Preparation of Pd-coated polymer electrolyte membranes and their application in direct methanol fuel cells

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Abstract

Nafion 117 was coated with thin layers of metallic Pd by electroless deposition from commercial plating baths. The deposits were well adhering and crack-free. In a purpose-built direct methanol fuel cell for liquid electrolyte, the methanol-blocking ability of the Nafion/Pd composites was studied. The cell construction allowed determining the methanol concentration directly in the catholyte while recording electrochemical parameters. Compared to bare Nafion, the Nafion/Pd composites considerably reduced methanol crossover. This resulted in enhanced cell performance, which was found to be somewhat dependent also on the potential of the Pd layer.
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1. Introduction

Direct methanol fuel cells (DMFCs) are promising candidates for the next generation of power sources for portable electronic devices. An increased customer's convenience is expected from the replacement of recharging by refueling and more reliable information on the energy status from the amount of fuel remaining in the tank. The use of a liquid fuel should result in fuel cell devices showing higher energy densities compared to systems based on hydrogen fuel cell technology. However, although remarkable progress has been made with respect to the power density and the fuel efficiency [1,2], a big effort is necessary in their further improvement, mainly under two aspects [3–8]:

(a) Improvement of the methanol oxidation catalysis at the anode and
(b) Reduction of the methanol crossover effect.

Recently, a combinatorial approach has been adopted [9–11] for the development of more efficient catalysts. For (b), several different strategies have been followed: the development of new polymer electrolyte membranes [12–14], the development of methanol-tolerant cathode catalysts [9,15], the application of an electrolyte cross-flow through the cell [16,17], the insertion of catalytically active particles into the polymer electrolyte membrane (PEM) [18] and the introduction of special coatings with methanol-blocking properties [19–21]. Among the latter layers of metallic palladium are of special interest [22], as palladium is impermeable to methanol and shows sufficient permeability for hydrogen [23]. The use of palladium foils is not recommended because of their thickness. Coating technologies offer possibilities to create thin layers of Pd on a suitable substrate. The method that has mainly been applied so far is sputtering [24–27]. This technique has a number of disadvantages, particularly the required vacuum conditions. Swelling due to (re-)hydration of the membrane during operation in the DMFC results in the formation of cracks in the vacuum-deposited Pd layer.

Here we report on the performance of palladium layers electroless plated on fully hydrated Nafion substrates.

Table 1
Materials properties of the electrodes used

Type	Catalyst layer	Diffusion layer
ELAT anode	60 wt.% Pt:Ru (1:1 a/o) on Vulcan XC-72, 4.0 mg cm^{-2}	Carbon cloth
ELAT cathode	80 wt.% Pt on Vulcan XC-72, 5.0 mg cm^{-2}	Carbon cloth
ESNS anode	60 wt.% Pt:Ru (1:1 a/o) on Vulcan XC-72, 4.0 mg cm^{-2}	Au-plated Ni-screen with microporous fluorocarbon backing
ESNS cathode	60 wt.% Pt on Vulcan XC-72, 4.0 mg cm^{-2}	Au-plated Ni-screen with microporous fluorocarbon backing

2. Experimental

2.1. Materials

Nafion 117 (Sigma Aldrich Co.) was pretreated in an aqueous solution of 2.5 mol l^{-1} nitric acid and 0.7 mol l^{-1} sulfuric acid for 3 h at 80 °C followed by several leaching steps in deionized water, until both nitric and sulfuric acids were completely removed. After this pretreatment, the membranes were kept in deionized water until further use.

Commercial electrodes (ETEK – DeNora, New Jersey, USA) were used for the electrochemical experiments. The properties of the different types are listed in Table 1.

Neoganth®, Pallatect PC® (Atotech, Berlin, Germany) and a solution of 0.125 M NaOH (Fisher Scientific) containing 1 g l^{-1} NaBH$_4$ (Alfa Aesar) were used for the electroless plating process. For the electrochemical experiments, an aqueous acidic electrolyte of 2.5 M H$_2$SO$_4$ (Merck) and 0.65 M Na$_2$SO$_4$·10H$_2$O (Fluka) was prepared.

2.2. Equipment

In order to characterize the surface of the Pd-coated Nafion, any technique requiring vacuum is not suitable, because the application of vacuum to the wet Pd–Nafion composite causes water to evaporate and the resulting shrinkage of the Nafion leads to cracks in the palladium layer. Therefore, we used environmental scanning electron microscopy (ESEM, Quanta 600 FEG, FEI, Hillsboro, USA) operating at 20 kV in this study. The working pressure was 564 Pa. This is slightly below the equilibrium vapor pressure of water at the temperature of 25 °C used here. Images were recorded with a GBS detector, spot 4.0 and 6.0 at a working distance of 10.8 mm.

A bipotentiostat RDP 98 (Bank-IC, Clausthal-Zellerfeld, Germany) with integrated electronic data recording was used for the electrochemical experiments.

The liquid acid electrolyte samples drawn from the cathode compartment were analyzed in a HP 6890 gas chromatograph (Agilent, Palo Alto, USA) with split/splitless injector, flame ionization detector (FID) and a HP INNOWax column. In order to prevent the gas chromatograph from corrosive components in the sample and to increase the sensitivity, solid-phase microextraction (SPME) was employed [28]. The signals of methanol and several expected reaction products were identified both by reference samples and parallel measurements on a gas chromatograph equipped with an MS-detector [29,30].

2.3. Procedures

2.3.1. Electroless plating

Electroless plating is a cheap and convenient method for depositing metallic layers on electrically non-conducting substrates. The plating solution contains the corresponding metal in ionic form, a reducing agent and additives. Among these additives, inhibitors play an important role preventing the reduction of the metal in the homogeneous liquid phase. A pretreatment of the substrates scheduled for metal deposition is necessary. The formation of small clusters of metallic palladium as described below produces catalytically active sites on the substrate for the deposition reaction to take place.

In order to obtain single-side plated Nafion, two samples were sandwiched and crimped in a suitable holder. Before the plating process, the samples were dipped into 0.1 M NaOH for a few seconds to adjust the Nafion surface to the alkaline conditions in the following step. For the plating process itself three steps were necessary [31–33]:

(a) Activation step: adsorption of Pd^{2+} complexes in Neoganth® for 5 min;
(b) Reduction step: reduction of the adsorbed Pd^{2+} complexes to form clusters of metallic palladium in 0.125 M NaOH containing 1 g l^{-1} NaBH$_4$ for 5 min;
(c) Plating step: autocatalytic deposition of palladium in Pallatect PC®.

Between these steps and afterwards the samples were rinsed in deionized water. The activation bath and Pallatect PC were operated at temperatures suggested by the manufacturer (45 and 65 °C), while the reduction bath was kept at ambient temperature.

2.3.2. Cyclic voltammetry

For cyclic voltammetry experiments, an electrolyte as described in Section 2.1 was used. The size of the samples used as working electrodes was 0.3 cm × 0.5 cm. A 1 cm × 1 cm platinum sheet was used as a counterelectrode and a saturated mercury sulfate electrode (SMSE) as reference electrode. The measurements were carried out in a glass cell, after nitrogen had been bubbling through the electrolyte for 15 min in order to remove oxygen.

2.3.3. Fuel cell experiments

The cylindrical test cell for the fuel cell experiments with an inner diameter of 35 mm was made from Plexiglas and is depicted in Fig. 1. It consisted of an anode and a cathode compartment separated by the Pd-coated Nafion membranes.
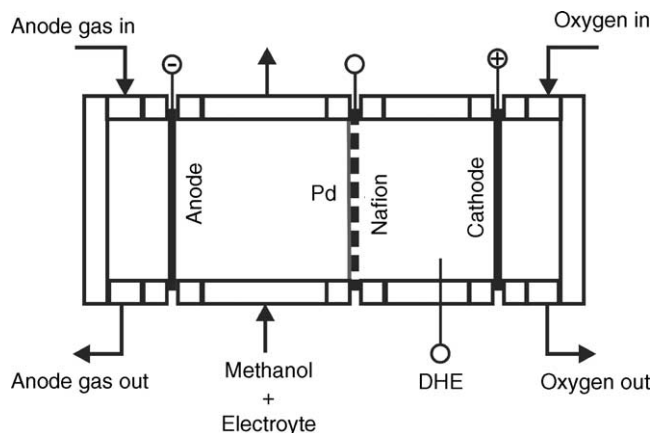
Fig. 1. Schematic side view of the cylindrical test cell for methanol crossover experiments.

Fig. 2. Cyclic voltammogram of Pd-coated Nafion in 2.5 M H_2SO_4/0.65 M Na_2SO_4 at ambient temperature, $v = 30\,mV\,s^{-1}$. Peak labels refer to the description in the text.

On both sides, commercially available fuel cell electrodes as described in Section 2.1 were used. The distance to the membrane was 17.5 mm for the anode and 27.5 mm for the cathode.

Through the anodic compartment, liquid electrolyte of the described composition was circulated from a large storage vessel, into which methanol was fed. This allowed keeping a constant methanol concentration inside the anodic compartment. For the results reported here, a concentration of 1 M methanol was used. The cathode compartment contained fittings for sampling and a dynamic hydrogen electrode (DHE) [34,35] and was filled with liquid acidic electrolyte as described above. The backside of the electrodes contained gas rooms, which were fed by an oxygen flow in the case of the cathode. For the anode, a nitrogen flow was applied in order to remove carbon dioxide produced by anodic oxidation of the fuel.

The test cell was fitted with electric contacts to the Pd layer. The potentials of the electrodes and the Pd layer versus DHE were controlled by a bipotentiostat. During the experiments, the test cell was kept in a temperature-controlled chamber. Electrochemical experiments were started with the injection of methanol into the storage vessel followed by tracking the open-circuit voltage (OCV). No current was drawn until stationary OCV values could be measured. As soon as the OCV remained constant, either voltage–current curves or galvanostatic experiments were recorded.

3. Results and discussion

Following the preparation procedure in Section 2.3.1, well-adhering smooth and bright palladium layers were obtained on Nafion 117. The deposition rate was determined to be 0.07 μm min⁻¹. The Pd–Nafion composite showed remarkable mechanical stability as long as no tensile stress was applied to the Pd/membrane plane.

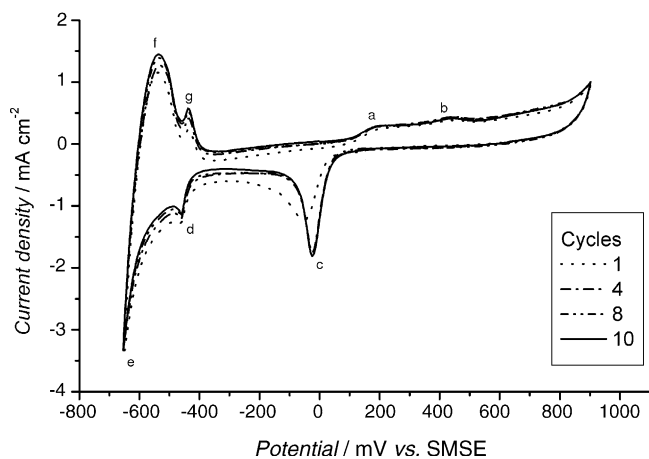The electrochemical behavior studied by cyclic voltammetry (Fig. 2) was as expected from polycrystalline palladium with the characteristic peaks for oxide formation (a, b) and oxide stripping (c), for hydrogen adsorption/desorption at −470 mV (d) and −434 mV (g) versus SMSE, respectively, and for hydrogen evolution (e) as well as hydrogen oxidation (f).

An initial problem concerning the quality of the layer was the appearance of pinholes. The reason for this was found to be bubbles of hydrogen formed by catalytic decomposition of $NaBH_4$ in the second preparation step (see Section 2.3.1). These tended to stick to the Nafion samples, thereby preventing the activation reaction on these locations. A series of experiments was carried out with various kinds of sample movement or electrolyte agitation in the reduction bath, including ultrasound generation, low-frequency vibrational sample movement and horizontal and vertical sample movements. Only the vertical sample movement resulted in an improvement of the process and allowed to reduce the number of pinholes significantly [36].

ESEM micrographs were taken to obtain information on the quality of the palladium deposits. The samples were always kept wet and the Nafion contained water in the pores and on the surface. The equipment (see Section 2.2) did not allow applying equilibrium vapor pressure, but a vapor pressure that was somewhat lower. Therefore, a certain loss of water occurred during these measurements. This was observed by shape changes of the sample. Fig. 3 shows the early stage of an ESEM measurement. The surface of the sample was flat, no pinholes or other defects could be found in the palladium coating. Fig. 4 shows the same sample after several minutes of measurement. The continuous loss of water led to a shrinkage of the Nafion membrane, causing the deformation of the Pd layer in form of crinkles. Nevertheless, the pictures obtained by ESEM did not show any cracks in the layer.

For the determination of the methanol crossover in a fuel cell or in an apparatus designed for the investigation of methanol transport phenomena, several methods have been
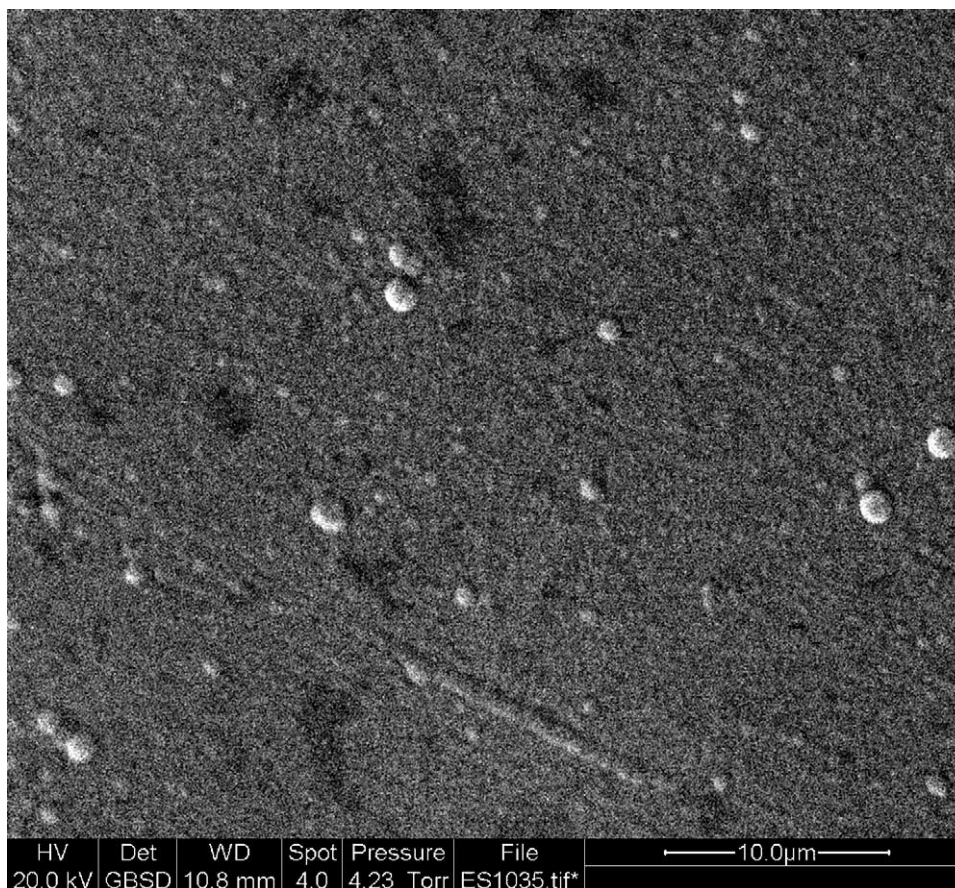
Fig. 3. ESEM micrograph of Pd-coated Nafion at an early stage of measurement.

described in the literature. The analysis of methanol and its reaction products—mainly CO_2—in the cathode exhaust gas [37–39] should be treated with caution, as other sources could be responsible for cathodic carbon dioxide [40,41]. Other ways of methanol determination are the measurement of partial pressure [12,42,43] or electrochemical detection [3,12,35,44].

In this study, the test cell shown in Fig. 1 and described in Section 2.3.3 in combination with a liquid acid electrolyte allowed measuring the concentration of methanol in the catholyte and recording electrochemical data in the same experiment. Thus information not only about the methanol crossover but also about the effects on overall performance was obtained.

The temperature in the test cell was measured at two different locations: in the atmosphere of the temperature-controlled chamber (T_a) and inside the storage vessel (T_i). The latter value was taken as a reference for the cell temperature. Measurements showed that the temperature difference ($\Delta T = T_a - T_i$) was always less than $5\,°C$, stationary operation mode provided. The rather large interelectrode gap in the test cell affected the cell performance due to the *iR* drop in the liquid electrolyte. The main target electrodes for the electrochemical experiments were of the ELAT type consisting of a carbon black supported catalyst on a carbon cloth carrier. Such elec-

trodes are used in membrane electrode assemblies (MEA) type DMFCs and have been designed for use in bipolar stacks requiring electric contact over the whole electrode area. Our test cell construction did not allow this. Instead, the electrode was contacted through a wire in the cell frame, resulting in an increased internal resistance and low current densities (Figs. 5 and 6). Fig. 5 shows the voltage–current characteristic of the test cell with ELAT electrodes at $65\,°C$ for Pd-coated Nafion and for bare Nafion. Although slightly higher cell voltages were measured with bare Nafion at current densities less than $0.2\,mA\,cm^{-2}$, the series with Pd-coated Nafion in the range of 0.2–$1.5\,mA\,cm^{-2}$ showed significant better performance, because of the reduction of methanol crossover. We believe that the lower cell voltage observed for the palladium-coated Nafion at very small current densities is due to an additional activation barrier for the hydrogen transport through the palladium layer.

In Fig. 6, the results of a constant current experiment with ELAT electrodes at $0.53\,mA\,cm^{-2}$ and $65\,°C$ are presented. The potential of the Pd layer was kept at $450\,mV$ versus DHE. With bare Nafion no stable cell voltage could be achieved, consequently the experiments were stopped after 2 h 30 min. In contrast, the values for Pd-coated Nafion were found to be stable for more than 8 h. Fig. 7 shows the methanol concentrations corresponding to the experiments displayed in
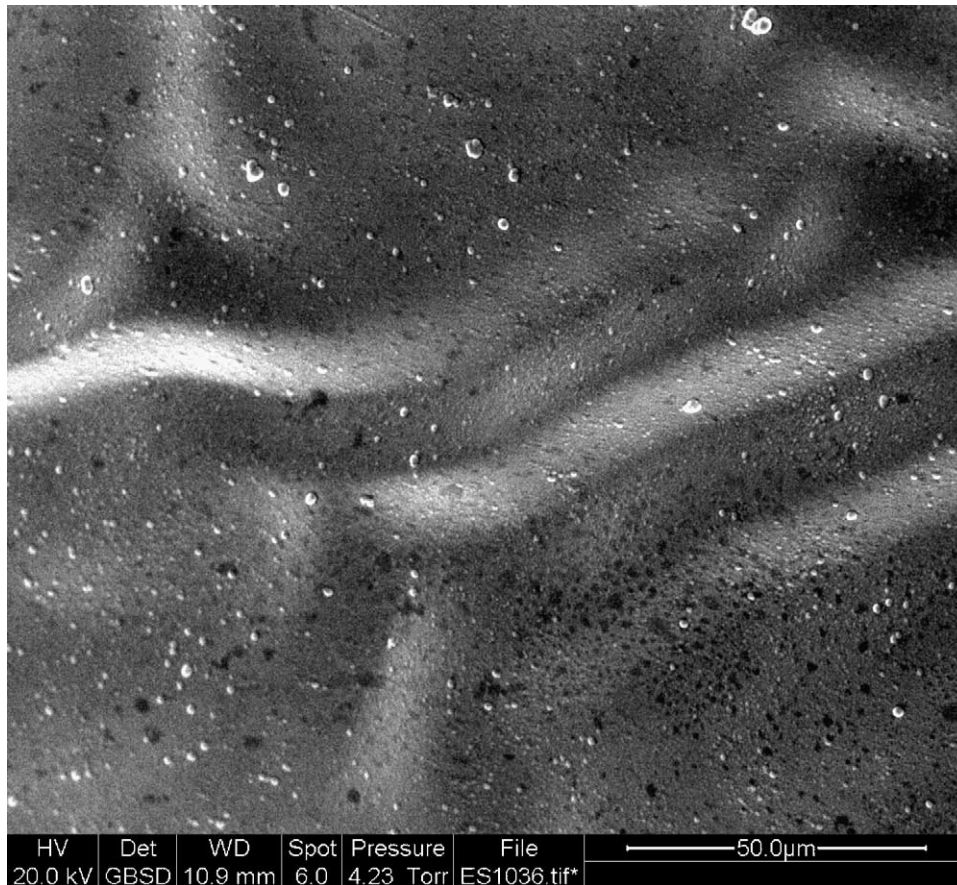
Fig. 4. ESEM micrograph of Pd-coated Nafion after several minutes of measurement.

Figs. 5 and 6. In the case of bare Nafion, a quick rise of the methanol concentration in the catholyte was found. With the Pd/Nafion composite, the methanol concentration in the cathode compartment remained constant at a low level. Presumably, the deposited Pd layers were not completely free of defects, since some methanol was still detectable in the catholyte.

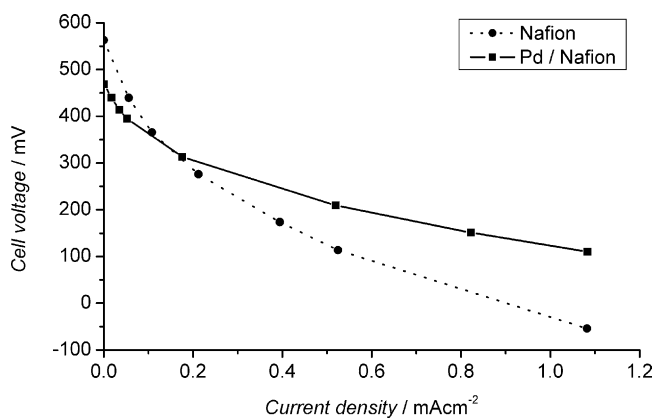Fig. 8 depicts the cell performance measured with ESNS electrodes at 50 °C and different membrane potentials. Posi-

tive values for the cell voltage were obtained for current densities up to $10 \, \text{mA cm}^{-2}$. A lower potential of the Pd membrane showed slightly better results for current densities higher than $1 \, \text{mA cm}^{-2}$.

Although better performance could be obtained with ESNS electrodes, the current densities achieved in our experiments are not yet in the range needed for commercial
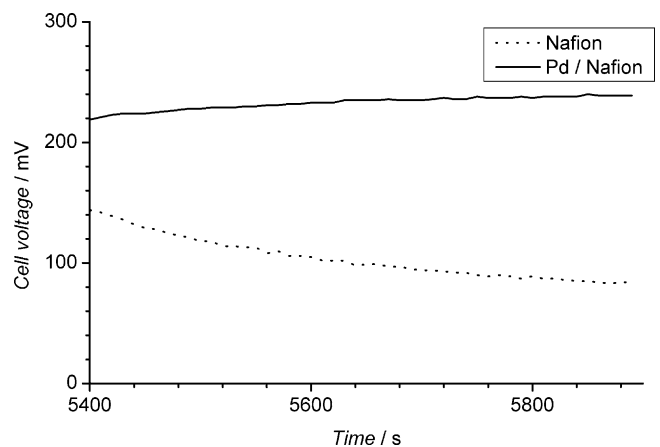

Fig. 5. Cell voltage–current density characteristics of the test cell with ELAT electrodes, for bare and Pd-coated Nafion at 65 °C, $E_{Pd} = 0.450 \, \text{V}$ vs. DHE.

Fig. 6. Performance of the test cell in constant current experiments at $0.53 \, \text{mA cm}^{-2}$ and 65 °C with ELAT electrodes for bare and Pd-coated Nafion, $E_{Pd} = 0.450 \, \text{V}$ vs. DHE. Methanol injection was at $t = 0 \, \text{s}$.
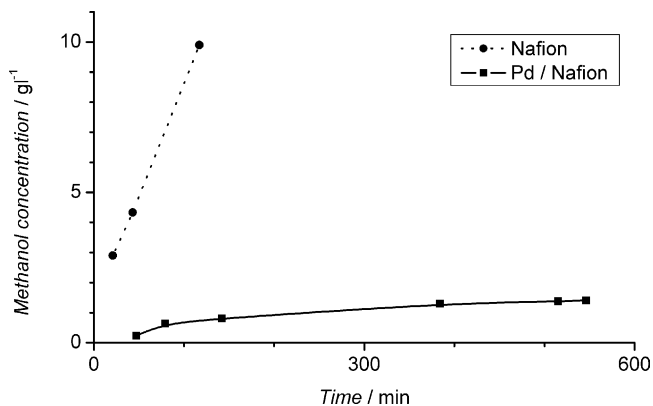
Fig. 7. Methanol concentrations in the cathode compartment as a function of time (0 min = methanol injection time).
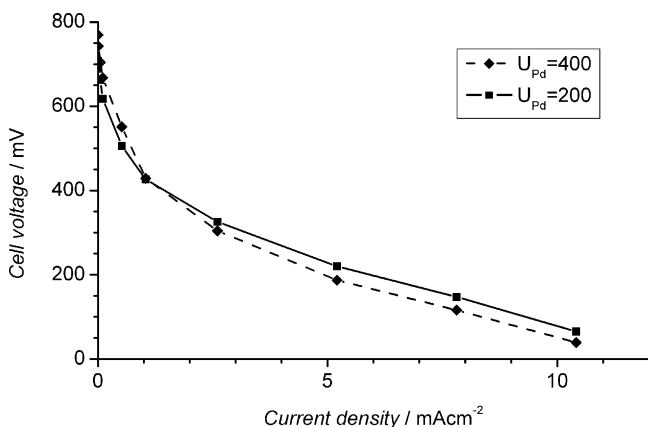

Fig. 8. Cell voltage–current density characteristics of the test cell with ESNS electrodes for different potentials of the Pd-layer vs. DHE at 50 °C.

cells, mainly because the cell voltage was suffering from the *iR* drop in the electrolyte. Besides, these types of electrodes are not suitable for use in MEA.

In order to keep the membrane potential at a certain level, maintenance currents were necessary. These currents decreased in the course of the experiment. Experiments with electrolyte, which had been refluxed under nitrogen atmosphere in order to remove dissolved oxygen, resulted in maintenance currents more than one order of magnitude lower for the same membrane potential. The maintenance currents could thus be related to the concentration of dissolved oxygen in the liquid phase. At 50 °C the maintenance current density was found to move towards $50\,\mu A\,cm^{-2}$ for a membrane potential of 400 mV versus SMSE and towards $200\,\mu A\,cm^{-2}$ for a membrane potential of 200 mV versus SMSE. At a nominal current density of $5\,mA\,cm^{-2}$ in the test cell, this is equivalent to 5% current loss at a membrane potential of 200 mV and 1% current loss at a membrane potential of 400 mV.

Sometimes the question arises, how the introduction of a further noble metal can contribute to a commercially successful direct methanol fuel cell. Based on average prices of precious metal quotations for palladium provided by Allgemeine Gold- und Silberscheideanstalt AG, Germany [45], cost data

were calculated for a 50-W unit using an area-related nominal power of $100\,mW\,cm^{-2}$, a Pd layer thickness of 1 μm and a proportion of material cost with respect to fabrication costs of 85%. For a wet chemical process like electroless plating material costs play a major role, so the latter value should be realistic. At the current price level of palladium metal, additional costs of about 5 EUR are expected.

4. Conclusions

Well-adhering crack-free Pd layers on a polymer electrolyte membrane could be produced by electroless plating from commercial baths. Care had to be taken to avoid the adhesion of hydrogen bubbles on the membrane during the plating process in order to obtain pinhole-free layers. A purpose-built electrochemical cell for liquid electrolyte allowed measuring the methanol concentration directly in the catholyte, while electrochemical parameters were recorded. Thus, a correlation of methanol crossover and cell performance was possible. The ability of palladium layers to reduce methanol crossover, as indicated in the literature, has been confirmed with electrodes, which are suitable for MEA. Due to the cell construction for liquid electrolytes and the resulting *iR* drop, only small current densities could be achieved. The results suggest, however, that the concept presented here can be transferred to MEA-type cells. With electrodes not suitable for MEA, better current densities were achieved and the effect of the membrane potential on the cell performance was studied. The results show a gain of performance for lower membrane potentials. Experiments are under way to study this effect in more detail.

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