porous Pt$_x$Ru$_y$ electrodes in HClO$_4$ solutions can be explained using a certain spatial distribution of sites for CH$_3$OH adsorption on PtRu first presented by Gasteiger et al. (9). In this model methanol is preferentially adsorbed on 3-fold Pt sites according reactions [2] - [4]. With a surface composition of around 90% Pt and 10% Ru these Pt ensembles are surrounded by one Ru atom on which water adsorption according

$$\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru-OH} + \text{H}^+ + e^- \quad [6]$$

occurs at potentials more negative compared to Pt. The enhanced reaction rate for methanol oxidation on Pt$_x$Ru$_y$ is then promoted by adsorbed water on Ru according the bifunctional mechanism proposed by Watanabe and Motoo (15)

$$\text{Pt-COH} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + 2\text{H}^+ + 2e^- \quad [7]$$

or

$$\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + e^- \quad [8]$$

Figs. 7 and 8 present results on the direct electrochemical oxidation of methanol in a PEMFC. The MEA in the single cell was activated at a current density of 0.25 A/cm$^2$ with humidified H$_2$ and O$_2$ at 100 °C and 2 bar until reproducible current-voltage curves were obtained. After introducing gaseous CH$_3$OH/H$_2$O with a volume ratio of 1:5 into the test station the open cell voltage drops from 1.05 V for H$_2$/O$_2$ to values of about 0.7 V after a period of 5 min (see Fig. 7). In the case of H$_2$/CO mixtures as fuels, however, the observed open circuit cell voltage is the same as for pure H$_2$ (16). The decrease of the cell voltage of a PEMFC in the presence of CH$_3$OH is explained by the diffusion of methanol through the Nafion membrane and the formation of a mixed potential at the cathode. Assuming a membrane thickness 170 μm, a diffusion coefficient of methanol in Nafion of $D = 4 \cdot 10^{-7}$ cm$^2$/s can roughly be estimated according the cell voltage transient in Fig. 7.

Current-voltage plots the single cell using Pt, Pt$_{0.7}$Ru$_{0.3}$ and Pt$_{0.3}$Ru$_{0.7}$ as anode catalyst is shown in Fig. 8. The use of PtRu anode catalysts lead to an improvement of the power density of the PEMFC. As expected from the DEMS data, Pt$_{0.7}$Ru$_{0.3}$ shows a better performance as Pt$_{0.3}$Ru$_{0.7}$. Using low catalyst loading of 1 mg/cm$^2$ current densities of $> 0.1$ A/cm$^2$ can be achieved at 0.4 V. It should be mentioned that the operating conditions are not optimized and improvements of the cell performance are possible. For a Pt content of $> 70\%$ a further enhancement of the power density is expected when regarding the experimental results obtained on porous Pt$_x$Ru$_y$ electrodes as discussed above. An additional aspect should be the catalyst loading. Literature data show higher performances at catalyst loading of $\geq 4$ mg/cm$^2$ (2-4). However, for the possible application of a DMFC in mobile systems, it should be kept in mind that high catalyst loading lead to higher costs of such fuel cell systems.
CONCLUSIONS

Adsorption and oxidation of methanol in 1 M HClO₄ solution were studied on porous PtₓRuₙ electrodes by means of cyclic voltammetry combined with on-line mass spectrometry. Beside CO₂ the formation of HCOOH coming from HCOOH was identified. The quantification of the product distribution showed that on Pt₀.₉Ru₀.₁ the complete oxidation of CH₃OH to CO₂ is favoured with respect to partial oxidation to HCOOH. The amount of poisoning adsorbate species decreases with increasing Ru content in the alloy. The onset potential of both oxidation of dissolved methanol and adsorbate oxidation is negative shifted by 0.15 V compared to pure Pt. The enhanced reaction rate for methanol oxidation on Pt₀.₉Ru₀.₁ was explained by the bifunctional mechanism.

Preliminary results on the direct electrochemical oxidation of gaseous CH₃OH/H₂O mixtures in a Proton Exchange Membrane Fuel Cell were presented. Membrane electrode assemblies were fabricated with catalyst loadings of 1 mg/cm². PtRu as anode catalyst improves the cell performance compared to a pure Pt catalyst. For a Pt₀.₉Ru₀.₁ catalyst current density of 0.1 A/cm² at 0.4 V were achieved.
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Figure 1:
Basic concept for a Direct Methanol Fuel Cell (DMFC) system.

Figure 2:
Test station for performance evaluation of PEM single cells using H₂/O₂(air) or CH₃OH/O₂(air).
Figure 3:
Potentiodynamic profiles for electrooxidation of 1 M CH₃OH in 1 M HClO₄ at porous Pt and Pt₀₉Ru₀₉; dU/dt = 0.01 V/s
CV; MSCVs for m/z = 44 (CO₂ formation) and m/z = 60 (formation of HCOOCH₃).

Figure 4:
Relative amount of m/z = 44 and m/z = 60 versus the Pt content in PtRu.
Figure 5:
Potentiodynamic methanol adsorbate formation on porous Pt\textsubscript{0.9}Ru\textsubscript{0.1} and Pt in 1 M HClO\textsubscript{4};
dU/dt = 0.01 V/s; CV (top); MSCV for m/z = 44;
\((-\)) first positive-going scan starting at 0.05 V; \((-\)) second scan; \((-\)) supporting electrolyte.

Figure 6:
Oxidation of adsorbed methanol on Pt and Pt\textsubscript{0.9}Ru\textsubscript{0.1} in 1 M HClO\textsubscript{4};
dU/dt = 0.01 V/s; CV (top); MSCV for m/z = 44.
solid line: first positive-going scan starting at $U_{at}$; dashed line: second potential scan.
Figure 7:
Open circuit cell voltage of a PEMFC after switching the fuel gas from pure H₂ to H₂O/CH₃OH (vol. 5 :1) mixtures using a Pt₇₀Ru₃₀ anode catalyst.

Figure 8:
Single cell measurements for direct oxidation of methanol in a PEMFC with Pt, Pt₆₇Ru₃₃ and Pt₅₃Ru₄₇ as anode catalysts and pure Pt for the cathode; catalyst loading on both gas diffusion electrodes: 1 mg/cm².