

ALTERNATIVE ANODES FOR DIRECT METHANOL FUEL CELLS

P. Holzhauser¹, M. Lange², K. Jüttner²

¹ *Institute of Chemical Technology, Department of Inorganic Technology, Prague, Czech Republic*

² *Karl-Winnacker Institut of DECHEMA e.V., Frankfurt am Main, Germany*

Introduction

Proton exchange membrane type fuel cells (PEMFC) are potentially an efficient and ecologically friendly power source of the future. Especially a PEMFC based on the methanol oxidation reaction (MOR) is proposed as suitable for supplying portable devices [1]. The present drawbacks of the methanol PEMFC are the low degree of utilisation of the catalyst and its poor resistivity to poisoning by carbon monoxide and other byproducts [2]. These two facts inflate the total price because the catalyst is usually based on platinum metals and their alloys.

The design of the catalyst layer is of key importance. The layer must enable the fuel to reach the metal particles and be able to conduct the protons and electrons that have been generated, this means to exhibit ionic and electronic conductivity. The present design of the catalyst layer is usually based on a carbon-black supported catalyst impregnated with Nafion, but the problem of three-phase contact often arises (Fig. 1).

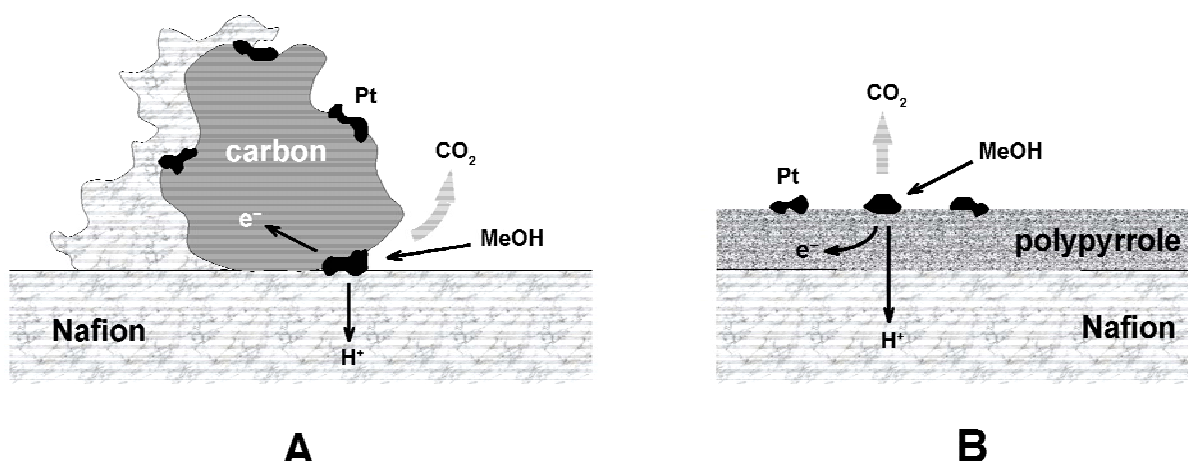


Fig. 1 A – the present design, B – the new approach

The use of conducting polymers (CP) has been suggested as an alternative solution to this problem. CPs exhibit intrinsic electronic conductivity as well as sufficient ionic conductivity, depending on the type of counter-ion present. Furthermore it has been reported that

incorporation of the catalyst into the CP improves its resistivity to poisoning [3]. Polypyrrole (PPy) was selected as a prospective material on account of its relatively high chemical stability in an acidic environment and its simple and reproducible (electro)synthesis. The aim of this study was to prepare catalyst layers directly on a Nafion membrane and to determine their activity for MOR.

Experimental

Nafion/PPy composite samples were prepared by the monomer-diffusion method, which provides PEM covered on one side with PPy. The Nafion membrane is sandwiched between two glass vessels, one compartment is filled with the monomer solution and the second one with the solution of sodium peroxodisulfate. The pyrrole molecules diffusing through the membrane are oxidised on its surface and form thin PPy film.

For the electrochemical experiments the Nafion/PPy composite was placed between two glass cells and contacted by platinum wire at PPy side. Corresponding compartment was filled by working electrolyte and equipped with the reference electrode and the counter electrode. The second compartment was filled with diluted sulphuric acid solution to keep Nafion wet and protonated. Then the platinum particles were deposited on the PPy surface by reduction from acidic platinate solution. The galvanostatic mode of deposition at $100 \mu\text{A cm}^{-2}$ was used and the samples with different platinum loadings (from 50 to $500 \mu\text{g cm}^{-2}$) were prepared.

The activity measurements were carried out in the dilute acidic solution of methanol in the same arrangement. The prepared composite anodes were tested for MOR by cyclic voltammetry (CV) and chronoamperometry at different potentials.

After the electrochemical testing the samples were dried and examined by scanning electron microscopy (SEM) to find the relation between the samples activity and size and morphology of Pt particles.

Results and Discussion

The Fig. 2 shows the cross-section of representative Nafion/PPy/Pt composite (Pt loading $200 \mu\text{g.cm}^{-2}$). In figure there is apparent only PPy layer with deposited Pt particles. From the picture it is evident that the particles grow only on the surface of the polymer, they are usually isolated, only sometimes form clumps grown together. Another characteristic feature common to all samples is half-sphere shape of particles, independent on Pt loading. For the highest Pt loading $500 \mu\text{g.cm}^{-2}$ there is already more or less compact layer of platinum on PPy surface.

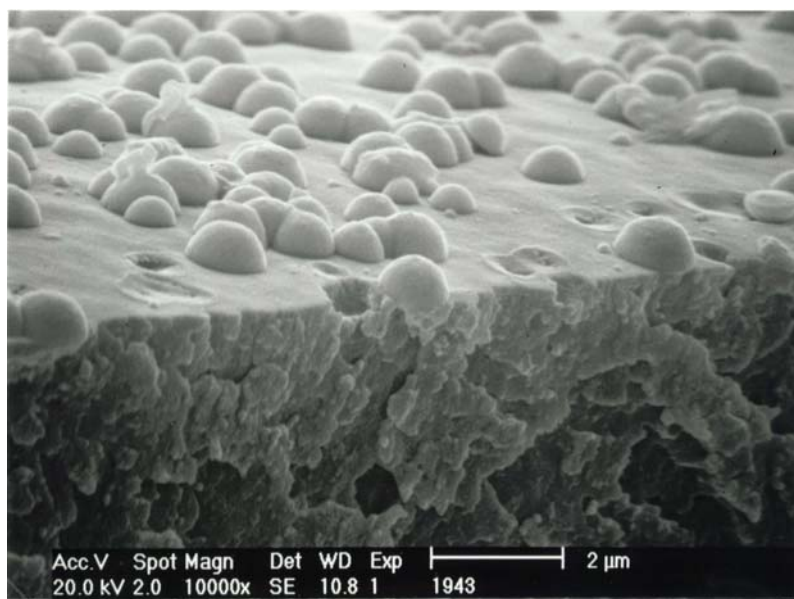


Fig. 2 SEM picture of cross-section of Nafion/PPy composite with $200 \mu\text{g cm}^{-2}$ Pt loading

The cyclic voltammograms measured in methanol solution are presented in Fig. 3. For the majority of samples it is not apparent any peak or wave characteristic for MOR. Only slight increase of currents is observable in anodic potential region (compared to CV in pure acid without methanol). Only for $500 \mu\text{g cm}^{-2}$ sample one can distinguish two peaks close to 0.8 V – the anodic peak corresponding to methanol oxidation and slight autooxidation peak in cathodic scan (methanol autooxidation peak is typical feature of bulk platinum). This effect can be simply explained by fact that only when the Pt particles begin to cover the PPy surface, the electrochemical behaviour characteristic for bulk Pt can be observed.

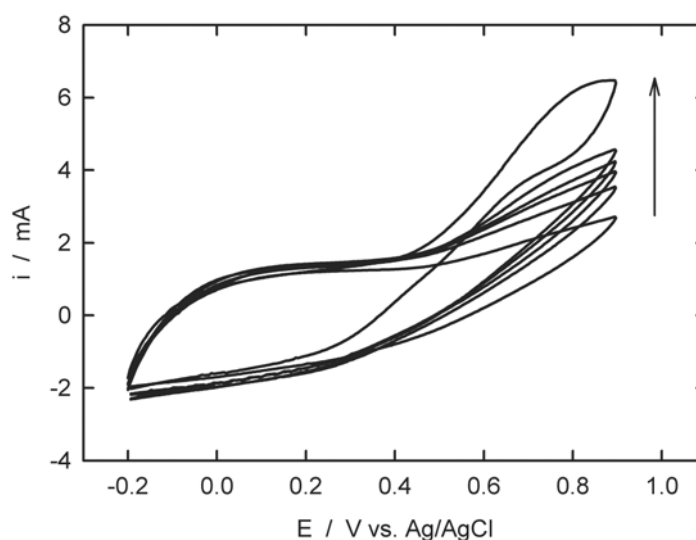


Fig. 3 The cyclovoltammograms of MOR (2M MeOH, 0.5M H_2SO_4 , $-0.2 \rightarrow 0.9$ V vs. Ag/AgCl, 20 mV s^{-1}) for 50, 100, 200, 300, 400 and $500 \mu\text{g cm}^{-2}$ (arrow direction ordered)

From the point of view of FC applications it is important to know the specific activity of platinum. As a variable describing the activity of composite the current density at anodic CV vertex point was considered. In Fig. 4 there is dependence of specific current density at this point on the total Pt loading. It is evident that with increasing Pt loading the specific activity decreases. This is in a good agreement with the SEM study, it was found that for lower Pt loading the particles are smaller and more isolated. Both these facts means higher surface of platinum and thus higher catalytic activity.

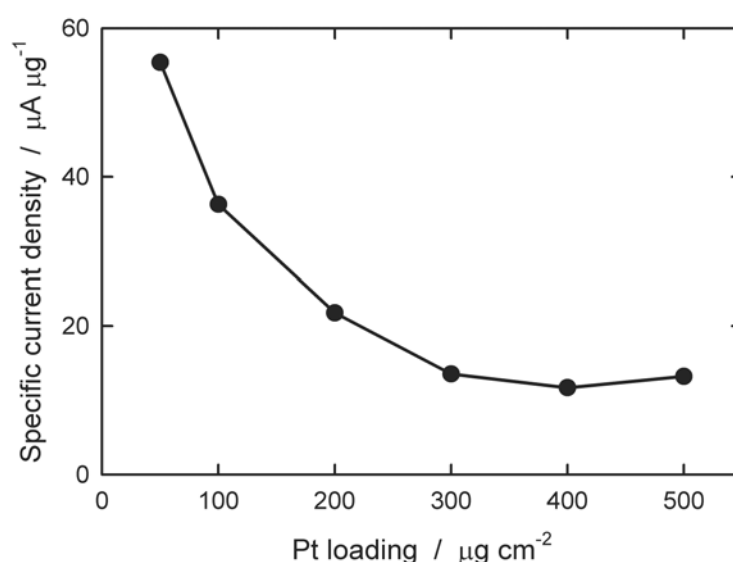


Fig. 4 Dependence of specific current densities in anodic CV vertex point (0.9 V vs. Ag/AgCl) on the total platinum loading

Conclusions

By monomer diffusion method and subsequent galvanostatic deposition it is possible to obtain composites with apparent electrocatalytic activity for MOR. The deposited particles have half-sphere shape and are grown on the PPy surface. The specific area of particles decreases with increasing Pt loading. The composites exhibit electrochemical activity different from bulk platinum, only for high Pt loading its behaviour begins to be similar. The specific activity is better for the lower Pt loading what is in agreement with higher surface area.

Acknowledgements

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