Enhanced electrocatalytic activity of CoTMPP-based catalysts for PEMFCs by plasma treatment

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Abstract

In this work, we developed a methodology of plasma-enhanced preparation of CoTMPP (tetramethoxyphenylporphyrin)-based electrocatalysts. A series of CoTMPP-based electrocatalysts were deposited on the porous gas diffusion substrate (titanium fibre felt) using plasma-enhanced impregnation method. Impregnated 1.5 mg cm^{-2} CoTMPP/Ti catalysts were treated by dielectric barrier discharge (DBD) plasma in Ar or N_2 atmosphere. Additionally, the pretreatment methods were utilized to improve the adhesion of CoTMPP on the diffusion layer surface. The plasma pretreatment methods included the a-C:H-layers deposition followed by an Ar:O_2 radio frequency (RF) plasma functionalization. The latter approach led to the formation of specific oxygen surface groups that influenced the catalysts activity. Obtained catalysts were compared in terms of activity, stability and structure. The catalytic activity for hydrogen peroxide (H_2O_2) reduction was tested in a proton exchange membrane fuel cell (PEMFC) using hydrogen peroxide on the cathode side. Surface elemental analysis and structure of catalysts were examined by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Our contribution shows the potential of a plasma treatment in the preparation of electrocatalysts for hydrogen peroxide reduction reaction in a PEMFC. Under the conditions of this study, improvement of the PEMFC performance up to 30% was achievable by a deposition of CoTMPP on the titanium diffusion substrate followed by plasma treatment. The large differences in catalytic activity of CoTMPP/Ti were observed, depending on the plasma treatment applied to the catalysts during their preparation.
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1. Introduction

Pt and Pt alloys have traditionally been employed as electrocatalysts in proton exchange membrane fuel cells PEMFCs [1–6]. Recently nanoparticles of Pt and its alloy supported on carbon black or newly developed nanosized materials such as carbon nanotubes or carbon nanofibers have been used as the catalysts [7–10]. However due to the Pt high cost, a strong motivation exists to find less expensive non-noble metal alternatives that are stable and exhibit catalytic activity comparable to that of Pt. Although it has been demonstrated that fuel cells utilizing hydrogen peroxide (H_2O_2) have numerous advantages for underwater application or space power systems [11,12], most efforts have almost exclusively been devoted to the development of non-precious catalysts for oxygen reduction. Jasinski [13] published in 1964 that transitions metal porphyrines and phtalocyanines show an electrochemical activity and can be used as cathode material in fuel cell. Janke et al. have demonstrated that the activity of the transition metal macrocycles can be improved by a pyrolytic heat treatment in an inert atmosphere [14]. Since that time many efforts have been devoted to enhance their electrochemical performance [15–27]. During the heat treatment, the molecular structure of metal complex is decomposed. For catalyst prepared by heat treatment in low and medium temperature ranges (up to 800 °C), the pyrolysis

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residual products (metal-N_4 moieties or their fragments) were found to be the active catalytic centre [15,17,18]. It is suggested that the metallic clusters surrounded by graphite layers can act as the catalytic sites when catalysts prepared at high pyrolysis temperatures [19]. Nevertheless, it has been shown that the thermal pyrolysis of porphyrines leads to an unfavourable morphology of the material [28,29]. Bogdanoff et al. [28] have demonstrated that melting and sintering of cobalt tetramethoxyphenylporphyrin (CoTMPP) during pyrolysis resulted in a nonporous product. This serious drawback of the preparation method can be overcome by using plasma treatment of the catalysts [30].

Low temperature plasma has been extensively utilized in catalysis, including plasma-assisted synthesis of catalytic active ultra-fine particles and their deposition on support, plasma regeneration or plasma treatment of catalysts [31–37]. Most of the conventional methods for preparation of catalysts include high-temperature calcinations/reduction or pyrolysis in an inert atmosphere. Replacement of heat treatment step by low-temperature plasma treatment minimizes some problem caused by high temperature such as aggregation, crystalline size grow and sublimation [32,38]. The plasma prepared catalysts or catalysts modified by plasma exhibit a much higher activity, enhanced selectivity and better stability [35,37,39]. A plasma modification of surface is known as a versatile approach to induce hydrophobic properties or improve wettability and adhesion of coatings [40]. These features help achieve a desirable metal–support interface in catalysts [36]. It was demonstrated that plasma treatment of CoTMPP-based catalysts suppressed particles aggregation [30]. In previous work, it was shown that low-temperature plasma treatment is suitable to transform CoTMPP into a catalytic material for the oxygen reduction reaction [30].

In this work we developed a methodology of plasma-enhanced preparation of CoTMPP-based electrocatalysts for hydrogen peroxide reduction. The purpose of this study was to show that plasma treatment allows to prepare CoTMPP-based catalysts for the cathode reduction of hydrogen peroxide in fuel cells. Fuel cells utilizing hydrogen peroxide as an oxidizer are of interest for underwater application [11,12]. From an operational point of view, these systems are more reliable. H_2O_2 is storable. It is environmentally compatible. When decomposed it gives only oxygen and water.

Though the porphyrines are considered to be the promising alternative to Pt, they are still a long way from being able to substitute it. A replacement of Pt by non-precious catalyst reduces the PEMFC performance. That makes it difficult to evaluate the efficiency of plasma treatment on catalytic activity of CoTMPP. For that reason, we did not replace the Pt-based catalysts by CoTMPP in PEMFC completely. Instead, we employed plasma treated CoTMPP-based catalyst additionally to the Pt. CoTMPP was deposited on the gas diffusion substrate at the cathode side in addition to the Pt catalysts on the membrane. In order to evaluate the efficiency of plasma treatment on the performance of non-precious catalysts, we tested the PEMFC with and without presence of CoTMPP-based catalyst on the diffusion substrate.

2. Experimental

2.1. Materials

Commercial (Sigma–Aldrich, Germany) cobalt tetramethoxyphenylporphyrin, CoTMPP ($C_{48}H_{36}CoN_4O_4$, 791.77 g mol^{-1}) was employed as a precursor of catalysts. Tetrahydrofuran (THF) was used to dissolve the CoTMPP. THF (GR for analysis) was purchased from Merck KGaA, Germany. Catalysts were deposited on the titanium fibre felt that was employed as a gas diffusion substrate at cathode side in a PEMFC. Titanium fibre felt (thickness of 0.4 mm, porosity of 79%) was purchased from STS Metalle GmbH. High purity methane (99.995%, Air Liquid, Germany), argon (99.999%, Air Liquid, Germany) and oxygen (99.999%, Air Liquid, Germany) were used for plasma treatment. Hydrogen (99.999%, Air Liquid, Germany) and hydrogen peroxide, 35% (GR for analysis, AppliChem GmbH, Germany) were used for PEMFC tests. The hydrogen peroxide was diluted with a distilled water to give a final concentration of 17.5%.

2.2. Preparation of CoTMPP catalysts

2.2.1. Plasma treatment of Ti substrate

Prior to use, the titanium fibre felts were washed in acetone and then dried. The amorphous hydrogenated carbon (a-C:H) films were deposited on the titanium fibre felts by a radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) method in a commercially available reactor (Piccolo, Plasma Electronic GmbH). All the samples were deposited from methane (CH_4) and argon (Ar) gas mixture at a total pressure of 15 Pa under gas flow conditions (CH_4:Ar = 15:15 sccm). The films were deposited at power of 100 W for 5 min on each side of substrate. The substrates were located either at the powered electrode or grounded electrode at the distance of 4 cm from the powered electrode. Additionally, a series of films was deposited on glass substrate for 10 and 5 min in order to calculate deposition rate and to measure the contact angle respectively. The radio-frequency (RF) power varied from 100 to 200 W.

The film thickness was determined using surface profilometer (Dektak 3ST, Veeco). The deposition rate was estimated by taking the film thickness and deposition duration into account.

After the deposition of a-C:H films, some of the samples were treated in Ar:O_2 RF-plasma. In order to avoid the undesirable influence of previous process, an Ar:O_2 RF-plasma treatment was carried out in another reactor. The reactor was described in detail in a previously published paper [30]. Plasma treatment was performed at RF-power of 80 W for 2 min at a total pressure of 10 Pa under gas flow conditions (Ar:O_2 = 15:15 sccm).

The contact angles of water on a-C:H films deposited on glass substrate were measured before and after treatment by Ar:O_2 RF-plasma. The contact angles were obtained using a commercial system (Digidrop, GBX Instrumetation Scientifique, France) equipped with a monochromatic light source for imaging the liquid drop placed on the sample surface. High quality and level optic (NIKON) are employed for measurement to avoid aberration problem. The instrument is equipped with a micro
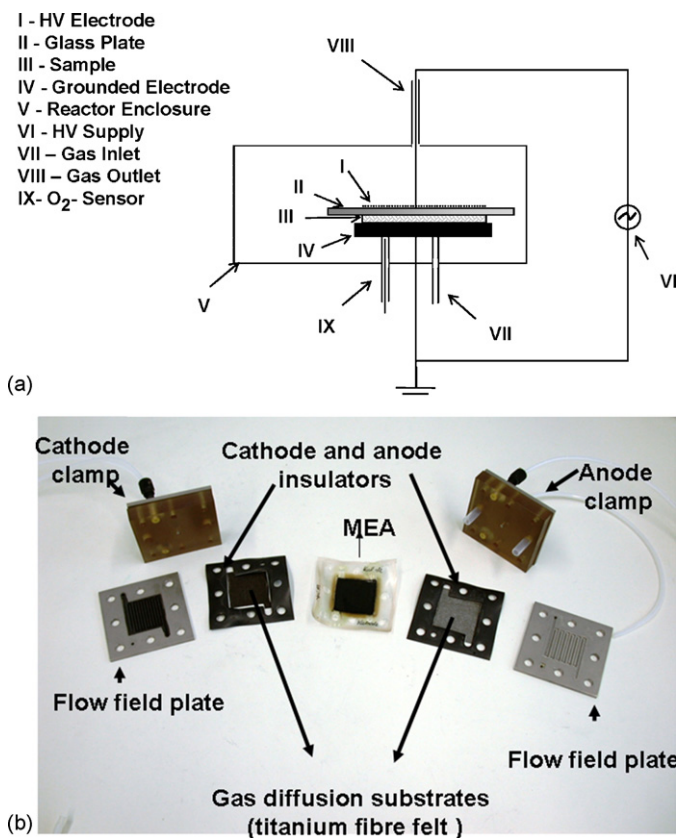
Fig. 1. A schematic configuration of a DBD reactor (a), and a photograph of a PEMFC (b).

regulator of droplets to disperse an accurate volume of liquid on the substrate. In this work, distilled water was used as the working liquid. The volume of water drop was 7 µl. The drop image was taken in 3 s after dispersing and stored, via a monochromatic video camera (CCD 2/3″), using PC-based control, acquisition and data processing.

2.2.2. Plasma treatment of CoTMPP/Ti catalysts

CoTMPP was deposited on Ti substrate using plasma-enhanced impregnation method. The pre-treated as described above Ti substrates were impregnated with a saturated solution of CoTMPP in THF. The final loading was about $1.5\,mg\,cm^{-2}$. After drying for a 24 h at room temperature, CoTMPP/Ti catalysts were treated in DBD plasma. A schematic diagram of the in-house build DBD-system used can be seen in Fig. 1a. The upper electrode is connected to an ac power source and covered with a glass plate (thickness = 2 mm). The lower electrode is connected to the earth. The applied voltage (peak-to-peak value) was in the 8–16 kV range. The applied voltage frequency was of 33.6 kHz.

The samples to be treated were located between the glass plate and the grounded electrode. Plasma treatment was carried out in Ar or N_2 environmental with gas flow rate of $200\,sccm\,min^{-1}$ at atmospheric pressure for treatments times of 24 or 2.4 min. Oxygen concentration inside the sealed chamber was monitored by oxygen sensor (Zyrox sensors and Electronics GmbH, Germany). During experiments, oxygen level ranged from 200 to

300 ppm. The electric energy (E_{el}) consumed by DBD was estimated as described in Ref. [41].

To examine the effect of plasma treatment on adhesion of CoTMPP to Ti fibre felt, the samples were treated ultrasonically in H_2O_2. The ultrasonic instrument was Transsonic 460/H (Elma, Germany).

2.3. Fuel cell test

Catalytic activity tests were performed in a PEMFC using H_2O_2 on the cathode side and H_2 on the anode side. The layer of electrocatalysts should be located in PEMFC between a gas diffusion substrate and the proton exchange membrane (PEM). The electrocatalysts can be deposited either on the gas diffusion substrate or on the PEM [5]. In our experiments, we used the PEMFC system with noble metal catalyst on the membrane. In order to evaluate the efficiency of plasma treatment on the performance of non-precious catalysts, CoTMPP was deposited on the gas diffusion substrate at the cathode side in addition to the Pt catalysts on the membrane. We tested the PEMFC with and without presence of CoTMPP-based catalyst on the diffusion substrate.

PEMFC test system set-up is shown in Fig. 1b. The membrane electrode assembly (MEA) with an active electrode area $6.25\,cm^2$ was purchased from AMT GmbH, Germany. A PtRu/C catalyst on anode side and a Pt/C catalyst on cathode side were employed with a noble metal loading of $2.0\,mg\,cm^{-2}$. Vulcan XC-72 was used as a catalyst support. For the anode catalyst, the Pt:Ru ratio was of 1:1. The deposition of CoTMPP onto the diffusion substrate was performed by plasma enhanced impregnation method described in Section 2.2. All of the component of the fuel cell that are shown in Fig. 1b were put together using eight bolts and nuts. The H_2O_2 was pumped through the cell with a tubing pump (REGLO, ISMATEC, Swiss) at a flow rate of $5\,ml\,min^{-1}$. H_2 was fed to the cell under $50\,sccm\,min^{-1}$. Humidification of the H_2 was carried out by bubbling the gas through water. The tests of PEMFC were performed under room temperature.

2.4. Characterization of catalysts

X-ray photoelectron spectroscopy analysis (XPS) was used for the analyses of the samples after different treatments. XPS was performed on an Axis Ultra (Kratos, Manchester, UK). For the excitation of the photoelectron spectra Al Kα ($h\nu = 1.4867\,keV$) was used. Two sets of measurements were performed. From measurements with a pass energy of 80 eV the composition of the surface was estimated. Moreover high resolution measurements of the C 1s line with a pass energy of 10 eV were performed. The scanning electron microscopy (SEM) investigation was performed in the usual way with a JEOL JSM 5800 4V instrument.

3. Results and discussion

3.1. Plasma treatment of catalysts

The plasma pretreatment of Ti substrates was aimed at improving of their adhesion to CoTMPP. On the other hand, it

Table 1
Deposition rate and contact angle of water on a-C:H films deposited on glass substrate at different RF-power followed by plasma treatment in Ar:O$_2$ atmosphere at power discharge of 80 W

Parameter of a-C:H film deposition power (W), substrate positioning	Deposition rate of a-C:H films (nm min^{-1})	Contact angle (°) before treatment by Ar:O$_2$ plasma	Contact angle (°) after treatment by Ar:O$_2$ plasma
100, on the HV-electrode	13.0	54	9
100, on the grounded electrode	7.5	69	15
150, on the HV-electrode	13.0	65	8
150, on the grounded electrode	7.7	72	11
200, on the HV-electrode	14.5	73	10
200, on the grounded electrode	10.0	77	15
No a-C:H film	–	80	15

All a-C:H films were deposited at a total pressure of 15 Pa under gas flow conditions (CH$_4$:Ar = 15:15 sccm). The a-C:H film deposition was carried out for 10 and 5 min for measurement of deposition rate and contact angle, respectively. RF-plasma treatment in Ar:O$_2$ atmosphere (functionalization) was performed for 2 min at a total pressure of 10 Pa under gas flow conditions (Ar:O$_2$ = 15:15 sccm).

is well known that the plasma treatment induces the functional groups on the surface (see for example [30,40] and references therein). These functionalities can improve the wettability and, in turn, influence on the impregnation of substrate with CoTMPP in THF solution. In addition, the enrichment of substrate with oxygen-containing groups was expected to enhance the catalytic performance of CoTMPP [42]. Prior to deposition on titanium, a series of a-C:H films was prepared on the glass substrates in order to illuminate the optimum deposition parameters. After

film deposition, the samples were treated in Ar:O$_2$ RF-plasma (functionalization). In order to follow the changes caused by plasma treatment and establish their correlation with plasma parameters, the contact angle was measured on a-C:H films.

Table 1 summarized the variation in deposition rate and contact angle with the deposition parameters. The variation in contact angle of water on a-C:H films were measured before and after treatment of samples in Ar:O$_2$ RF-plasma. It can be seen that wettability of a-C:H films tends to decrease with increasing

Table 2
Summary of plasma treatment conditions

Preparation route number	a-C:H film deposition: substrate positioning	Functionalization	Treatment by DBD plasma gas, voltage (peak-to-peak) (V), time of the treatment (min)	Lost of the catalyst loading after sonication in H$_2$O$_2$ for 1 h (%)
1	On the HV-electrode	Yes	N$_2$, 14, 24	33.0
2	On the grounded electrode	No	N$_2$, 14, 24	55.0
3	On the HV-electrode	Yes	N$_2$, 14, 24	61.0
4	On the grounded electrode	No	N$_2$, 14, 24	64.0
5	No a-C:H film	Yes	N$_2$, 14, 24	50.0
6	No a-C:H film	No	N$_2$, 14, 24	100.0
7	On the HV-electrode	Yes	N$_2$, 14, 2.4	35.0
8	On the grounded electrode	No	N$_2$, 14, 2.4	26.0
9	On the HV-electrode	Yes	N$_2$, 14, 2.4	54.0
10	On the grounded electrode	No	N$_2$, 14, 2.4	48.0
11	No a-C:H film	Yes	N$_2$, 14, 2.4	58.0
12	No a-C:H film	No	N$_2$, 14, 2.4	48.0
13	On the HV-electrode	Yes	N$_2$, 8, 24	74.0
14	On the grounded electrode	No	N$_2$, 8, 24	66.0
15	On the HV-electrode	Yes	N$_2$, 8, 24	85.0
16	On the grounded electrode	No	N$_2$, 8, 24	66.0
17	No a-C:H film	Yes	N$_2$, 8, 24	84.0
18	No a-C:H film	No	N$_2$, 8, 24	88.0
19	On the HV-electrode	Yes	Ar, 8, 24	100.0
20	On the grounded electrode	No	Ar, 8, 24	100.0
21	On the HV-electrode	Yes	Ar, 8, 24	100.0
22	On the grounded electrode	No	Ar, 8, 24	100.0
23	No a-C:H film	Yes	Ar, 8, 24	100.0
24	No a-C:H film	No	Ar, 8, 24	100.0
25	No a-C:H film	No	No	81.0

All a-C:H films were deposited on Ti substrate for 5 min at power discharge of 100 W from Ar:CH$_4$ RF-plasma under gas flow conditions (CH$_4$:Ar = 15:15 sccm). A total pressure in the deposition chamber was of 15 Pa. RF-plasma treatment of Ti in Ar:O$_2$ (functionalization) was curried out for 2 min at power discharge of 80 W under gas flow conditions (Ar:O$_2$ = 15:15 sccm). A total pressure was of 10 Pa. After impregnation with CoTMPP, the samples were treated by DBD-plasma.

RF-power during deposition process. At the same RF-power, the wettability of an a-C:H film was higher (contact angle was lower) if the substrate was located at the powered electrode. Ar:O$_2$ RF-plasma treatment of a-C:H films resulted in significant increase in wettability. The increase in wettability might be attributed to the surface covering with oxygen functional groups, which is confirmed by the XPS analysis later on. For the RF-power ranged from 100 to 200 W, the deposition rates were found to be in range from 7.5 to 14.5 nm min^{-1}. The dependence of deposition rate on substrate positioning can be ascribed to an influence of ionized species in plasma on a film deposition process. The different influence of ions on the film growth is likely due to the ions acceleration in the vicinity of the HV electrode.

On the titanium fibre felt, the a-C:H films were deposited at RF-power of 100 W. The titanium substrates were positioned at powered as well as grounded electrodes. An Ar:O$_2$ RF-plasma treatment was performed for Ti substrate with and without a-C:H films. After impregnation with CoTMPP, samples were treated in DBD plasma. The samples undergone to the plasma treatment are summarized in Table 2.

When plasma treatment is conducted to replace the pyrolysis, the temperature does not seem to play a key role in transforming CoTMPP into catalytic active material [30,32]. The conditions of DBD plasma are characterized by a low temperature of the neutral gas. DBD plasma comprises the electrons of high mean energy, excited molecules and radicals that can contribute to modification of CoTMPP. The generation of these species is governed by the electric energy (E_{el}) consumed by DBD per voltage cycle. Taking this into account, E_{el} can be considered as a parameter to characterize the DBD treatment of catalysts. The value of E_{el} was higher for N$_2$ (0.06 mJ per voltage cycle) than for Ar (0.02 mJ per voltage cycle) for the same voltage of 8 kV applied at the HV electrode. The energy, as expected, increased with the increase in voltage. For feeding voltage of 14 kV, the energy consumed by DBD in N$_2$ was found to be of 0.2 mJ per voltage cycle (i.e. 10 times more than in Ar at 8 kV). Under such circumstances, it might be expected that the difference in performance of the catalysts treated by DBD in Ar and N$_2$ cased by difference in E_{el}. In order to illuminate a role of treatment time, a series of samples was treated by DBD for exposure time of 2.4 min (i.e. 10 times shorter than for the most of the catalyst).

To limit the number of parameters, throughout of catalyst performance test in fuel cell, the preliminary test of catalysts stability against the H$_2$O$_2$ was carried out. The test was aimed to examine the effect of different plasma treatment conditions on the CoTMPP adhesion to the titanium fibre felt. The samples were treated ultrasonically in H$_2$O$_2$ for an hour. A lost of catalysts loading was monitored during sonication. A difference in bonding CoTMPP to a Ti was expressed in terms of relative loading lost (L):

$$L = \frac{(m_{CoTMPP\_0}/(m_{Ti} + m_{CoTMPP\_0})) - (m_{CoTMPP\_t}/(m_{Ti} + m_{CoTMPP\_t}))}{m_{CoTMPP\_0}/(m_{Ti} + m_{CoTMPP\_0})} \times 100\% \qquad (1)$$

Here m_{CoTMPP_0} is the mass of CoTMPP in a sample before sonication, m_{CoTMPP_t} the mass of CoTMPP in a sample after
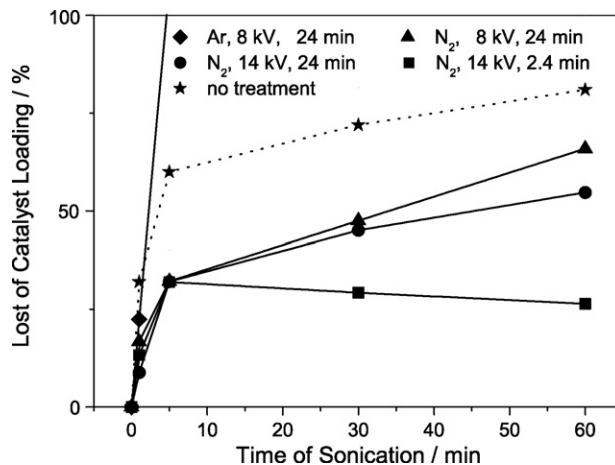

Fig. 2. The lost of loading of the plasma treated and untreated CoTMPP/Ti catalysts as a function of time of sonication. For plasma treated catalysts, Ti substrate were covered with a-C:H films without functionalization.

sonication for a time t, and m_{Ti} is the mass of titanium substrate. The data on catalyst loading lost (L) after 1 h of sonication are listed in Table 2. The following general observations were made. For the samples treated by DBD in N$_2$, the deposition of a-C:H films seems to improve the CoTMPP adhesion to titanium substrate. In case of CoTMPP deposition on not pre-treated titanium substrate (preparation routes 6, 12, 18, and 24), the loading lost was found to be of 50–100% in 1 h of sonication. On the contrast, an a-C:H film deposition on Ti substrate allowed decreasing the catalyst loading lost till 30% (preparation routes 1, 7, and 8). It is worthwhile to note, that the treatment by DBD for shorter time (2.4 min) appeared to be sufficient to improve CoTMPP bonding to the substrate. For all catalyst treated by DBD for 2.4 min, loading lost ranged from 26 to 57%. As a general trend, deposition of a-C:H film by locating the substrate on the HV-electrode led to more pronounced improvement of adhesion between CoTMPP and Ti.

The role of substrate functionalization in Ar:O$_2$ RF-plasma was unambiguous. In the most cases, that resulted in slight deterioration of CoTMPP/Ti bonding. But for catalysts treated by DBD at 14 kV (preparation routes 1 and 2), additional functionalization of Ti substrate led to decrease in loading lost from 54 to 33%. For all catalysts treated by DBD in Ar, the lost of loading exceeded 100% after 5 min of sonication. For selected catalysts, the lost of their loading is shown in Fig. 2 as a function of time of sonication. It summarized the influence of DBD parameters on CoTMPP adhesion on Ti substrate. For all catalysts presented in the Fig. 2, CoTMPP was deposited on the Ti substrate covered with a-C:H film but without further fictionalization in Ar:O$_2$ RF-plasma (preparation routes 2, 8, 14, and 20 in Table 2). As a reference, the data on untreated sample is also presented (preparation route 25 in Table 2). It can be seen that lost of catalyst loading occurred rapidly in the first 5 min of sonication. Catalyst treated in Ar loosed CoTMPP completely after 5 min of sonication. Further ultrasonic treatment seemed to destruct the titanium substrate. For catalysts treated in N$_2$, the bonding the CoTMPP to a Ti increased with increase of voltage applied. Taking into account the differences in values of E_{el} for

Ar- and N_2-DBD, it reached the conclusion that the improvement of adhesion of CoTMPP to the Ti is strongly dependent on the energy consumed by DBD. The DBD-plasma treatment is based on a conversion of electric field energy to chemical or physical processes on the surface of the sample treated. From this it follows that the effectiveness of treatment depends on energy consumed by a discharge. Taking this into consideration, the effectiveness of N_2-DBD plasma treatment (E_{el} ranged from 0.06 to 0.2 mJ per voltage cycle) is expected to be higher than that of Ar-plasma ($E_{el} = 0.02$ mJ per voltage cycle). This coincides with results presented in Fig. 2 and Table 2.

For the catalytic activity test in fuel cell, six samples were chosen (preparation routes 1, 2, 7, 8, 19, and 20 in Table 2). For all catalysts, a-C:H films were deposited by positioning the Ti substrate on HV electrode. A half of all samples were additionally functionalized in Ar:O_2 RF-plasma. After an impregnation with CoTMPP, the catalysts were treated by DBD in Ar at 8 kV (peak-to-peak value) for 24 min, and in N_2 at 14 kV (peak-to-peak value) for 24 and 2.4 min.

3.2. Fuel cell tests

Fig. 3 shows the performance of PEMFC with diffusion substrate containing CoTMPP (denoted further as catalyzed substrate) and original (untreated, without catalyst) diffusion substrate. In former case, the untreated titanium substrate was impregnated with CoTMPP without any further plasma treatment. For both diffusion substrates, an open cell potential of 900 mV was observed. When current was drawn from the cell, the cell potential fell. At low cell potential, the PEMFC with catalyzed diffusion substrate gave the lower current density than the PEMFC with original diffusion substrate (Fig. 3a). In Fig. 3b, the results from Fig. 3a are plotted in terms of power density. The maximum power density, W_{max}, of 12 mW cm^{-2} was observed for PEMFC with original diffusion substrate. The impregnation of diffusion substrate with CoTMPP without further treatment resulted in only a decrease in W_{max}. That indicates that deposition of untreated CoTMPP on diffusion layer does not impose the improvements of PEMFC performance. A further study is
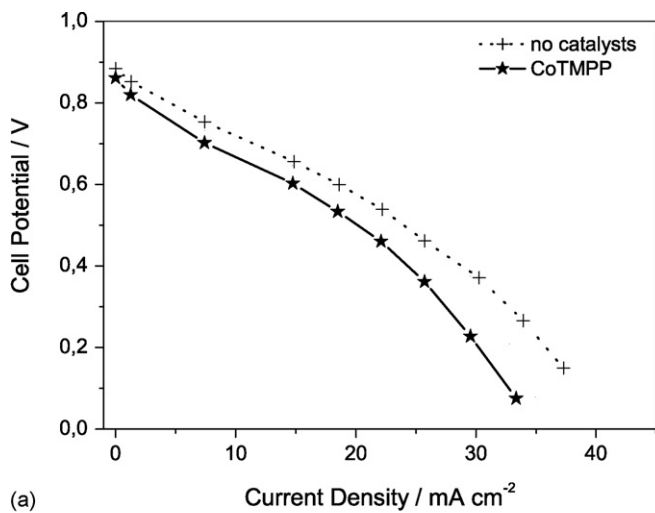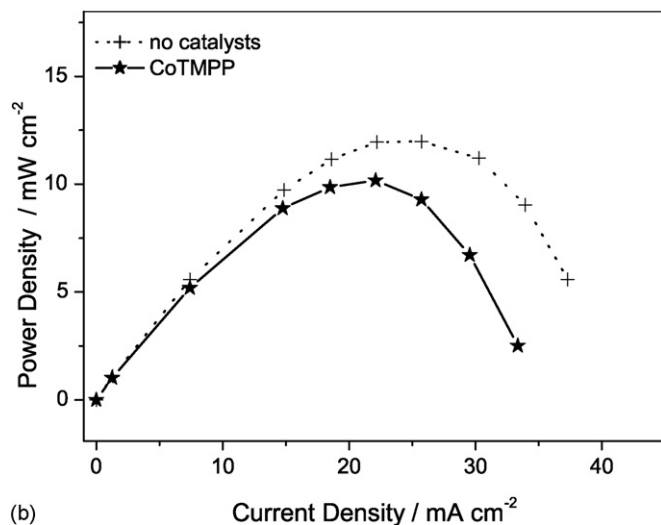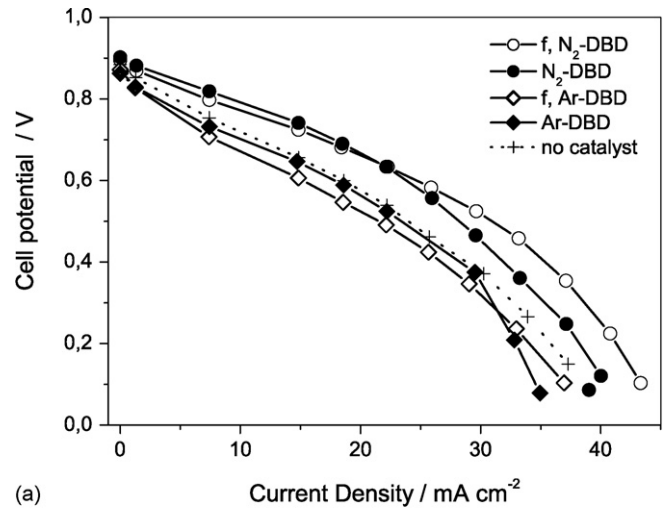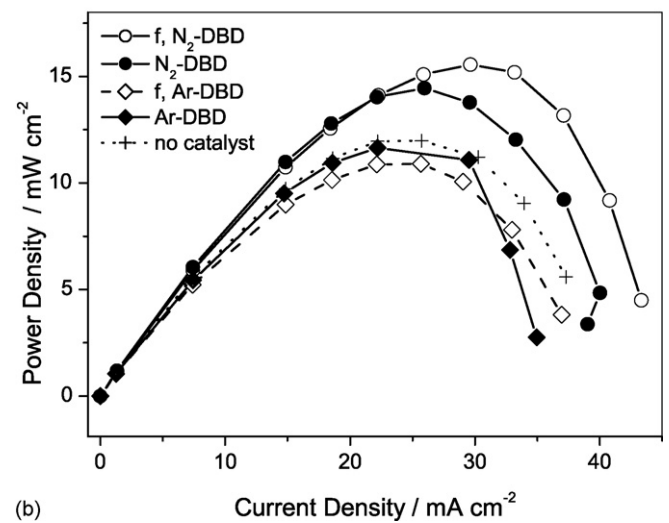

Fig. 3. The cell potential (a) and power density curves (b) for PEMFC with and without CoTMPP on untreated diffusion substrate.

Fig. 4. The cell potential (a) and power density curves (b) vs. different diffusion substrates. The catalyzed diffusion substrates were treated for 24 min in Ar- or in N_2-DBD plasma without and with functionalization (denoted as (f)).

needed to understand the performance drop for untreated catalyzed diffusion substrate.

Fig. 4 shows the effect of different plasma treatment routes on the performance of PEMFC with catalyzed diffusion substrate. The preparation of catalyzed diffusion substrates was carried out by plasma enhanced impregnation method. The substrate pretreatment procedure included a-C:H film deposition with or without functionalization. Then substrates were impregnated with CoTMPP. As a final step, the samples were treated in plasma under two different conditions. The samples were either exposed to Ar-DBD plasma for 24 min applying high voltage of 8 kV (peak-to-peak value) or N_2-DBD plasma at 14 kV (peak-to-peak value) for 24 min according to the routes 1, 2, 19 and 20 in Table 2. Additionally data on the performance of PEMFC with original titanium diffusion substrate are presented as the reference.

An improvement of the PEM performance was observed, when using the catalysts treated by DBD in N_2. Clearly, the

PEMFC with catalyzed diffusion substrate treated in N_2-DBD plasma generated the highest current density over the entire cell potential range (Fig. 4a). The performance of PEMFC with catalyzed diffusion substrate treated in Ar-DBD plasma did not differ much from that with original substrate. For all catalyst, the functionalization of substrate in Ar:O_2 RF-plasma gave a slight rise in current density for lower cell potential. But for catalysts treated in Ar-DBD plasma, the influence of functionalization on their performance can be only seen at currency of around 35 mA cm^{-2}. In either case, an open circuit voltage was around 900 mV.

For catalysts treated in N_2-DBD plasma, performance was enhanced up to 30%. The measured maximum power density, W_{max}, was 12 mW cm^{-2} for original diffusion substrate and it increased to 16 mW cm^{-2}, when using the catalysts treated by N_2-DBD plasma (Fig. 4b). For catalyst treated in N_2-DBD plasma, the additional functionalization of substrate in Ar:O_2 RF-plasma lead to a slight increase (up to 8%) in the W_{max} According to Fig. 4b, the functionalization resulted also in shifting of curve maxima to higher value of current density. For catalysts treated by DBD in Ar, the W_{max} decreased in a slight degree to compare to that of original titanium diffusion substrate.

Fig. 5 shows the effect of plasma treatment time of the catalysts on PEMFC performance. Tacking in to account data on bonding CoTMPP to Ti (Fig. 2), it can be expected that treatments for 24 min is too long for really improving the catalysts performance, leading actually to the bad CoTMPP adhesion to titanium or even to surface degradation. In fact, no improvement in performance was achieved for catalysts treated for shorter time. Concerning influence of functionalization, all trends observed for catalysts treated by N_2-DBD for longer time remain for catalysts treated for shorter time. The maximum power density occurred at two different current density points for functionalized and unfunctionalized CoTMPP/Ti diffusion substrates.
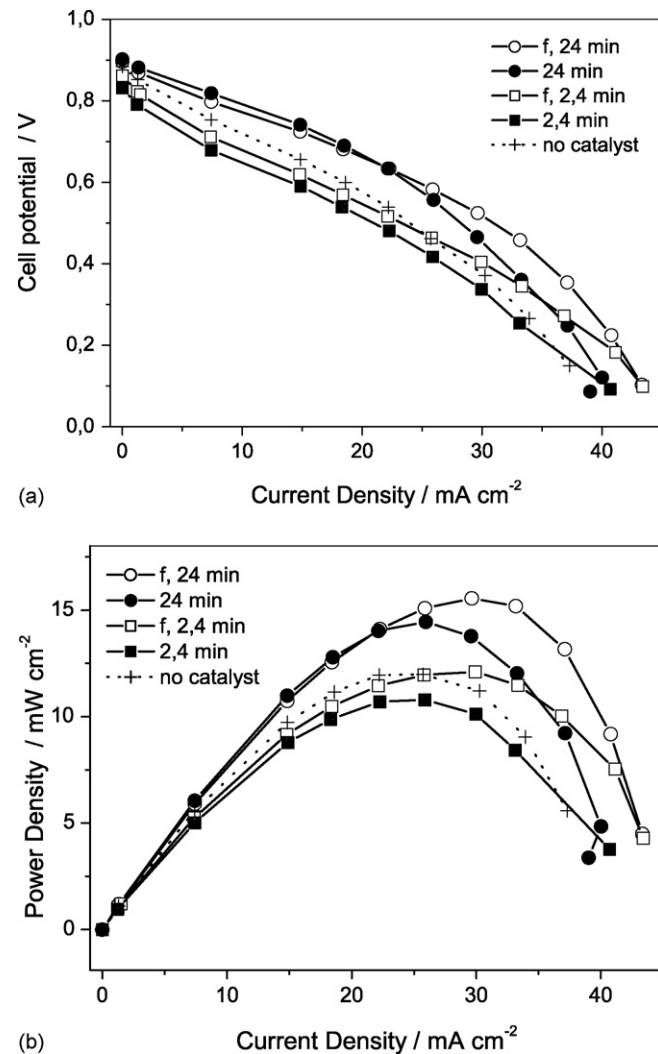

(a)

(b)

Fig. 5. The cell potential (a) and power density curves (b) vs. two different times of plasma treatment. The catalyzed diffusion substrates were treated in N_2-DBD plasma at 14 kV (peak-to-peak value without and with functionalization (denoted as (f)).
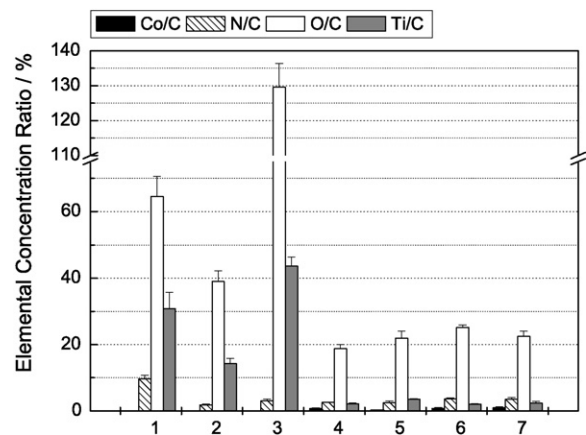

Fig. 6. The surface elemental concentration of Co, N, O and Ti on the diffusion substrates after various steps of CoTMPP/Ti catalysts preparation: untreated Ti (1); Ti covered with a-C:H film before(2) and after functionalization (3); Ti covered with a-C:H film, impregnated with CoTMPP and treated by Ar-DBD (4) and N_2-DBD (5) plasma; Ti covered with a-C:H film, functionalized in Ar:O_2 RF-plasma, impregnated with CoTMPP and treated by Ar-DBD (6) and N_2-DBD (7) plasma.

These results imply that PEMFC performance depends on the catalysts preparation. While addition of untreated CoTMPP on the diffusion substrate reduced the maximum power density, Ar-DBD plasma treated CoTMPP/Ti diffusion substrate seemed to have no significant effect on the fuel performance. The treatment by N_2-DBD plasma improved the PEMFC performance. The energy consumed by DBD discharge was a factor of 10 higher for N_2 than for Ar. On the other hand, CoTMPP/Ti substrate treated for a longer time improved the fuel cell performance. Hence, it appears that energy consumed by DBD during treatment have a decisive role in catalysts activity. High energetic electrons and excited species are generated in DBD plasma. These species react at the catalyst surface or change the surface morphology. Their amount is in general proportional to the energy consumed by discharge. The results of PEM performance tests imply that the conditions of only N_2-DBD are suitable to transform CoTMPP into a catalytic material. The PEMFC performed poorly when using untreated or Ar-DBD plasma treated CoTMPP/Ti. The adhesion of CoTMPP to Ti was found to be weak for untreated or Ar-DBD treated samples (see Fig. 2). On the contrary, the binding of CoTMPP to Ti seemed to be the stronger the shorter time of the plasma treatment in N_2. But catalysts treated for longer time showed the higher activity. Therefore, the PEMFC performance degradation cannot be ascribed to the weak CoTMPP adhesion to the diffusion substrate. An improvement of CoTMPP performance caused by substrate functionalization in Ar:O_2 RF-plasma can be explained by higher content of oxygen groups on the surface [42].

3.3. Catalyst characterization

A XPS and SEM analysis were undertaken in order to explain the difference in catalytic behaviour of plasma treated CoTMPP catalysts.

The XPS analysis was used to determine the elemental concentration on the catalysts surface after various steps of their preparation. Fig. 6 depicts the surface O, N, Ti and Co concentration for untreated titanium surface (original diffusion substrate), Ti covered with a-C:H film before and after functionalization as
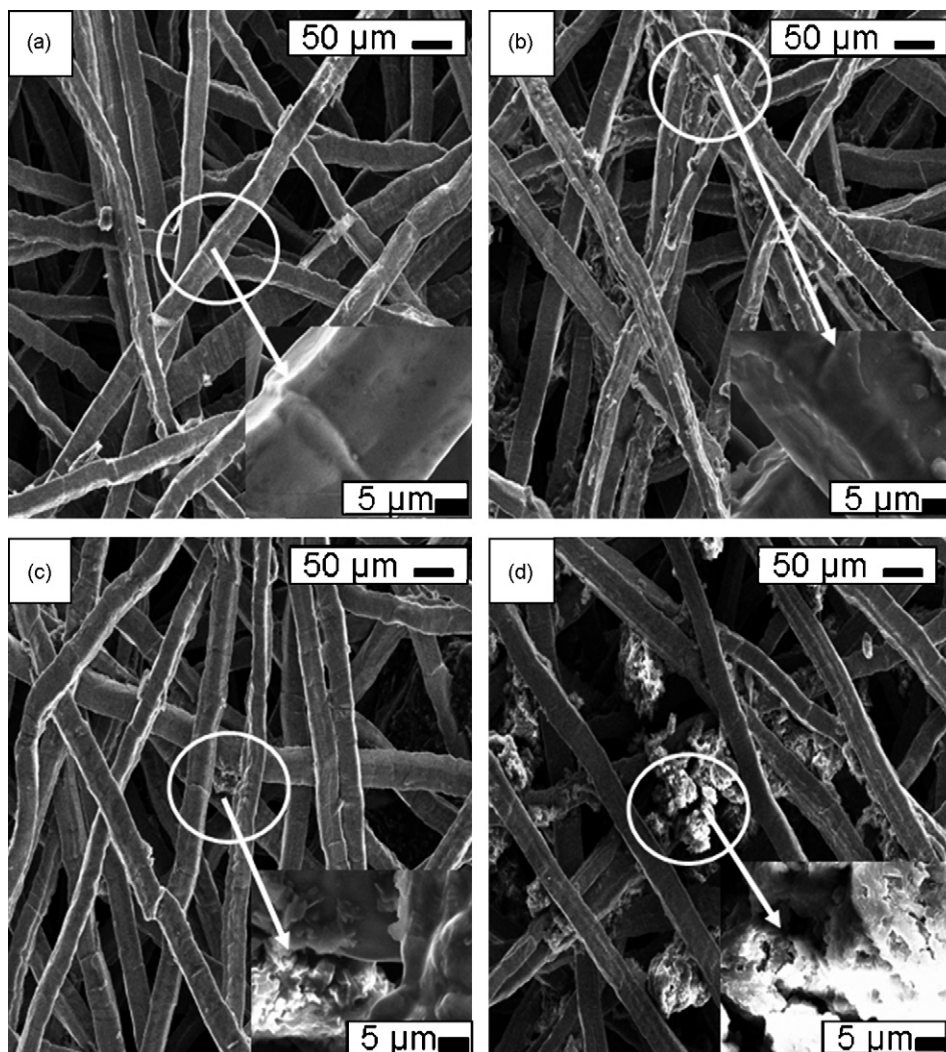

Fig. 7. The SEM images of untreated Ti (a), Ar-DBD (b) and N_2-DBD (c), (d) plasma treated CoTMPP/Ti catalysts. The time of plasma exposure was 24 min (b), (c) or 2.4 min (d).

well as for catalyst treated by DBD in Ar and N_2 with and without functionalization (preparation routes 1, 2, 19, and 20 in Table 2). The surface concentration of these elements is expressed relative to carbon. From Fig. 6 it can be observed: (i) untreated Ti surface contained O, N and C; (ii) a-C:H film deposition led to increase in C concentration; (iii) functionalization resulted in increasing of oxygen surface concentration, (iv) after treatment by DBD plasma, the difference in oxygen content on the surface of catalysts prepared with and without functionalization can be negligible; (v) a very weak tendency to increase in N content for functionalized catalysts was observed; (vi) the elemental composition of the Ar and N_2 DBD—plasma-treated catalyst is almost identical.

XPS analysis confirmed the higher content of oxygen on the functionalized surfaces. On the other hand, no increase of O content on the surface of catalysts was observed after treatment of catalyst by the DBD-plasma. In other words, the increase in activity of functionalized catalysts can be associated rather with promotion of catalytic centres formation than with oxidation of catalyst surface. DBD treatment in different gases did not resulted in a significant change in elemental composition of the catalyst surface.

SEM was used to investigate the morphology changes produced by DBD treatment in Ar and N_2 for different time. Fig. 7 shows the SEM images of untreated Ti and plasma treated CoTMPP/Ti catalysts (preparation routes 1, 7, 19). No difference in morphology caused by functionalization was observed. Therefore the SEM images of unfunctionalized catalysts are not shown. For all samples, the diameter of individual titanium fibre is of 15–45 μm. The untreated fibres have smooth surface (Fig. 7a). Ar-DBD treatment caused increasing of surface roughness (Fig. 7b). Nevertheless, this morphological change did not influence the catalytic activity. As it was shown in fuel cell tests, the PEMFC performance with untreated titanium substrate with smooth surface and Ar-DBD treated rough substrate were very similar. Moreover, the morphology changes obtained by Ar-DBD treatment showed a similarity with that of N_2-DBD treatment (Fig. 7b and c), though Ar- and N_2-DBD treated samples exhibited rather different catalytic activity (Fig. 3). The 2.4 min treated surface (Fig. 7d) was similar to the 24 min treated one (Fig. 7c), confirming that very rapid modification of surface occurred.

4. Conclusions

In this work we developed a methodology of plasma-enhanced preparation of CoTMPP-based electrocatalysts. Our contribution shows the potential of a plasma treatment in the preparation of electrocatalysts for hydrogen peroxide reduction in a PEMFC. Deposition of CoTMPP on the titanium diffusion substrate followed by plasma treatment improved the PEMFC performance up to 30%. The results of experiments suggest that PEMFC performance depends on the catalysts plasma treatment procedure used. While addition of untreated CoTMPP on the diffusion substrate reduced the maximum power density, Ar-DBD plasma treated CoTMPP/Ti diffusion substrate seemed to have no significant effect on the fuel performance. The high-

est performance enhancement was achieved by treatment of the CoTMPP/Ti diffusion layer in N_2-DBD plasma. In the process of catalysts treatment, plasma serves as a special supply of high energetic electrons and excited molecules that can modify the catalysts. In general, their amount is proportional to the energy consumed by discharge. The results of our experiment imply that both activity and stability of DBD-plasma treated catalysts increased with increasing energy consumed by discharge. Even for the same feeding voltage, the energy, consumed by DBD was higher for N_2 than for Ar. That suggests that the conditions of N_2-DBD plasma are more suitable to transform CoTMPP into a catalytic material. Deposition of a-C:H films on titanium surface (pretreatment) enhanced adhesion of CoTMPP on titanium. Additional functionalization of titanium surface in Ar:O_2 RF-plasma led to a slight increase in catalyst activity. Both DBD treatment in different gases and additional functionalization in Ar:O_2 RF-plasma did not result neither in a significant change in elemental composition nor in a morphology of the catalyst surface. This implies that increase in activity of plasma treated catalysts can be attributed rather with plasma influence on catalytic centres formation than with changes in morphology of catalyst surface.

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