

Gas diffusion electrodes for high temperature PEM-type fuel cells: role of a polymer binder and method of the catalyst layer deposition

P. Mazúr · J. Soukup · M. Paidar · K. Bouzek

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Abstract The topic of this study is the optimization of the preparation procedure and chemical composition of a gas diffusion electrode (GDE) for utilization in high-temperature PEM fuel cells. A phosphoric acid-doped polybenzimidazole derivative membrane was used as a polymer electrolyte. The following parameters were studied: nature and content of the polymeric binder (PTFE—hydrophobic, PBI—hydrophilic) in the catalytic layer (CL) and concentration of platinum in catalytic powder (affecting the thickness of the CL). Brushing and spraying were selected as the most suitable techniques of CL deposition. Surprisingly, both polymeric binders investigated in the framework of this study were found to provide a similar GDE performance for CL deposited on the gas diffusion layer surface by spraying.

Keywords Gas diffusion electrode · Polymer electrolyte · Polybenzimidazole · Fuel cell · Catalytic layer · Binder

1 Introduction

Polymer electrolyte membrane (PEM) fuel cells are being intensively studied as one of the future alternative energy converters. Their advantage is the high efficiency of the energy conversion—when compared to currently widespread energy sources (e.g., combustion engines or thermal power plants) [1]. Although considerable attention has been paid to the topic of PEM-type fuel cells in the last two decades [2], there still remain several serious drawbacks to

deal with. They are mainly related to the slow electrode kinetics and susceptibility of the Pt catalyst to poisoning. This results in the necessity of a high-platinum catalyst loading to attain the desired intensity of energy production [3]. It seriously increases the cost of this technology. At the same time, it represents a factor that prevents its widespread use due to the limited world resources of this element. The majority of these problems can be solved by increasing the operating temperature of the fuel cell, thus improving the electrode kinetics, enhancing catalyst resistivity to poisoning and simplifying the heat and water management of the fuel cell [4, 5].

The operating temperature of a PEM-type fuel cell based on a perfluorinated sulphonated acid (PFSA) membrane (low temperature) is limited by the boiling point of water under atmospheric pressure due to the danger of loss of conductivity of the electrolyte above this temperature [6]. Among numerous possible candidates to replace the PFSA membrane for this type of technology cited in the literature, only a membrane based on phosphoric acid supported by polybenzimidazole (PBI) or its derivatives has received general acceptance within the community [5, 7, 8]. It is clear that the structure and composition of the gas diffusion electrode (GDE) has to be compatible with a membrane used as a polymer electrolyte. Whereas significant attention has been paid in the past to the optimization of the GDE for the classical PEM fuel cell utilizing a PFSA membrane, reviewed by Wee et al. [9], scarcely any systematic studies have been published on the optimization of the GDE for a PEM fuel cell based on phosphoric acid-doped PBI [10–16].

Several techniques can be used to deposit catalytic layer (CL) in the form of catalyst ink on the top of the GDL. As the most commonly used ones brushing, spraying, doctor blade, and screen printing can be mentioned here [3, 9, 17].

P. Mazúr · J. Soukup · M. Paidar · K. Bouzek (✉)
Department of Inorganic Technology, Institute of Chemical
Technology Prague, Technická 5, 16628 Prague, Czech Republic
e-mail: bouzekk@vscht.cz

These techniques were originally proven in PFSA-based fuel cell technology. Because of substantial similarities between these two technologies, they can also be easily adapted for the fuel cell utilizing a PBI membrane. The polymeric binder plays an important role in the CL's performance. This is connected, on the one hand, with the CL's mechanical properties and on the other hand with the use of a platinum catalyst [5]. In the case of the high-temperature PEM fuel cell, phosphoric acid soaked into the porous structure is assumed to play a key role in the proton conductivity of the CL [18].

Modestov et al. [14] investigated the utilization of Nafion and fluorinated ethylenepropylene (FEP) as a CL binder. He found that the first polymer had a detrimental effect on the performance of this type of fuel cell. He suggested that the minimum content of binder, just to maintain the integrity of CL, was optimal. In their work, Lobato et al. [10] used PBI as a CL binder. The CL was deposited by the spraying method using two forms of polymer binder differing according to the solvent used. The *colloidal method* used acetone as a solvent. As it follows from the name, in the catalytic ink polymer binder was present in the form of a suspension. In the case of the *solution method*, *N,N*-dimethylacetamide was used as a solvent. In this case, PBI was present in the catalytic ink in the form of a homogeneous solution. The CL prepared by the colloidal method exhibits better properties with respect to catalyst utilization and transport of reactants. On the other hand, the GDE prepared by the solution method showed a less open CL structure. This had a positive influence on the PBI membrane conductivity due to the retention of humidity inside MEA. The same group [11] dealt with the concentration of platinum on a catalyst support, again using PBI as the binder. As an optimum, 40 wt% of Pt on the carbon support was identified.

Pan et al. [12] increased the porosity of GDE prepared by the tape-casting method with PBI used as the CL binder by means of an additive (ammonium oxalate, ZnO, etc.) promoting the porous structure present in the catalyst slurry. A positive effect on the fuel cell performance was observed. Mamlouk and Scott [13] investigated the amount of PBI binder and its phosphoric acid doping level, separately on the cathode and the anode. The permeability of gases through the catalyst layer, the conductivity of the catalyst layer and the electrode overpotential were determined. The same group [15] investigated the influence of the platinum catalyst alloying with other metals (Pt–Fe, Pt–Ni, Pt–Co, and Pt–Ru) on the oxygen reduction reaction and fuel cell performance. PTFE was used as a binder of the CL of the cathode. Kannan et al. [16] published a parametric study of PBI membrane-based MEAs, investigating the role of carbon, electrocatalyst, and PTFE binder content in the GDL as well as in the CL of the GDE.

The objective of this study was to investigate the influence of CL composition and method of its preparation on the performance of such electrodes in high temperature PEM-type fuel cells.

2 Experimental

2.1 Catalytic ink preparation

The procedure of the catalytic ink preparation was as follows: (1) preparation of the corresponding amount of water–isopropanol mixture (1:1 by weight); (2) addition of required amount of carbon-supported Pt catalyst powder; (3) addition of appropriate amount of solvent(s)—amount of solvent dependent on the amount of catalyst, ensuring the constant viscosity of the catalytic ink; (4) addition of polymeric binder; and (5) homogenization for 30 min in an ultrasonic bath.

In the case of PTFE-bonded electrodes, polymeric binder was applied in the form of 10 wt% water suspension and a mixture of water and isopropanol (1:1 weight ratio) was added to the ink as the solvent. PBI was applied as a binder in the form of 10 wt% solution in *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) was used as the solvent during ink preparation.

2.2 Method of GDE preparation

GDEs were prepared by applying catalytic ink onto the GDL in several layers. Brushing or spraying was employed for this purpose. The amount of deposited catalyst was detected by weighing. A Pt load of 0.5 mg cm^{-2} was used throughout the study. The final electrode treatment consisted of heating at 190 °C for 30 min under inert atmosphere in the case of the PBI binder, to remove the traces of solvents. In the case of PTFE binder, a temperature of 350 °C was used for 30 min to melt the polymer particles and thus to achieve a binding effect in the CL.

2.3 Fuel cells tests

During all fuel cell experiments, commercial PBI derivative membranes were doped with 85 wt% phosphoric acid at a doping level of 300 wt%. In all cases, a laboratory single fuel cell (active area 6.25 cm^2) was assembled in an identical way to minimize the influence of this step on the observed fuel cell performance. The intensity of MEA compression was controlled by the force moment of fuel cell constriction (typically 5 Nm). The flow rate of hydrogen and oxygen was set at 30 and 20 mL min^{-1} , respectively. Gases were not externally humidified. The fuel cell was operated under atmospheric pressure, at

temperature of 160 °C and potential of 0.6 V for about 350 h until its performance reached a steady value. After conditioning of the fuel cell, subsequent measurements were carried out at temperatures of 160, 140, 120, and 95 °C in the indicated order.

2.4 CL morphology

Scanning electron microscopy (SEM) analysis with a Hitachi S4700 microscope was used to study the morphology and thickness of the CL.

2.5 Materials used

Non-woven carbon paper covered with a hydrophobic layer (SGL[®]-34 BC type) was utilized as the GDL within the framework of this study. Two catalysts differing in Pt concentration on the support were tested: 30 wt% Pt on the carbon support (HP Pt on Vulcan XC-72R) by BASF[®] and 60 wt% Pt on the carbon support (HiSPEC[®]t 9000) by Alfa Aesar[®]. AB-PBI membranes obtained from Fumatech[®] were used as the polymer electrolyte.

The following chemicals were used: 60 wt% PTFE suspension (Sigma-Aldrich[®]) diluted by demineralized water to a concentration of 10 wt%; 10 wt% PBI solution in *N,N*-dimethylacetamide (Celanese[®]); *N,N*-dimethylformamide p.a. (Penta[®]); 85 wt% phosphoric acid p.a. (Penta[®]); isopropanol p.a. (Penta[®]); and demineralized water (conductivity below 1 $\mu\text{S cm}^{-1}$). For fuel cell testing, hydrogen and oxygen with a degree of purity of 5.5 and 4.0, respectively (SIAD[®]), were used.

3 Results and discussion

3.1 Influence of the method of CL preparation (brushing vs. spraying)

The first preparation method was to brush catalyst ink onto the GDL, resulting in relatively effective deposition of the catalyst. Nevertheless, electrodes prepared by this method suffered from an occurrence of cracks. Moreover, the reproducibility of this technique was not satisfactory because of the subjectivity of the process of manual brushing. This is documented by SEM photographs shown in Fig. 1. As the same figure shows, in the case of the GDE prepared by the spraying method, the structure of the resulting CL was more homogeneous. The spraying technique allowed the application of less viscous catalytic ink. Thus, the amount of deposited material in a single layer decreased, which improved the homogeneity of the CL. This led to an increase in the fuel cell performance, see Fig. 2. This accounts for the improved contact of the CL to

the GDL and to the membrane. Better catalyst utilization may also be expected due to the homogeneous CL structure. An additional positive aspect is the enhanced reproducibility of the electrode properties. The only drawback of the spraying method is the high amount of waste material resulting from the necessity to wash the spraying nozzle. However, the effect of this aspect is significantly reduced by the production of larger electrode areas. Therefore, spraying was used for CL deposition in all remaining experiments reported in this study.

3.2 Role of the CL binder

Two different types of CL polymeric binders, characterized by different degrees of hydrophilicity, were used. PTFE was selected as a typical representative of hydrophobic binders and PBI as representative of hydrophilic binders, both stable under the operational conditions of the high temperature PEM fuel cell. The danger of insufficient compatibility of

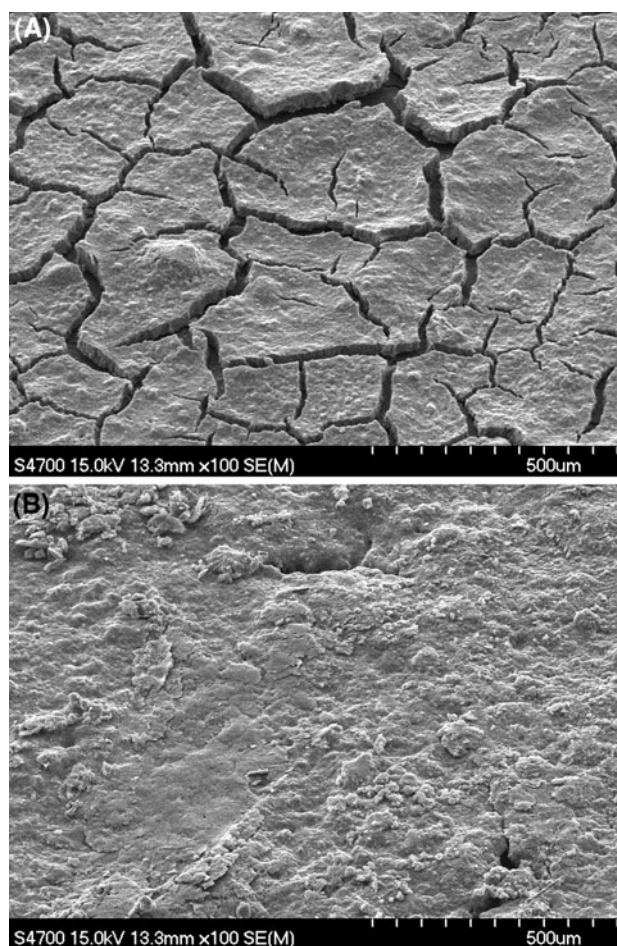


Fig. 1 SEM images of CL deposited by **a** brushing (3 layers), **b** spraying (10 layers) of catalyst ink on top of the GDL. Identical composition of CL: 15 wt% PBI binder, 30 wt% Pt/C catalyst, 0.5 mg Pt cm^{-2}

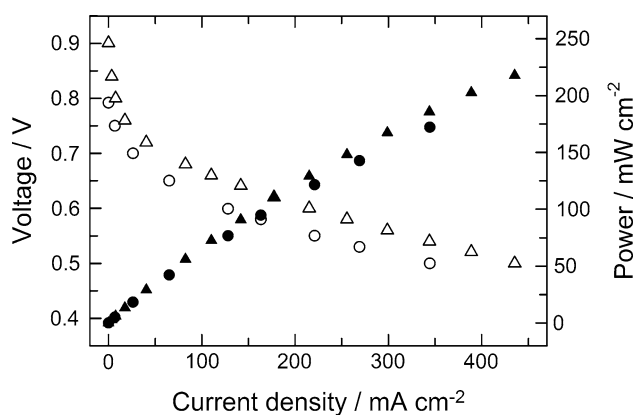


Fig. 2 Influence of CL deposition method on the fuel cell's performance. U - j (empty symbol) and P - j (filled symbols) curves of CLs deposited by: triangle spraying, circle brushing. Identical composition of CL: 15 wt% PBI binder, 30 wt% Pt/C catalyst, 0.5 mg Pt cm⁻². Operated at 160 °C, atm. pressure, 5 Nm moment force of constriction, hydrogen and oxygen flow rates of 30 and 20 mL min⁻¹, respectively

membrane material and CL binder is not relevant in this case. This is due to the fact that proton-conducting contact between these two fuel cell components is provided by phosphoric acid pressed out of the membrane during the assembly of the cell. The aim was to identify the importance of penetration of this phosphoric acid into the bulk of the CL structure. It is clear that the intensive penetration leads to flooding of the electrode. At the same time, this is connected with the corrosion of the catalyst. Insufficient phosphoric acid penetration results in a low degree of catalyst utilization. As is known from low-temperature PEM fuel cell technology, the degree of CL hydrophilicity is decisive for the performance of the GDE. Surprisingly, in the fuel cell tests similar performances of the CL were obtained for both binder materials. This is documented by Fig. 3.

Figure 3a shows the U - j curves recorded using CLs with different PBI contents. 11 wt% was determined as the optimum binder content. It provided a smooth, compact CL. The single laboratory fuel cell shows power outputs up to 225 mW cm⁻² at 0.6 V. Similarly, Fig. 3b summarizes the behavior of CLs with different contents of PTFE binder. In this case, an even higher maximum power output of 255 mW cm⁻² at a cell voltage of 0.6 V and a temperature of 160 °C was obtained for 12 wt% PTFE content in the CL. However, generally it was observed that the dependence of CL performance on the amount of the polymer binder is significantly lower for PTFE binder within the content range studied, i.e., from 5 to 15 wt%.

The reason for the observed behavior consists in the different hydrophobicity of the two binders. In the case of PBI, the polymer content in a CL up to 11 wt% is not sufficient to cause CL flooding by phosphoric acid. PBI is probably located inside the CL in separated domains, not well interconnected, or the PBI film deposited on the individual particles of the supported catalyst is extremely thin in comparison to the void volume. Phosphoric acid pressed against the CL from the membrane during the compression of the fuel cell thus does not penetrate the PBI phase through the entire, or a significant amount of, CL volume. The electrode reaction takes place just near the membrane/CL interface. An increase in PBI content results in exceeding this level and in flooding of the electrode by the acid.

In the case of PTFE the situation is different. As a hydrophobic polymer, it repels phosphoric acid and therefore even with higher polymer contents it does not cause flooding of the CL. Conversely, it may prevent phosphoric acid from penetrating into the CL and thus reducing the degree of catalyst utilization. The reason why this does not happen is that PTFE is incorporated into the CL in the form of a suspension. Its potential to form

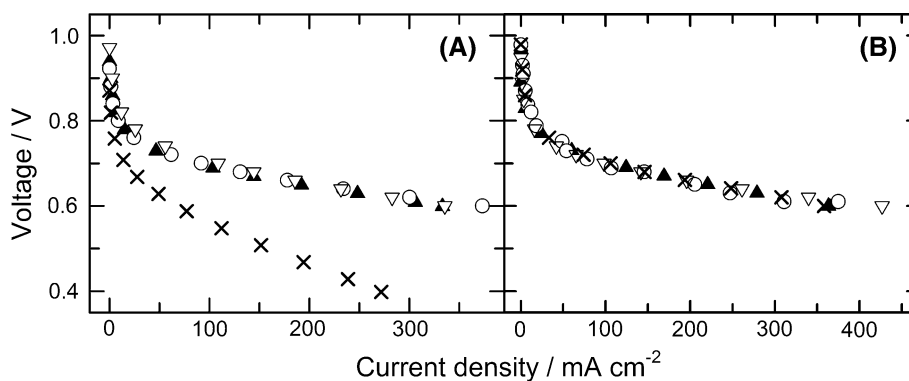


Fig. 3 U - j curves of GDE with **a** PBI as a binder. PBI content in CL (wt%): filled triangle 8.4, open circle 11.0, downward pointing open triangle 13.0, times 15.0; **b** PTFE as a binder. PTFE content in CL (wt%): open triangle 5.1, filled circle 10.1, downward pointing open triangle 12.0, times 15.1. Composition of CL: 30 wt% Pt/C catalyst,

0.5 mg Pt cm⁻², prepared by spraying on GDL. Single fuel cell operated at 160 °C, atm. pressure, 5 Nm moment force of constriction, hydrogen and oxygen flow rates of 30 and 20 mL min⁻¹, respectively

a homogeneous hydrophobic phase in the CL volume is thus limited, even after thermal heating of the GDE after CL deposition. Another possible explanation is the gradually moving front of the CL domain flooded by phosphoric acid. In the case of a low-PTFE content, it is located relatively deep in the electrode structure, but still a sufficient part of the CL is free of acid and thus operates freely. With increasing content of PTFE in the CL, the phosphoric acid front gradually moves out of the CL, leaving a significantly larger part free. However, this aspect does not cause significant change in performance, because only a relatively narrow domain in the neighborhood of the acid front is catalytically active. Another aspect influencing this behavior is the visually identified increased compactness of the CL caused by the increased content of the polymeric binder. This is documented in Fig. 4. A more compact layer less readily allows penetration of phosphoric acid into its internal structure. In the case of PBI, this influence was not observed. Therefore, SEM pictures are not shown here.

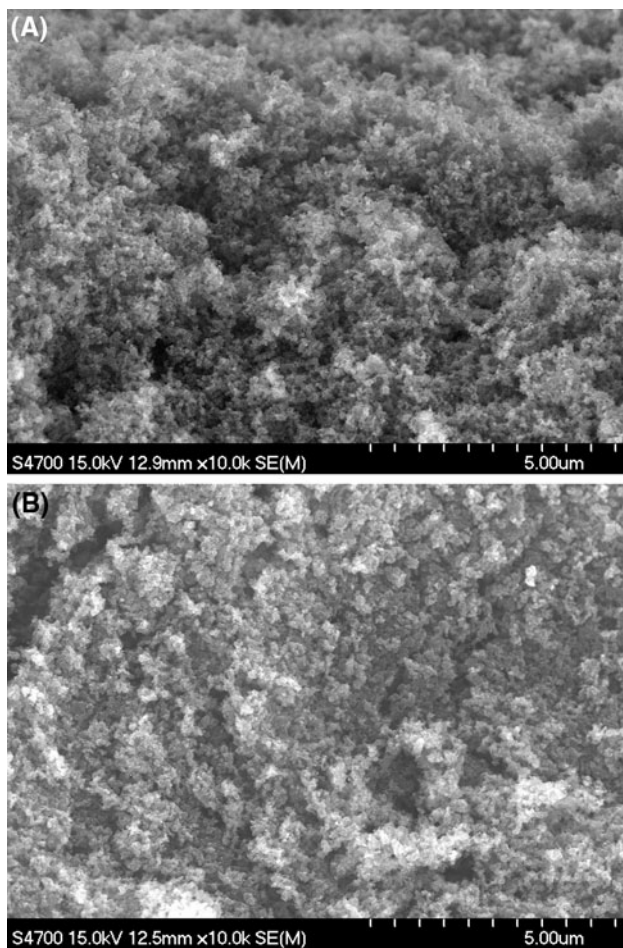


Fig. 4 SEM pictures of GDE cross-sections, documenting the influence of the polymer binder content on the morphology of the CL at constant Pt load 0.5 mg cm^{-2} . Content of Teflon binder: **a** 10.4 wt% and **b** 15.0 wt%

3.3 Influence of platinum concentration in the catalyst

Two catalysts with different contents of platinum (30 and 60 wt%) on a carbon support were used. GDEs were prepared keeping a constant platinum load of 0.5 mg cm^{-2} . This resulted in CLs of different thicknesses. This experiment was performed to investigate the utilization of the catalyst across the CL cross-section. Figure 5 shows SEM pictures of the cross-sections of the electrodes used to establish the thickness and morphology of the CL. As can be seen, the thickness of the CL was reduced from 30 μm observed for 30 wt% Pt/C (Fig. 5a) to 15 μm for 60 wt% Pt/C (Fig. 5b).

The influence of the PTFE binder content in the CL, prepared by means of the catalyst containing 60 wt% of Pt, on the resulting U - j curve is summarized in Fig. 6. As is visible, in the majority of cases the performance is lower than in the case of the CL based on the catalyst containing 30 wt% of Pt (compare with Fig. 3b). One possible

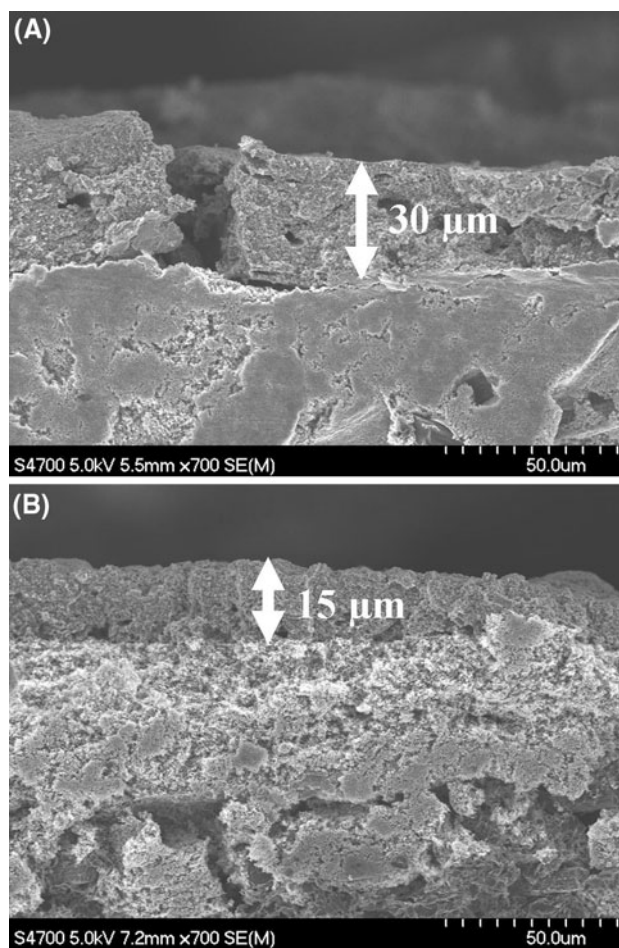


Fig. 5 SEM pictures of GDE cross-sections, documenting the relation between the platinum concentration in the catalyst and the CL thickness (constant Pt load 0.5 mg cm^{-2}): **a** 30 wt% Pt/C and **b** 60 wt% Pt/C

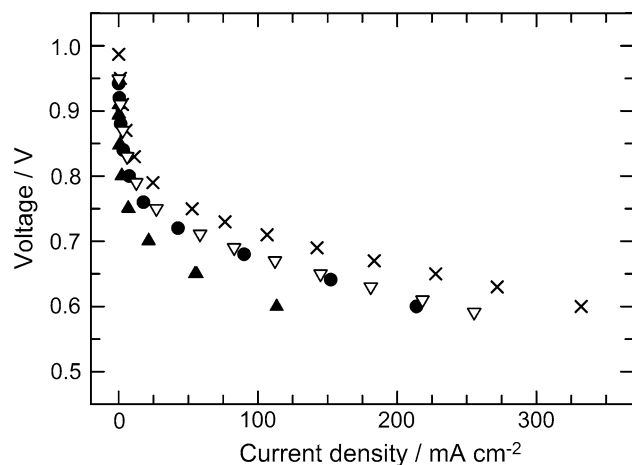


Fig. 6 U - j curves of GDE with PTFE as a binder. PTFE content in CL (wt%): filled triangle 5.0, filled circle 9.2, times 15.7, and downward pointing open triangle 20.0. Composition of CL: 60 wt% Pt/C catalyst, 0.5 mg Pt/cm², prepared by spraying on GDL. Operated at 160 °C, atm. pressure, 5 Nm moment force of constriction, hydrogen and oxygen flow rates of 30 and 20 mL min⁻¹, respectively

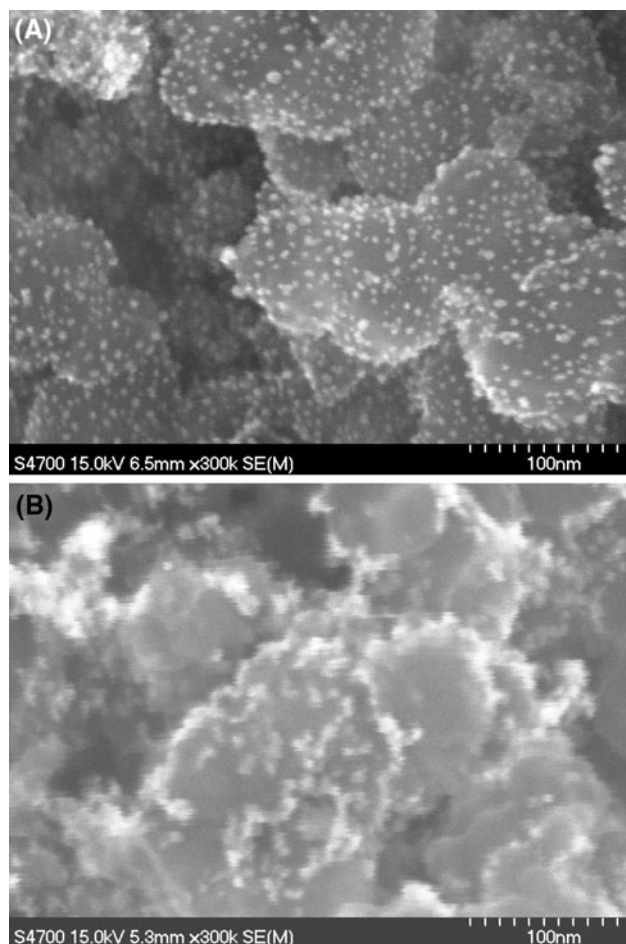


Fig. 7 SEM pictures of catalysts with different contents of platinum on a carbon support: **a** 30 wt% Pt/C and **b** 60 wt% Pt/C

explanation is the different dispersion of Pt particles on the catalyst support, which is documented by the SEM pictures shown in Fig. 7. This analysis manifests better Pt particle distribution in the case of the catalyst with a lower Pt concentration. It is also confirmed by an analysis of the XRD diffraction: in the case of 60 wt% catalyst, the average platinum particle size (3.6 nm) was nearly twice that in the case of the 30 wt% one (2.0 nm). Related XRD spectra are not shown here.

A closer analysis of this phenomenon offers an alternative, more probable explanation. In contrast to the catalyst containing 30 wt% of Pt, in the case of 60 wt% Pt/C

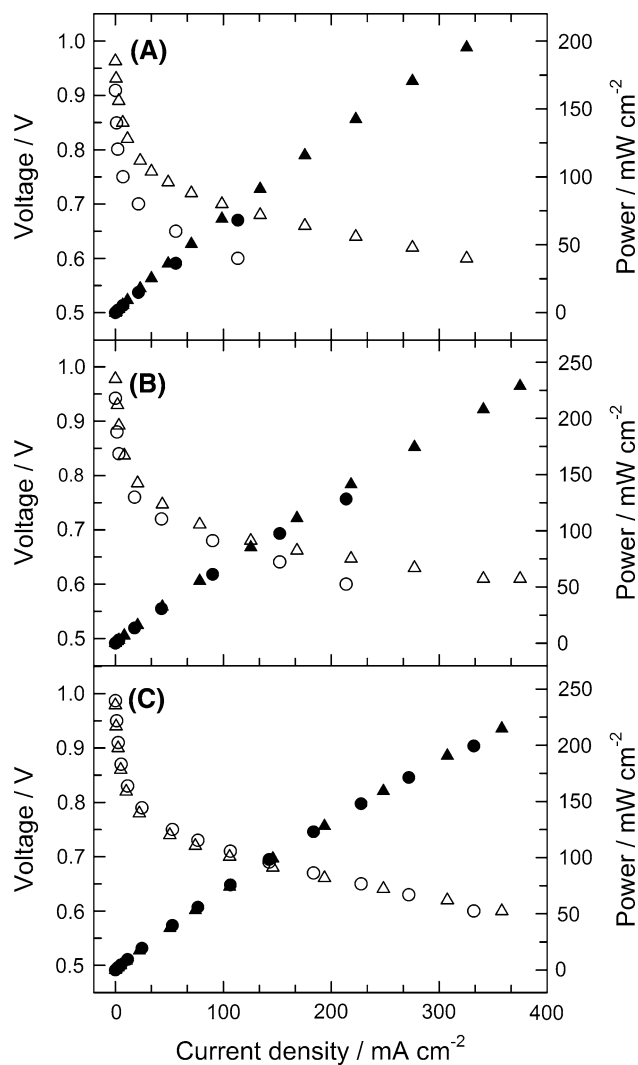


Fig. 8 Influence of the platinum concentration in the catalyst on the fuel cell's performance. U - j (empty symbol) and P - j (filled symbols) dependences of electrodes prepared from: open triangle 30 wt% Pt/C, open circle 60 wt% Pt/C catalyst. PTFE binder content in CL: **a** 5 wt%, **b** 10 wt%, **c** 15 wt% in CL, 0.5 mg Pt cm⁻², prepared by spraying. Operated at 160 °C, atm. pressure, 5 Nm moment force of constriction and hydrogen and oxygen flow rates of 30 and 20 mL min⁻¹, respectively

catalyst the fuel cell performance is significantly dependent on the PTFE content in the CL. The performance increase with increasing PTFE concentration up to 15.7 wt% indicates a significantly higher danger of CL flooding by phosphoric acid. This is in agreement with the decreased CL thickness. It indicates that the relatively high resistance to flooding of the CL, based on the catalyst containing 30 wt% of Pt, is connected mainly with its relatively high thickness. With decreasing value of this parameter, the role of the binding polymer content and its nature becomes more significant. This is documented by Fig. 8. By exceeding the optimal level of PTFE content (15.7 wt%), penetration of phosphoric acid into the CL is hindered due to strongly hydrophobic character of CL. This results in reduced catalyst utilization and in deterioration of the CL's performance, see Fig. 6.

4 Conclusions

Within this study, the spraying technique provided a significantly more homogeneous and reproducible deposition of the CL onto the GDL, compared with brushing. From the results obtained in this study, it is evident that a GDE for high temperature PEM-type fuel cells can be manufactured utilizing both PBI as well as PTFE binder in the CL. The difference consists in the significantly higher danger of the CL flooding by phosphoric acid when using hydrophilic PBI as a binder. In the case of PTFE, the danger of such behavior is relatively low with a sufficiently thick CL (30 μm or more). For the thinner CL, a sufficiently high-PTFE content has to be used. A laboratory FC utilizing GDE with optimal composition of CL displayed more than 250 mW cm^{-2} power output at 0.6 V. Of the

two catalysts examined for the purpose of CL construction, 30 wt% platinum on a carbon support exhibited better results in the majority of cases. This fact can be explained by the higher resistivity of the CL prepared from the less concentrated catalyst to the electrode flooding by phosphoric acid.

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