

METHANOL AND CO OXIDATION ON Pt AND Pt-COLLOID CATALYSTS FOR DMFC

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Introduction

The use of nanocolloidal particles on catalysts in fuel cell is advantageous because of their large surface to volume ratio. In this study we compared the activity of different carbon supported Pt-nanoparticles for methanol oxidation with that of smooth electrodes. We also studied the influence of temperature on adsorption of methanol.

Experimental

The carbon supported colloids were obtained from the MPI in Mülheim [1] (M. Lopez and M. Reetz). Glassy carbon (GC) disk electrodes with a diameter of 10 mm, polished to a mirror finish, were used as a substrate for the carbon supported catalysts. The total platinum loading was 10 $\mu\text{g Pt}\cdot\text{cm}^{-2}$. Nafion was used in order to mechanically stabilize the catalyst layer [2].

Dual thin layer flow-through cells [3], made of Kel-F and titanium (for temperature dependent experiments), were used for DEMS in combination with a quadrupole mass spectrometers (Balzers QMG-511 and QMG 422).

The real surface area of the colloid was estimated from the amount of CO_2 formed during oxidation of adsorbed CO. Thus, the colloid surface utility was checked. The pre-adsorbed CO was oxidized to CO_2 during the anodic scan of potential.

Results and Discussion

Electrocatalytic oxidation of adsorbed CO on colloid catalysts

The activity of the catalysts was first tested by oxidation of adsorbed CO. This also allows for a determination of the real surface (assuming complete coverage). Within a factor of two this real surface agrees with that determined from the particle size and a simple bulk model, showing that the catalyst is completely active.

Some CO stripping experiments are shown in Fig. 1.1. The oxidation of pre-adsorbed CO starts around 0.4 V for PtRu and PtRuOslr.

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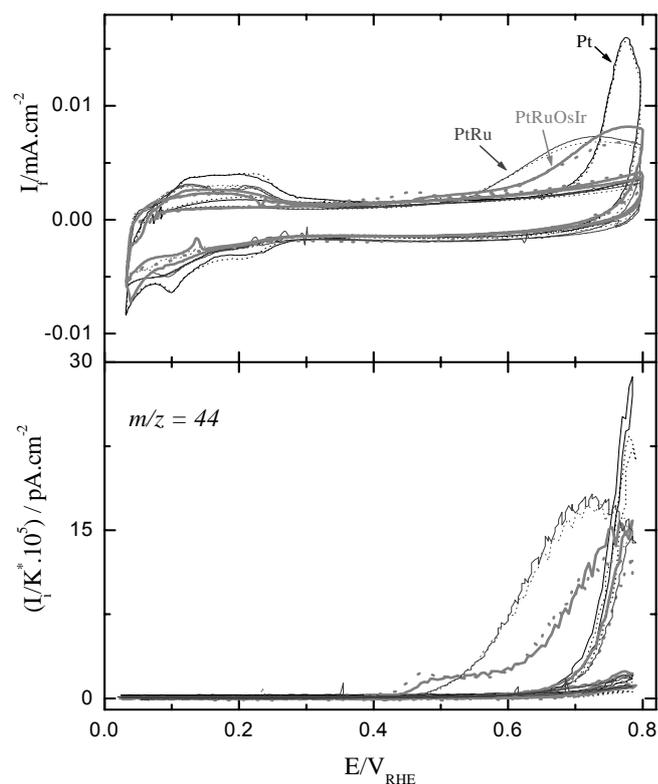


Fig. 1.1 Simultaneously recorded CV and MSCV $m/z=44$ for the oxidation of pre-adsorbed CO on three different electrochemically reduced colloid catalyst at 25 °C - Pt (LOP-LB-625) (—) before and (---) after MetOH; PtRu (LOP-LB-677) (—) before and (---) after MetOH; PtRuOsIr (LOP-LB-764) (—) before and (---) after MetOH - (loading - 10 μg of Pt. cm^{-2} of GC) in 0.5M H_2SO_4 solution in the dual thin layer flow through cell. Scan rate: 10mV/s. Electrolyte flow rate: 5 $\mu\text{L}\cdot\text{s}^{-1}$.

We found some kind of pre-peak for PtRuOsIr colloid catalyst. This pre-peak shows no maximum. The main peak at around 0.8 V for CO_{ad} oxidation for Pt, PtRuOsIr and PtRuMo and broader main peak at 0.7 for PtRu, are observed in CV and MSCV. Afterwards, we adsorbed again CO. Possible shift of CO oxidation to high potentials on PtRu catalyst may indicate a loss of Ru.

Electrocatalytic bulk oxidation of Methanol on colloid catalysts

Fig. 1.2 shows the cyclic voltammograms (CVs) of 0.1M methanol dissolved in 0.5M H_2SO_4 and the simultaneously recorded mass spectrometric cyclic voltammograms (MSCVs) for $m/z = 44$ due to CO_2 formation and for $m/z = 60$. This signal is assigned to the molecular peak of methyl formate (HCOOCH_3) and indicates the formation of HCOOH as a partial oxidation product of methanol.

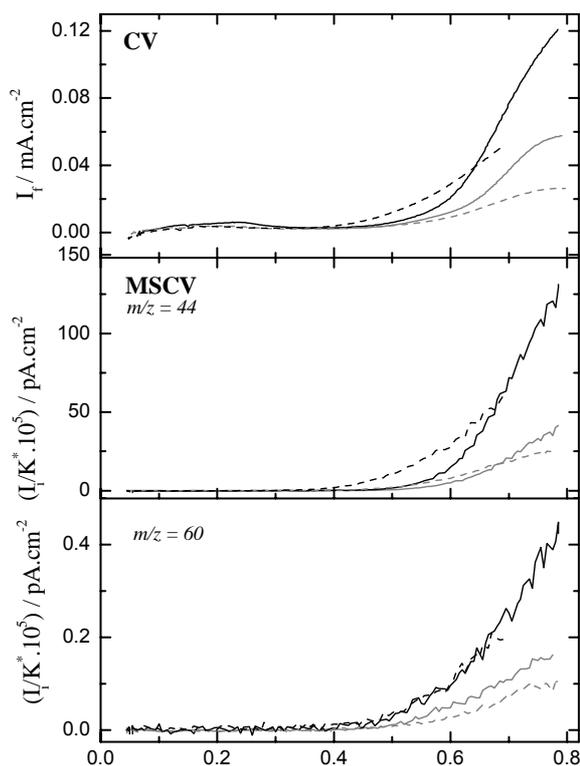


Fig. 1.2 Simultaneously recorded CV, MSCV $m/z=44$ and $m/z=60$ on three different electrochemically reduced colloid catalyst in 0.1M methanol + 0.5M H_2SO_4 solution at two different temperatures - Pt (LOP-LB-625) at 25°C (—) and at 50°C (---); PtRu (LOP-LB-677) at 25°C (—) and at 50°C (---) (loading - 10 μg of Pt / cm^2 of GC) in the dual thin layer flow through cell. Scan rate: 10mV/s. Electrolyte flow rate: 5 μ L/s

The PtRuOslr catalyst is less active than PtRu, which is less active than Pt colloid catalyst. However, a careful look shows that CO_2 formation starts at lower potentials at PtRu, and in case of colloid catalysts with Ru content, the current efficiencies are higher than in case of pure Pt colloid catalysts.

In order to obtain more detailed information on the potential dependence of the methanol oxidation under stationary conditions, we performed potential step experiments on different surfaces. An information on the stationary coverage with the adsorbate and the adsorption rate was obtained by adsorbing methanol for 2 min at a given potential and the stepping back to 0.05 V, where no adsorption occurs. In control experiments with different adsorption times it was checked that after 2 min saturation is achieved indeed. After an electrolyte exchange with pure sulfuric acid, the adsorbate was oxidized.

For the stripping of CO formed for adsorption of methanol, here, the effect of Ru is clearly visible again.

From the integrated ion current of CO_2 of methanol adsorbate and ion current of CO_2 which correspondent to full monolayer adsorption of CO, the coverage of methanol adsorbate can be determined by equation $\Theta = \Gamma_{CO} / \Gamma_{CO}^{max} = Q_i(44) / Q_i^{max}(44)$.

The experimental results show that methanol adsorbate is mainly composed of CO. It is observed that at the low potentials the saturated coverage of methanol adsorbate increases with the increase of adsorption potentials, at the high potentials above 0.6 V decreases, due to the oxidation of methanol adsorbate.

In colloid catalysts with presence of Ru, the onset of methanol adsorbate oxidation is shifted to the more negative potentials. This could be explained by bifunctional mechanism. In the case of PtRuMo catalysts, there is a very small catalytic effect on the oxidation of methanol adsorbate.

Effect of temperature

In order to obtain informations on the stationary coverage with the adsorbed methanol and adsorption rate at 0°C and 50°C, we performed the following experiments with different temperature on different colloid catalysts. The faradaic oxidation charge and the amount of CO₂ was determined. From these the electron number for the oxidation of adsorbed methanol on Pt was calculated, which is approximately 2 for the high coverage achieved at 0.5 V (demonstrating that the adsorbed methanol is formed as CO, but approaches values near 3 for low coverage. Such high values might indicate adsorbate structures like COH or CHO, but it is more probable that they are caused by double layer charging effects, which become relatively more prominent at low coverage. Interestingly, oxidation rate at the low potential side is independent of coverage. Independent of temperature, the current efficiency for Pt colloid catalyst and smooth polycrystalline platinum is shown in Fig.1.3.

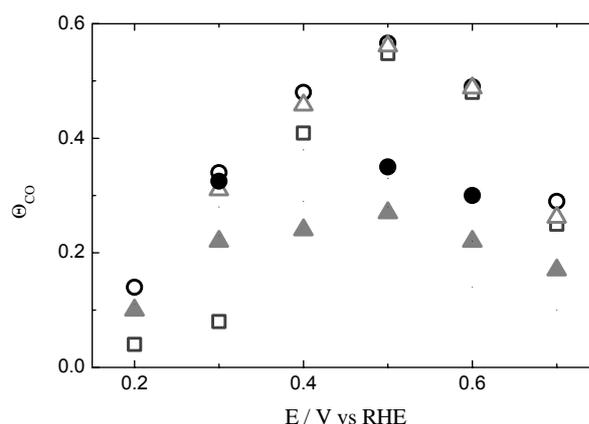


Fig.1.3 CO saturated coverage degrees at different step potentials on pcPt (open symbols) at 0°C (□), 25°C (△) 50°C (○) and Pt (LOP-LB-625) (solid symbols) 25°C (▲) and 50°C (●). The adsorption of methanol was carried out at different step potentials for 2 minutes.

At low potentials, the coverage is increased by a higher temperature, whereas at high potentials it is not much influenced, probably because adsorption rate and desorption rate are influenced in the same way. At higher temperature, the oxidation peaks are in all cases shifted to negative potentials.

Acknowledgements

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