THE INFLUENCE OF THE CATALYST LOADING AND THE IONOMER CONTENT ON THE PERFORMANCE OF DMFC ANODES

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Abstract
The influence of the catalyst loading (0.5 – 6 mg/cm²) and the Nafion content (5 – 16 wt%) on the electrochemical and structural properties of DMFC anode catalyst layers based on unsupported Pt/Ru was investigated. It turns out, that Pt/Ru loadings of more than 1.5 - 3 mg/cm² do not significantly improve the performance of the DMFC anode, depending on the current density of methanol oxidation. At moderate current densities, the best performance is achieved with 7 wt% Nafion. The highest active catalyst surface calculated from hydrogen desorption peaks of CV’s is obtained with 10 wt% Nafion. From porosimetric measurements, it turns out, that the highest fraction of ‘hydrophobic’ pores is obtained with a Nafion content of 5 wt%. It is assumed, that a high fraction of hydrophobic pores is advantageous for a fast transport of CO₂ and gaseous methanol. We conclude, that the best performance is achieved with a Nafion content of 7 wt%, because it provides the best combination of a large active surface area and a fast mass transport, which is favourable for obtaining high performance of the DMFC anode.

Introduction
The performance of a Direct Methanol Fuel Cell (DMFC) anode catalyst layer is mainly affected by the catalytic activity, utilisation and active surface of the catalyst, the mass transport of methanol / CO₂ and the electrical, i.e. ionical / electronical conductivity. Except the catalytic activity, these properties are influenced by both the catalyst loading and the ionomer content, because the following structural parameters of the catalyst layer are changed:

A variation of the catalyst loading at a constant composition of the catalyst layer means, that mainly the thickness of the layer is affected. From literature data (2,3) it turns out, that
loadings of more than 8 mg/cm² of Pt/Ru black do not improve the cell performance. This ‘upper limit’ can be explained by contrary effects: a) the active surface of the catalyst is increasing with the catalyst loading b) the thickness of the catalyst layer is also increasing with catalyst loading and thus causing a mass transport limitation of methanol and CO₂. Additionally, the limited ‘penetration depth’ of the electric field has to be considered. E.g., if the thickness of the catalyst layer exceeds the penetration depth, the electrochemical reaction is predominantly taking place in the ‘inner’ part of the catalyst layer (4,5), whereas the ‘outer’ part is less active and a further increase of the loading and layer thickness will only slightly increase the performance of the catalyst layer. However, a thicker anode catalyst layer can be advantageous for the cell performance, because a part of the methanol is consumed in the outer part of the layer and the permeation of methanol to the cathode is reduced (1).

By varying the ionomer content, a. the porosity b. the fraction of ‘hydrophilic’ and ‘hydrophobic’ pores and c. the microstructure of the pores and the catalyst / ionomer phases are changed. ‘Hydrophilic’ pores means the volume fraction of the open pores of the catalyst layer, which is filled by water. Under fuel cell operation, these pores could be used for the transport of liquid methanol. Nevertheless, the diffusion of the gaseous methanol should be dominating. This means, that the ‘hydrophobic’ pores, which are not filled by water, should mainly serve for the mass transport, i.e. the diffusion of gaseous methanol and the removal of CO₂. A suitable, non-destructing porosimetric method to determine these structural parameters is the so-called ‘standard porosimetry’ developed by Y.M. Volfkovich et al. (6-8). Up to now, only few work was dedicated to the influence of the ionomer content in anode catalyst layers made of Pt/Ru black in the direct methanol fuel cell. S.C. Thomas et al. (9) have used Pt/Ru catalysts with a protonic conducting phase of Ru oxide. They found out that up to a temperature of 80 – 90 °C the best performance is obtained with a Nafion content of 6.5 wt%, whereas at higher temperature, the catalyst layer without the addition of Nafion gives the best result (9).
Experimental

Anode catalyst layers:
- Preparation method: spraying onto the backing layer, i.e. carbon cloth with 13 wt% PTFE, 87 wt% carbon black (Vulcan XC72)
- Ink: Pt/Ru (1:1) black (Johnson Matthey), 5% Nafion solution (Aldrich), isopropanol
- Variation of Nafion content: 5, 7, 10, 13 and 16 wt%; Pt/Ru loading: about 2 mg/cm²
- Variation of catalyst loading: 0.5 - 6.0 mg/cm², composition: 7 wt% Nafion / 93 wt% Pt/Ru

Cathode catalyst layers:
- same preparation method as described above, Pt-black, 9 wt% Nafion, cathodes acted as counter (disc) and reference (ring) electrodes (reversible hydrogen electrodes !)

MEA’s:
- Electrodes (catalyst layer + backing layer) were hot-pressed (T = 130 °C) onto Nafion 117 membranes

Electrochemical measurements:
- 3-electrode arrangement, CV’s, quasi-stationary current potential curves, impedance spectra

Porosimetric measurements:
- identical Pt/Ru catalyst layers sprayed onto PTFE substrates;
- overall porosity: pore volume filled by decane (pressure of 20 Pa), decane contact angle of 0 (6); ‘hydrophilic’ pores: pore volume filled by water; ‘hydrophobic’ pores: subtraction of the hydrophilic pore volume from the overall pore volume

Results and discussion

Influence of the catalyst loading
At first, current/potential curves of methanol oxidation were recorded with anode catalyst layers containing different Pt/Ru loadings. Fig.1 shows the current density of methanol oxidation as a function of the Pt/Ru loading for different temperatures at the example of an electrode
potential of 0.3 V. It can be seen from this figure that at lower Pt/Ru loadings up to a critical value, the current density is significantly increasing with the Pt/Ru loading. If the critical value of the loading is exceeded, the anode performance is only slightly improving. This so-called ‘upper limit’ of the Pt/Ru loading is decreasing with rising temperature, i.e. the upper limit is about 3 mg/cm² for 40°C, 2 mg/cm² for 60°C and 1.5 mg/cm² at 80°C. These values can be explained by the limited penetration depth of the electric field, which decreases with increasing current density and temperature, respectively.

Fig. 1: Current density of CH₃OH oxidation in dependence on the Pt/Ru loading, 1M CH₃OH, T = 40 - 80 °C, U = 0.3 V, data for T = 80 °C calculated from an Arrhenius plot

As described in /5/, the penetration depth, \( \lambda \), is defined as

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\lambda = \sqrt{\sigma H^+ * R_i}
\]
with the specific protonic conductivity, $\sigma_{H^+} / \text{S}\cdot\text{cm}^{-1}$ and the electrochemical volume resistivity, $R_i / \Omega\cdot\text{cm}^3$. The equation is valid only for linear regimes of current/potential curves, a condition, which is fulfilled in the range of about $U = 0.35 - 0.45$ V. Based on the above equation, we have calculated penetration depths of $\lambda = 8 - 14$ $\mu$m for ranges of $U = 0.35 - 0.4$ V and $T = 40 - 60$ °C. A detailed description of the determination of the specific protonic conductivities and the electrochemical volume resistivities will be given elsewhere (10). Because a Pt/Ru loading of 1 mg/cm² corresponds to a thickness of about 4 - 5 $\mu$m, considering the preparation conditions described above, the loadings of 1.5 – 3 mg/cm² correlate with a thickness of the layers which is close to the calculated penetration depths of 8 – 14 $\mu$m. This explains, why Pt/Ru loadings of more than 1.5 - 3 mg/cm² and thus a layer thickness higher than the penetration depth does not enhance the performance of the DMFC anode considerably. However, thicker anode catalyst layers could be useful under operation conditions of DMFC, because the methanol permeation is reduced, as discussed above. This effect can not be observed with half cell measurements as reported here and it can explain the ‘upper limit’ of Pt/Ru loading of about 8 mg/cm² determined from single cell measurements (2,3), which is considerably higher than the values presented in this work.

**Influence of the ionomer content**

Current/potential curves of the methanol oxidation in the Pt/Ru catalyst layers for different Nafion contents (5 – 16 wt%) and temperatures (40 – 80 °C) were recorded. Up to a potential of about 400 mV the best performance is obtained with 7 wt% of Nafion, which confirms the findings of S.C. Thomas et al. (9) at temperatures lower than 90 °C. This is evident from Fig.2, where the current density is plotted as a function of the Nafion content for different electrode potentials. With increasing potential and temperature (not shown here), i.e. increasing current density, the performance obtained with 5 wt% Nafion is more and more improving. This means, that at high current densities, a low Nafion content is favourable to obtain anode catalyst layers with good performance.
After the electrochemical characterisation of the anode catalyst layers containing different amounts of Nafion, equal catalyst layers prepared on Teflon blanks were investigated by means of porosimetric measurements. For this purpose, the catalyst layers were filled by decane and water and the overall porosity as well as the relative amounts of the ‘hydrophilic’ and ‘hydrophobic’ pores were determined (see experimental section). These fractions are plotted in Fig.3 in dependence on the Nafion content. As can be seen, the ‘hydrophobic’ pores are dominating. The fraction of ‘hydrophilic’ pores increases with the Nafion content, which can be explained by the mainly hydrophilic behaviour of the Nafion phase. Thus, the highest amount of ‘hydrophobic’ pores (80 Vol%) and the lowest fraction of ‘hydrophilic pores’ (20 Vol%) is reached with a Nafion content of 5 wt%. Because a high amount of ‘hydrophobic’ pores is favourable for a fast transport of CO₂ and gaseous methanol, the catalyst layer with a Nafion content of 5 wt% should provide the best mass transport compared to the other catalyst layers investigated.
Fig. 3: Fraction of the volume of ‘hydrophilic’ and ‘hydrophobic’ pores in Pt/Ru catalyst layers in dependence on the Nafion content

From cyclic voltammograms, the charge of the hydrogen desorption peaks and the active surface of the catalyst was calculated as a function of the Nafion content. As a result, the highest active surface is obtained with a medium Nafion content of 10 wt%, which could be explained by a distribution of Nafion and Pt/Ru close to a percolation threshold.

A correlation between electrochemical and structural data is shown in Fig.4. In order to eliminate the influence of the size of the reaction zone, the current density is normalized to the active surface area of the Pt/Ru catalyst and plotted as a function of the amount of ‘hydrophilic’ pores. It is evident that the highest ‘true’ current density is obtained with the lowest fraction of ‘hydrophilic’ pores, corresponding to a Nafion fraction of 5 wt%. This means, that not only a large active catalyst surface, but also a high amount of ‘hydrophobic’ pores is favourable to achieve a high performance of the DMFC anode.
Fig. 4: ‘True’ current density as a function of the fraction of ‘hydrophilic pores’, i.e. current density normalized to the Pt/Ru loading and to the dimensionless active surface area of Pt/Ru

**Conclusions**

We have studied both the influence of the Pt/Ru loading (0.5 – 6 mg/cm²) and the effect of the Nafion content (5 – 16 wt%) of anode catalyst layers based on Pt/Ru (1:1) black on the electrochemical and structural properties of DMFC anodes.

From half cell measurements, it turns out that in the temperature range of 40 – 80 °C Pt/Ru loadings higher than 1.5 - 3 mg/cm² do not improve the performance of the DMFC anode significantly. These ‘upper limits’ of the Pt/Ru loading correlate with a thickness of the catalyst layers, which is similar to the penetration depth \( d \) of the electric field, i.e. 8 – 14 µm. Because the penetration depth tends to decrease with increasing current density, we expect that under practical operation conditions of DMFC (\( T \geq 80 \) °C, \( j \geq 200 \) mA/cm²), the penetration depth should be less than 7 µm, which corresponds to a catalyst loading of \( \leq 1.5 \) mg/cm². In the literature, much higher values of the ‘upper limit’ of 8 mg/cm² were reported (2,3). These results are not contradicting, because the literature data were obtained from single cell experiments. If we
operate a membrane electrode assembly under DMFC operating conditions, we have to consider that a thick anode catalyst layer with a high Pt/Ru loading can reduce the methanol permeation from the anode to the cathode and thus improve the cell performance, as described in (1). Vice versa, the anode catalyst loading could be lowered, if modified membranes with a reduced methanol permeation would be developed.

For $U \leq 0.4 \text{ V}$ and $T < 80 \text{ °C}$, i.e. moderate current densities, the best performance of the DMFC anode is achieved with a Nafion content of 7 wt%, which is in accordance with literature data (9). At higher current densities, Nafion fractions lower than 7 wt% seem to be more favourable. The active surface of the catalyst exhibits a maximum at 10 wt% of Nafion. From porosimetric experiments, the highest fraction of ‘hydrophobic’ pores in the anode catalyst layer is obtained with a Nafion content of 5 wt%. From the correlation of the electrochemical and porosimetric measurements, it turns out, that both a large active catalyst surface and a high amount of ‘hydrophobic’ pores is favourable to achieve a high performance of the DMFC anode. We conclude, that at moderate current densities, a Nafion content of about 7 wt% provides the best combination of a large active surface and a fast mass transport. With increasing current density, the influence of the mass transport gets more and more important and thus Nafion fractions lower than 7 wt% could be more advantageous under these conditions.

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**References**


(10) A. Havránek, K. Klafki and K. Wippermann, unpublished results