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

B. Lánová, *H. Baltruschat*

Institut für Theoretische und Physikalische Chemie der Universität Bonn, Germany

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 carbon supported Pt, PtRu and PtRuOsIr nanoparticles for methanol oxidation with that of smooth electrodes. Colloids, with a diameter in the lower nanometer range, where obtained from the MPI, Mühlheim [1]. The carbon supported colloids were suspended in water and deposited on glassy carbon substrates. Ethylene glycol was added in order to obtain a more uniform distribution. Nafion was used in order to mechanically stabilize the catalyst layer [2]. The oxides were reduced directly before the measurement in situ at constant potential. The total surface loading was 10 μg of Pt/cm^2 on GC. Preadsorbed CO oxidation experiments and also oxidation experiments of methanol adsorbates at different potentials were performed in 0.5 H_2SO_4 solution in electrochemical dual compartment thin layer flow through cell [3]. Bulk oxidation measurements were performed in 0.1M methanol + 0.5M H_2SO_4 solution using 10 mV/s with electrolyte flow through – 5 ml/s.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 catalytic activity for CO oxidation as given by the oxidative potentials was identical to smooth polycrystalline Pt. For methanol oxidation, the current efficiency was around 50% and thus similar to polycrystalline Pt. Therefore, dissolved intermediates are also formed at the small colloid particles and, because the catalysts layer is thin enough, able to diffuse into the bulk of the convecting electrolyte.

In order to obtain informations on the stationary coverage with the adsorbed methanol and adsorption rate at 0^oC and 50^oC, we performed the following experiments with different temperature on Pt and different Pt-colloid catalysts. The faradaic oxidation charge and the amount of CO_2 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 0.5V (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. 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.

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