ELSEVIER

Chemical Engineering Journal 133 (2007) 113–119

Chemical Engineering Journal

www.elsevier.com/locate/cej

Preparation and characterization of Pt direct deposition on polypyrrole modified Nafion composite membranes for direct methanol fuel cell applications

Lei Li[a,*], Yongming Zhang[a], Jean-Francois Drillet[b],
Roland Dittmeyer[b], Klaus-Michael Jüttner[b]

[a] *School of Chemistry and Chemical Technology, Shanghai Jiaotong University, Shanghai 200240, China*
[b] *Karl Winnacker-Institut, DECHEMA e.V., Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main, Germany*

Received 9 August 2006; received in revised form 13 February 2007; accepted 17 February 2007

Abstract

A novel method of Pt catalyst direct deposition on polypyrrole (ppy)-modified Nafion composite membranes for direct methanol fuel cell (DMFC) is proposed in this paper. Proton conductivity and methanol permeability of polypyrrole-modified Nafion composite membranes were investigated. The Pt particles were directly deposited on the PPy-modified Nafion composite membranes by using chemical reduction of platinic chloride at room temperature. Scanning electron microscopy measurements showed that Pt particles with a porous structure uniformly exist in the Pt/PPy/Nafion electrodes. The roughness factor and the active surface area of the Pt catalyst increased with increasing PPy loading. The performance of the Pt/PPy/Nafion electrodes was evaluated in a single DMFC.

Keywords: Polypyrrole; Direct methanol fuel cell; PPy/Nafion composite membrane; Pt/PPy/Nafion electrode

1. Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention due to its simple system design, low operating temperature and convenient fuel storage and supply. Conventional membrane electrode assemblies (MEAs) for DMFCs are prepared from catalyst inks containing a matrix of polyelectrolyte, a carbon supported catalyst, and in some cases a binder, e.g. polytetrafluoroethylene (PTFE), forming an interface with the proton exchange membrane (mostly Nafion®, DuPont) [1]. The multiphase boundary among carbon, noble metal catalyst, polyelectrolyte (binder), and the proton exchange membrane allows for the transport of fuel and water as well as for the diffusion of protons to and from the catalytic sites. However, carbon is impermeable to gases and liquids and does not conduct protons, which limits the achievable performance of the catalyst and results in low catalyst utilization and reduces cell performance. Therefore, it is important to find new catalyst supports instead of carbon, which improve catalyst utilization and cell performance.

Conducting polymers (CPs) are promising candidate materials for the catalyst support, as they allow to replace both the carbon and the polyelectrolyte (binder) in the catalyst layer of MEAs [2–10]. Polypyrrole (PPy) is mechanically and chemically stable and easy to prepare. It is permeable to gases and water, and exhibits both electronic and ionic conductivity [2]. Due to these unusual properties, a two-phase boundary in the catalyst layer is sufficient for the electron and proton transfer for the electrochemical reaction, as compared to the multiphase boundary when carbon is used as catalyst support. For this reason, a better utilization of the novel catalyst support material is expected. In addition, PPy in situ polymerisation inside proton exchange membranes can result in an efficient barrier to methanol crossover from the anode to the cathode [11–14].

Until now, however, most of the research related to the use of CPs for DMFC applications is focused on the performance of PPy modified membranes by using different polymerisation methods and reaction conditions, such as concentration of monomer, and oxidant types [11–16]. The transport properties of some PPy modified membranes from the literature are

---

[*] Corresponding author.
E-mail address: lilei0323@yahoo.com.cn (L. Li).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.02.008

Table 1
Transport properties of PPy modified composite membranes described in the literature

	Oxidant	Water uptake (wt%)	Relative conductivity	Relative methanol permeability	Ref.
Nafion 115	–	24.6	1 (0.032 S cm^{-1})	1 (2.6×10^{-6} cm^2 sec^{-1})	[14,16]
PPy/Nafion	H_2O_2	19.2	0.712	0.381	[14,16]
PPy/Nafion	H_2O_2		0.561	0.580	[11]
	H_2O_2/H_2SO_4 (aq)		0.545	0.804	[11]
PPy/Nafion	$Fe(NO_3)_3$	18.5	0.727	0.832	[12]
PPy/Nafion	$(NH_4)_2S_2O_8$	22	0.5	0.616	[13]
SPEEK*			1 (0.049 S cm^{-1})	1 (4.1×10^{-6} cm^2 sec^{-1})	[15]
PPy/SPEEK*	H_2O_2		0.531	0.375	[15]

*SPEEK: sulfonated poly(ether ether ketone), the degree of sulfonation 0.65.

summarised in Table 1. Studies dealing with the direct application of CPs as the catalyst support in the fuel cell are rare, it appears that only Jüttner et al. [3] and Qi et al. [2] have reported the direct application of PPy as a catalyst support in MEAs. Qi has used hot pressing of polystyrene sulfonate-doped PPy particles impregnated with Pt particles and bonded by Teflon on the Nafion membrane surface. Although the electrocatalytic activity of this electrode has been proved, the negative influence of high temperature on the properties of PPy particles and poor adherence between the catalyst layer and the membrane must be considered. Recently, a novel method for direct deposition of thin Pt catalyst layers on Nafion membranes impregnated with PPy was proposed for unitized regenerative fuel cells (URFC) [6]. This new method has been considered as an alternative way of preparation, avoiding the application of high temperature and poor adherence.

For this reason, the preparation and characterization of new MEAs based on PPy modified Nafion membranes as a catalyst support for DMFC application is reported in this study. The chemical and electrochemical properties of the prepared PPy-modified Nafion composite membranes and Pt/PPy/Nafion MEAs were studied.

2. Experimental

2.1. Membrane pre-treatment

Nafion 117 membranes were cleaned by immersion in boiling 3% H_2O_2 and 1 M H_2SO_4 for 1 h each. The membranes were then rinsed in boiling de-ionized water for 1 h, and the procedure was repeated at least twice to remove sulphuric acid completely. After this purification procedure, the membranes were stored in de-ionized water at room temperature before use.

2.2. PPy/Nafion composite membrane

Polypyrrole-modified Nafion composite membranes were prepared by the following procedure. First, the Nafion membrane was impregnated in 0.1 M pyrrole monomer aqueous solution at room temperature. In our experiments, the impregnation times were 5, 20 and 40 min, respectively. Pyrrole monomers were absorbed into the membrane during the impregnation process, which caused the colour of the membrane to change from transparent to yellowish. Then the membrane was placed in a two-compartment glass cell, and one side of it was exposed to 0.5 M $FeCl_3$ solution for 1 h at room temperature. After polymerisation, the resulting PPy/Nafion composite membrane was boiled in 1 M H_2SO_4 and de-ionized water for 1 h each. All the PPy/Nafion composite membranes were black.

2.3. Characterization of PPy/Nafion composite membrane

2.3.1. Thermal analysis

To analyze the thermal stability of PPy/Nafion composite membranes, thermogravimetric analysis (TGA) was carried out using a thermal balance (LCT-2, Beijing Optical Instruments Co.). Samples of approximately 15–20 mg were first dried at 100 °C for 24 h, and then programmed from 30 to 500 °C at the rate of 10 °C/min under a nitrogen atmosphere.

2.3.2. Proton conductivity

The proton conductivity of the PPy/Nafion composite membranes was derived from DC measurements using a potentiostatic four-electrode technique at room temperature [17,18]. For this the test membrane was placed in a two-compartment glass cell. Each compartment was filled with 1 M H_2SO_4 and contained a Pt counter electrode as well as an Ag–AgCl reference electrode with Luggin capillary. All electrodes were connected to the terminals of a potentiostat (EG&G Princeton Applied Research, Model 273 Potentiostat/Galvanostat). The ionic current I through the membrane was measured as a function of the potentiostatically controlled potential difference ΔE between the tips of the Luggin capillaries. The proton conductivity σ was calculated as follows:

$$\sigma = \frac{l}{RA}$$

where R is the resistance of the PPy/Nafion composite membrane which was calculated from the slope of the linear plot I versus ΔE, l is the thickness, and A is the membrane area. To determine the electrolyte resistance between the membrane and the two Luggin capillaries, a measurement was carried out without membrane.

2.3.3. Methanol permeability

In our experiments, two methods were used to measure the methanol permeability of samples. Methanol permeability was measured using a diaphragm cell at room temperature

[19], and under fuel cell conditions at 80 °C [20], respectively.

Method 1: The glass cell consisted of two identical compartments (V = 16 ml), separated by the test membrane and containing 1 M methanol solution on one side and de-ionized water on the other side. Both compartments were magnetically stirred during the experiment. The methanol permeated through the membrane into the de-ionized water with increasing time. The concentration of permeated methanol was measured by GC (FULI 9790 Gas Chromatograph). The methanol permeability was calculated from the slope of the linearized plot of the methanol concentration versus the permeation time.

Method 2: Methanol permeability of membranes at 80 °C was tested under fuel cell condition (electrolysis mode) [20]. The fuel cell configuration is shown in Fig. 1. One molar methanol solution was fed to the left side electrode as in a DMFC. Then methanol permeated through the left carbon cloth backing, the thin Pt catalyst layer and the membrane tested. The flux rate of permeating methanol was determined by measuring the steady-state limiting current density (J_{lim}) resulting from the complete methanol oxidation at the membrane/Pt catalyst interface on the right side in a nitrogen-saturated water atmosphere. The membrane electrode assembly (MEA) was manufactured by hot pressing at 6 bar and 130 °C during 4 min. The PPy film of the PPy/Nafion composite membranes was contacted with the cathode (electrolysis mode). Linear sweep voltammograms (LSV) was recorded with EG&G potentiostat with sweep rate 1 mV s^{-1} at 80 °C.

2.3.4. Water uptake

Equilibrium absorption of deionized water in membrane samples was determined at room temperature. The wet weight (G_w) of membrane samples was measured immediately after removing excess water from the membrane surfaces. The membrane dry weight (G_d) was obtained after drying the wet membrane in an vacuum oven for 24 h at 80 °C. The water uptake of the membrane at room temperature was calculated as follows:

$$\text{Water uptake} = \frac{G_w - G_d}{G_d} \times 100\%$$

2.4. Pt/PPy/Nafion electrode

The Pt catalyst deposited onto the PPy/Nafion composite membrane was prepared by using H_2PtCl_6 as Pt precursor and $NaBH_4$ as reducing agent. The PPy/Nafion membrane was placed in a two-compartment cell with 10 mM H_2PtCl_6 solution on one side and 1 M $NaBH_4$ solution on the other side. The reaction was carried out at room temperature, and the reduction time was fixed to 1.5 h. The opposite face of the Pt/PPy/Nafion electrode was deposited by the same method. After deposition, the resulting electrode was soaked in 1 M H_2SO_4 for 24 h and then washed with de-ionized water at room temperature. All electrodes were stored in de-ionized water before testing.

Cyclic voltammetry (CV) and methanol oxidation measurements on Pt/PPy/Nafion electrodes were carried out using a conventional 3-electrode technique with a Model 273 Potentiostat/Galvanostat, EG&G Princeton Applied Research. A Pt/PPy/Nafion electrode connected to a stainless steel ring acted as the working electrode. The geometric area of the electrode was 0.785 cm^2. A Pt-foil was used as the counter electrode, and an Ag–AgCl electrode as the reference electrode. The temperature was controlled at 25 °C during the experiments. The electrolyte solution in CV was 1 M H_2SO_4.

The morphology of the Pt/PPy/Nafion electrode surface was studied by scanning electron microscopy (SEM, Philips XL-40).

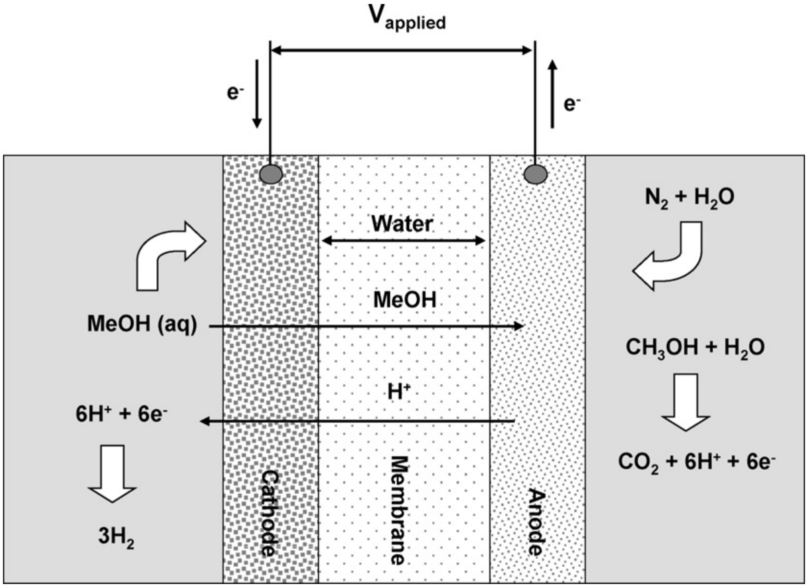

Fig. 1. Schematic diagram of the methanol permeation measurement in DMFC configuration. Methanol solution flows on the cathode side functioning as reference and counter electrode and humidified nitrogen on the anode that functions as the working electrode. Operating conditions: 1 M methanol solution with 10 ml min^{-1}, nitrogen-saturated water with 400 ml min^{-1}, 1.2 bar and 80 °C. Pt loading for anode and cathode were 1.0 mg cm^{-2}.

2.5. DMFC test

The fuel cell performance was evaluated by using a DMFC with an active area of 4 cm^2. The operating temperature of the cell was 80 °C. Two molar methanol solution was pumped through the DMFC anode at a flow rate of 10 ml min^{-1} at atmospheric pressure, and humidified oxygen gas was fed to the cathode at a pressure of 0.1 MPa.

3. Results and discussion

3.1. Characteristics of the PPy/Nafion composite membrane

In our experiments, several kinds of PPy modified Nafion composite membranes with different impregnation time of the Nafion in the pyrrole solution were investigated. These modified membranes are named P/N005 for 5 min, P/N020 for 20 min, and P/N040 for 40 min of impregnation time, respectively. The degree of polymerisation of pyrrole and the amount of polypyrrole inside the PPy/Nafion composite membranes increased with increasing impregnation time.

Fig. 2 shows the TGA curves of Nafion and PPy modified Nafion composite membrane. The first weight loss appears in the temperature 80–250 °C, which is believed to be due to the loss of water. Despite drying each sample at 100 °C for 24 h, membrane had residual water which was freezingly boundary water [21]. Vaporization behaviour of this water is different from that of bulk water. It could not be removed completely at 100 °C, due to the interaction with the sulfonic acid groups of Nafion. The second weight loss appears in the temperature 250–500 °C, which was associated with a dedulfonation process. Due to the ionic interaction between the secondary ammonium groups of the polypyrrole and the sulfonated acid groups of Nafion in the PPy/Nafion composite membranes, it reduced the weight loss of composite membranes compared with the pure Nafion membrane in the temperature 250–500 °C. This means the incorporation of PPy can improve the thermal stability of membranes. The same behavior has been obtained by Park et al. [14].

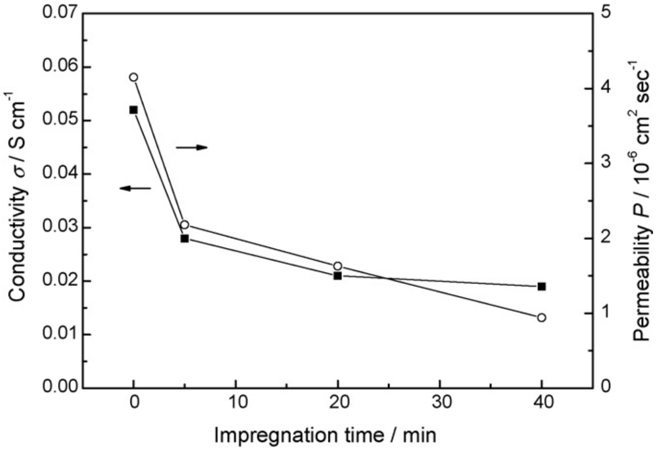

Fig. 3. Proton conductivity and methanol permeability of Nafion 117 and PPy/Nafion composite membranes at room temperature.

The cell performance in a DMFC, apart from the Pt-loading, is mainly determined by the proton conductivity and the methanol crossover. In general, a good performance requires that the proton exchange membranes show high proton conductivity and low methanol crossover. Fig. 3 gives the proton conductivity and the methanol permeability of these composite membranes at room temperature as a function of the impregnation time. Clearly, with increasing impregnation time, both proton conductivity and methanol permeability of the composite membranes decrease. A similar phenomenon has been reported in the literature [11–14,16,22]. Fig. 4 shows LSVs between 100 and 900 mV at a 1 mV s^{-1} sweep rate for Nafion 117 and P/N composite membranes. Cell voltage is controlled by the cathodic hydrogen evolution and anodic methanol oxidation. The cell current limitation under 650 mV is caused by transport limitation of the methanol oxidant through membrane. In the kinetically

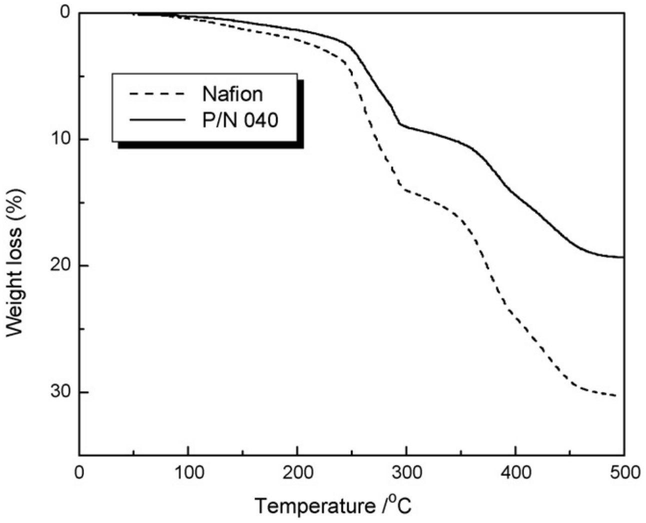

Fig. 2. TGA curves of Nafion 117 and P/N 040 composite membrane.

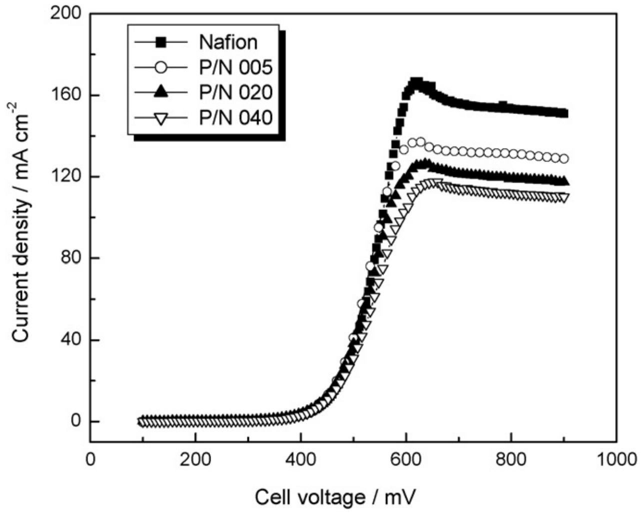

Fig. 4. Methanol permeation measurement of PPy/Nafion composite membranes at 80 °C in DMFC configuration.

controlled region (400–550 mV) the overpotential values are similar for all membranes. The small current peak near 600 mV results from oxidation of the methanol stored in the reaction and backing layers of the GDE anode. Permeation-controlled methanol oxidation takes place only after total consumption of the methanol in the GDE structure (650–900 mV). As expected, the limiting diffusion current density decreases with the increasing impregnation time. For Nafion 117, the limiting diffusion current density is about 150 mA cm^{-2}, which is in good agreement with data reported by Ren et al. [20]. The limiting values of the PPy modified Nafion composite membranes correlate well with the methanol permeation experiments in Fig. 4.

There are two main factors affecting the conductivity and the methanol permeability of PPy/Nafion composite membranes. One is the ion association of PPy and the sulfonic acid groups of Nafion, which leads to electrostatic crosslinking inside the Nafion ionomer, a decreased mobility of the ionic clusters, contraction of pores, and therefore a decrease of the water uptake, the proton conductivity and the methanol permeation of the membranes. Another factor is that the volume physically occupied by PPy reduces the free volume of the Nafion pores (if it is assumed that the membrane does not swell to accommodate the PPy).

Table 2 shows that the relative proton conductivity of the composite membranes is higher than the relative methanol permeability. This means that the methanol permeability was reduced more than the proton conductivity despite the swelling effect of the ionic clusters. Hence, PPy modified Nafion composite membranes are promising new membranes for DMFC applications. This has been verified in DMFC tests by several groups [12,14,22].

Table 2
Transport properties of Nafion and PPy/Nafion composite membranes at room temperature

	Nafion 117	P/N 005	P/N 020	P/N 040
Water uptake (wt%)	25.3	23.4	22.3	20.1
Relative proton conductivity	1	0.538	0.404	0.365
Relative methanol Permeability	1	0.525	0.393	0.227
Thickness	185	187	190	195
Amount of PPy (wt%)	0	2.5	5.8	9.2

3.2. Electrochemical properties of Pt/PPy/Nafion electrode

When the Pt/Nafion electrode was fabricated in the absence of polypyrrole, the Pt particles formed on the Nafion surface were easily peeled off. In the presence of polypyrrole, we found that the Pt particles as well as adhered well to the Nafion surface. The difference of adhesion can be explained by considering the mechanism of the Pt reduction process. Liu et al. [23] reported that platinum nucleation is initiated by chemical reduction after introducing the reductant into the platinic chloride solution. As the size of the particles increases, the growth mechanism of the particles and their aggregation to clusters is turned into a predominantly electroless reaction, i.e. the electron

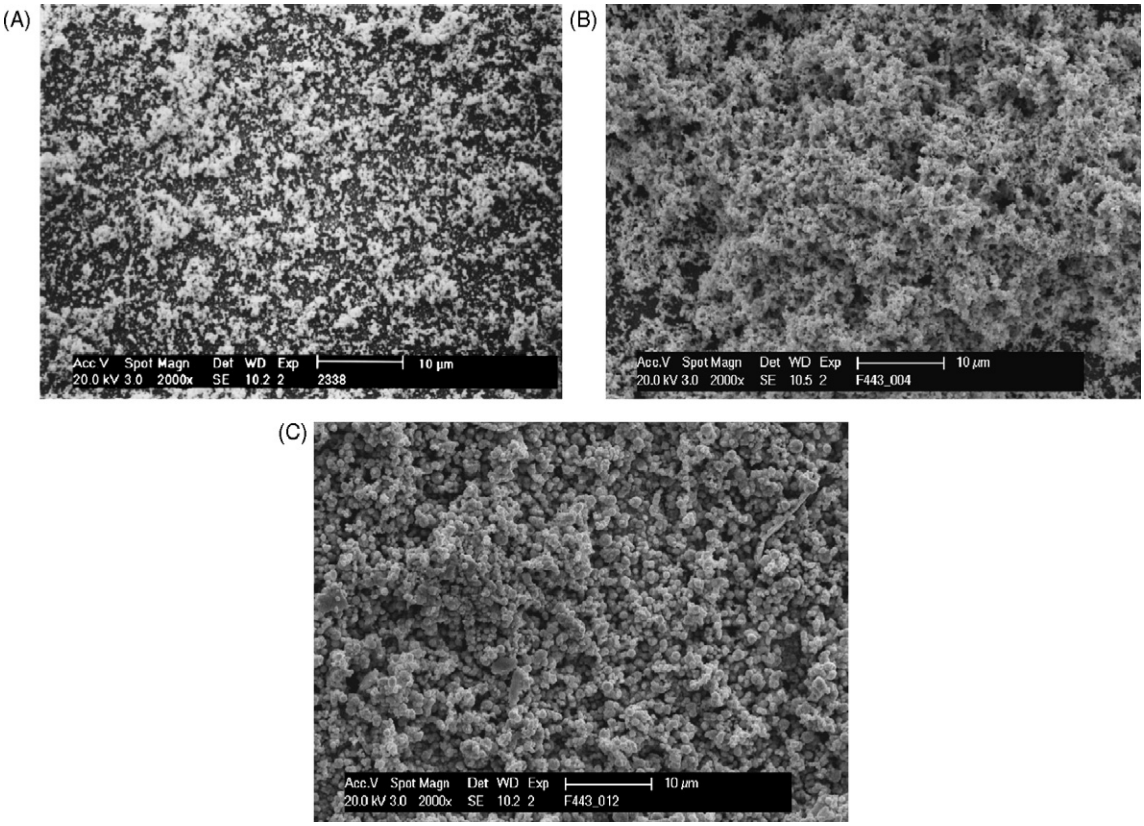

Fig. 5. SEM images of Pt/PPy/Nafion electrode surfaces with different Pt loadings. (A) 0.15 mg cm^{-2}, (B) 0.54 mg cm^{-2} and (C) 0.67 mg cm^{-2}.

is produced by an electroless reaction. The electron cannot be transported inside the poorly electron-conductive Nafion membrane. However, because the modification of the polypyrrole induces electronic conduction, the adhesion of Pt on the membrane surface is significantly enhanced. Therefore, the oxidation state of polypyrrole bonded with sulfonic acid groups to the Nafion membrane is an important factor to control the dispersion and the location of the Pt catalyst.

In our experiments, the Pt loading could be controlled by the impregnation time of the Nafion in the pyrrole monomer solution. When the impregnation time was 5, 20 and 40 min, the loading of Pt was 0.14, 0.54 and 0.67 mg cm^{-2}, respectively. Fig. 5 shows the morphology of the Pt/PPy/Nafion electrode surface for various Pt loadings. It is observed that Pt particles with a porous structure uniformly exist in the electrodes with a size less than 1 μm. The thickness of the catalyst layer in our electrodes was found to be about 3–6 μm. Because the deposition of Pt particles is predominantly controlled by an electroless reaction, as mentioned above, the electrode prepared for 5 min of impregnation time has a low PPy amount so that there are less Pt particles growing on the PPy/Nafion composite membrane surface.

Fig. 6 shows typical cyclic voltammograms (CV) of the Pt/PPy/Nafion electrodes in 1 M H_2SO_4 at room temperature. The measurements were carried out in the potential range from −0.25 to 1.2 V versus Ag–AgCl at a scan rate of 40 mV s^{-1}. In our experiments, the CV measurements of our electrodes were cycled continuously for 1000 times. The CV results of samples did not change, which means the electrodes were very stable. The cathodic and anodic peaks observed between –0.25 and 0.1 V correspond to the adsorption and desorption of hydrogen ions on the Pt catalysts, respectively. The active area of the Pt catalyst was calculated from the area of the hydrogen absorption region obtained by multiplying the current density with the scan time and comparing it to the area of the hydrogen adsorption region of a mono-layer of platinum, which is about 210 μC cm^{-2} [24]. The roughness factor and the active surface area of the prepared Pt/PPy/Nafion electrodes are given in Table 3. The roughness factor is the ratio of the actual adsorption charge to the theoretical adsorption charge on smooth platinum. The active surface area is the ratio of the roughness factor to the Pt loading. From the data in Table 3, it is found that the roughness factor and the active surface area of the Pt/PPy/Nafion electrodes increased with increasing time of impregnation of Nafion in the pyrrole monomer solution. It is assumed that the formation and the amount of Pt particles formed on Nafion are affected by the degree of polymerization of pyrrole. The active surface area of the electrode with a loading of 0.67 mg cm^{-2} Pt was 176 cm^2 mg^{-1} in our experiments, which is still lower than that of a commercial Pt/C electrode (e.g. for a loading of 2 mg cm^{-2} Pt ca. 575 cm^2 mg^{-1} [25]). The Pt particle size of the commercial Pt/C electrode is normally around 3–5 nm. However, our Pt particle size was about 100–200 nm.

3.3. DMFC performance of Pt/PPy/Nafion electrode

Fig. 7 shows the current–voltage performance curves of a single DMFC prepared with Pt/PPy/Nafion electrodes with different Pt loadings. Because both sides of the Pt/PPy/Nafion electrodes were made one after the other, the resulting Pt loading on either side is not exactly the same. Therefore, the side with the higher Pt loading was selected as the anode side in our experiments. The performance of the fuel cells equipped with the Pt/PPy/Nafion electrodes with different Pt loadings was evaluated in presence of 2 M methanol solution and water-saturated oxygen gas with an active area of 4 cm^2 at 80 °C. The best performance was obtained for the MEA with 0.67 mg cm^{-2} of Pt for the anode and 0.56 mg cm^{-2} of Pt for the cathode. The maximum of power density of 12.25 mW cm^{-2} was obtained at 0.175 V. To confirm the durability of cell performance in our electrode, the cell performance of the P/N 040 electrode was continuously tested in a single DMFC for 100 h. From Fig. 8, it can be found that the cell performance of the P/N 040 electrode was maintained for long time.

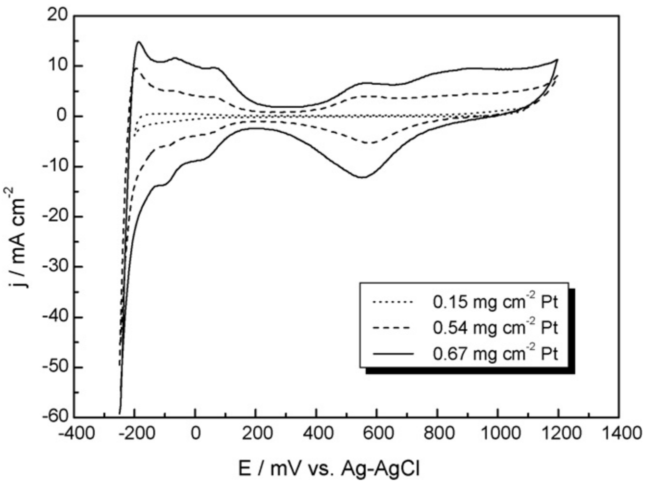

Fig. 6. Cyclic voltammograms of Pt/PPy/Nafion membrane electrodes with different Pt loadings. Scan rate: 40 mV s^{-1}; temperature: 25 °C; electrolyte: 1 M H_2SO_4.

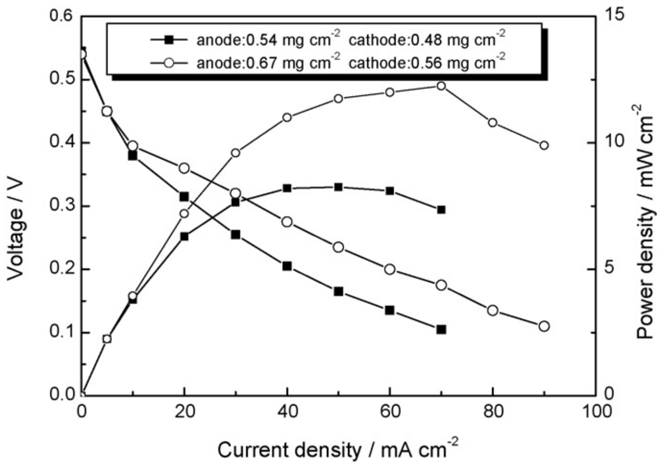

Fig. 7. DMFC performances of Pt/PPy/Nafion electrodes with different Pt loadings. Operating conditions: 2 M methanol solution (10 ml min^{-1}); pure O_2 (0.1 MPa) and 80 °C.

Table 3
Electrochemical properties of Pt/PPy/Nafion electrodes

Electrode	Impregnation time (min)	Pt loading (mg cm^{-2})	Charge density (mC cm^{-2})	Roughness factor	Pt surface area (m^2 g^{-1})
P/N 005	5	0.15	0.902	4.3	2.86
P/N 020	20	0.54	18.67	89	16.5
P/N 040	40	0.67	24.76	118	17.6

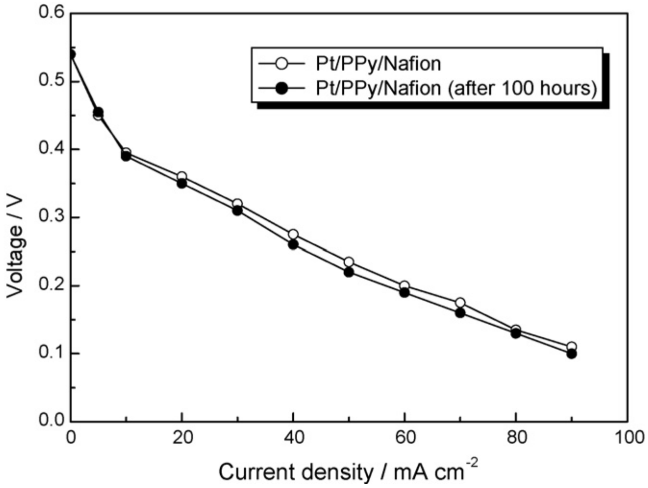

Fig. 8. The durability of P/N 040 electrode in running DMFC condition. Operating conditions: 2 M methanol solution (10 ml min^{-1}); pure O_2 (0.1 MPa) and 80 °C.

4. Conclusion

A novel membrane electrode assembly based on direct deposition of the Pt catalyst on the membrane for DMFC applications was prepared in this study. Both proton conductivity and methanol permeability of the PPy-modified Nafion composite membranes decrease with increasing impregnation time of the Nafion membrane in the pyrrole monomer solution. The methanol permeability of the PPy/Nafion composite membranes was reduced more than the proton conductivity despite the swelling effect of the ionic clusters. Pt particles can be easily deposited on the Nafion membrane in presence of PPy. The roughness factor and the active surface area of the Pt catalysts increased with increasing PPy loading. Among single DMFCs with different Pt loadings, the MEA with 0.67 mg cm^{-2} of Pt on the anode and 0.56 mg cm^{-2} of Pt on the cathode showed the best performance.

The results show that direct deposition of the Pt catalyst on a polypyrrole-modified Nafion membrane is a promising method for the preparation of new MEAs for DMFC applications. Further investigations will be needed to establish the optimal conditions for the fabrication of Pt/PPy/Nafion electrodes. In addition, for the DMFC anode, it would also be necessary to deposit a mixed Pt and Ru metal or alloy catalyst to reach high activity for methanol oxidation.

Acknowledgements

This work was financially supported by the Sino-German Center for Research Promotion in Beijing and by the German Science Foundation (Deutsche Forschungsgemeinschaft) under contract JU 201/10.

References

[1] S.S. Kocha, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells, Fundamentals Technology and Applications, vol. 3, John Wiley & Sons, New York, 2003, pp. 538–565.
[2] Z. Qi, M.C. Lefebvre, P.G. Pickup, J. Electroanal. Chem. 459 (1998) 9.
[3] K. Jüttner, K.-M. Mangold, M. Lange, K. Bouzek, Russ. J. Electrochem. 40 (2004) 359.
[4] H. Laborde, J.-M. Leger, C. Lamy, J. Appl. Electrochem. 24 (1994) 219.
[5] H. Laborde, J.-M. Leger, C. Lamy, J. Appl. Electrochem. 24 (1994) 1019.
[6] H. Lee, J. Kim, J. Park, Y. Joe, T. Lee, J. Power Sources 131 (2004) 188.
[7] J.-H. Park, J.-H. Kim, H.-K. Lee, T.-H. Lee, Y.-I. Joe, Electrochim. Acta 50 (2004) 769.
[8] K. Jüttner, K.-M. Mangold, M. Lange, K. Bouzek, Russ. J. Electrochem. 40 (2004) 17.
[9] P.G. Pickup, C.L. Kean, M.C. Lefebvre, G. Li, Z. Qi, J. Shan, J. New Mater. Electrochem. Syst. 3 (2000) 21.
[10] J.-F. Drillet, R. Dittmeyer, K. Jüttner, L. Li, K.-M. Mangold, Fuel Cells, in press.
[11] J. Zhu, R.R. Sattler, A. Garsuch, O. Yepez, P.G. Pickup, Electrochim. Acta 51 (2006) 4052.
[12] E.B. Easton, B.L. Langsdorf, J.A. Hughes, J. Sultan, Z. Qi, A. Kaufman, P.G. Pickup, J. Electrochem. Soc. 150 (2003) 735.
[13] F. Xu, C. Innocent, B. Bonnet, D.J. Jones, J. Rozière, Fuel Cells 5 (2005) 398.
[14] H.S. Park, Y.J. Kim, W.H. Hong, H.K. Lee, J. Membr. Sci. 272 (2006) 28.
[15] S. Xue, G. Yin, Electrochim. Acta 52 (2006) 847.
[16] H.S. Park, Y.J. Kim, W.H. Hong, Y.S. Choi, H.K. Lee, Macromolecules 38 (2005) 2289.
[17] C. Ehrenbeck, K. Jüttner, Electrochim. Acta 41 (1996) 1815.
[18] R.H.J. Schmitz, K. Jüttner, Electrochim. Acta 44 (1999) 1627.
[19] V. Tricoli, J. Electrochem. Soc. 145 (1998) 3798.
[20] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
[21] Y.S. Kim, L. Dong, M.A. Hickner, T.E. Glass, V. Webb, J.E. McGrath, Macromolecules 36 (2003) 6281.
[22] N. Jia, M.C. Lefebvre, J. Halfyard, Z. Qi, P.G. Pickup, Electrochem. Solid-State Lett. 3 (2000) 529.
[23] R. Liu, W.H. Her, P.S. Fedkiw, J. Electrochem. Soc. 139 (1992) 15.
[24] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, Electrochim. Acta 43 (1998) 3693.
[25] M. Shen, S. Roy, K. Scott, J. Appl. Electrochem. 35 (2005) 1103.