Desalination and Water Treatment
www.deswater.com

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doi: 10.5004/dwt.2010.1103

14 (2010) 101–105
February

Preparation of gas diffusion electrodes for high temperature PEM-type fuel cells

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Received 3 August 2009; accepted 22 December 2009

ABSTRACT

Gas diffusion electrodes (GDEs) were prepared and optimized for testing a novel electrolyte for PEM-type fuel cells operating at elevated temperatures based on polymer-supported ionic liquid (IL). For the construction of the GDE, a commercial E-TEK gas diffusion layer was employed. On its surface, a catalyst layer (CL) was deposited by the brushing technique. The catalyst ink contained a commercial, carbon-supported platinum catalyst (30 wt.% – E-TEK), polymer binder and solvents. As a binder, polytetrafluoroethylene (PTFE) or polybenzimidazole (PBI) was applied. Various amounts of binder were used in the CL. The utilization of PBI was found to be more advantageous than PTFE. 15 wt.% PBI was identified as the optimum amount in the CL. Such electrodes exhibit a relatively good performance in a laboratory-scale single fuel cell employing commercial PBI–based membranes doped by H_3PO_4 (50 mW/cm^2 at 0.4 V and 140°C). Although polymer-supported IL-based membranes exhibit relatively high ionic conductivity, the performance of a fuel cell utilizing these membranes produced power output approximately 30 times lower compared to PBI-based membranes.

Keywords: Gas diffusion electrode; Polymer electrolyte; Ionic liquid; PBI; Fuel cell

1. Introduction

Proton Exchange Membrane Fuel Cells (PEM FCs) represent a prospective alternative as an energy source, mainly for mobile applications (vehicles, notebooks). At present, however, they suffer from several serious drawbacks which are mainly related to the slow electrode reactions kinetics. They thus require a high loading of platinum metal-based electrocatalysts. At the same time it is sensitive to several catalyst poisons. The majority of these problems may be solved by increasing PEM FCs' operating temperature up to 200°C. An increase in operating temperature results in important changes in the water management of the fuel cells. This concerns the polymer electrolyte membrane as well as the gas diffusion electrode (GDE). Whereas significant attention has been paid to the first issue during the last few years [1–5], attempts to solve the problem of the related GDE have been significantly less systematic.

There are two main concepts currently used for GDE preparation. The first one is based on the method used in phosphoric acid fuel cell technology. Here PTFE is used as a binder in the catalyst layer (CL). Ionic contact is provided by phosphoric acid added directly or squeezed out of the membrane [5]. The second concept is based on the conventional low temperature PEM fuel cell [4,5]. Here the incorporation of a suitable

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Presented at the Fourth Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2009), Prague, 7-11 June, 2009.

polymer as a binder into the CL represents an important problem. At the same time it enables the occurrence of a three-phase contact (*i.e.* access of gas, electric contact with the current collector and proton conducting contact with the electrolyte on one site). Regarding this problem, Modestov *et al.* [6] found Nafion to be more suitable than Teflon at temperatures up to 160°C. They suggested keeping the minimal concentration of the binder in the CL necessary just to maintain the integrity of the layer. The usage of polybenzimidazole (PBI) or a blend of PBI with other polymers as a binder in the CL was also often reported in the literature [7].

The present research is devoted to the development of novel high temperature PEM FC membranes based on polymer-supported ionic liquid (IL). ILs [8,9] are salts characterized by their liquid state at relatively low temperatures, now often even at the room temperature. They are ion-conductive, have negligible vapour pressure up to their decomposition temperature and exhibit good thermal and electrochemical stability. On account of these advantageous properties, they have good potential for applications in high temperature PEM FCs as a proton conductor.

The aim of this contribution was to develop an electrode compatible with a novel type of membrane based on IL. It should permit the reproducible determination of the performance of a fuel cell equipped with such a membrane. In order to develop such GDE, commercially available PBI-based phosphoric acid doped membranes were employed. The data achieved by this means were used as a reference for the evaluation of the newly developed membranes. Afterwards the compatibility of GDEs with novel IL-based membranes was examined and means of refining it were tested.

For this purpose, a 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][Tf])-based, Nafion-supported membrane was chosen as a model IL-based membrane. The reason was its satisfactory mechanical properties and its ionic conductivity determined during the preceding part of this study. [BMIM][Tf] is miscible with water in the entire concentration range and it has thus higher potential for the proton conductivity.

2. Experimental

2.1. Membrane preparation and characterization

IL-based membranes were prepared by dissolving Nafion and [BMIM][Tf] in propan-2-ol, casting the film on a Nalgen dish and evaporating the solvent. The evaporation time was 48 h at 40°C. The content of [BMIM][Tf] in the membranes used in this contribution was 50 wt.%.

The ionic conductivity both of the bulk [BMIM][Tf] and of the IL-based Nafion membranes was measured using a Solartron SI 1250 frequency response analyzer connected to a Solartron SI 1287 electrochemical interface. The conductivity of the bulk IL was measured in a capillary cell using a two-electrode arrangement. The conductivity of the membranes was determined in the longitudinal direction in a tempered box under nitrogen atmosphere at controlled humidity in a four-electrode arrangement.

2.2. GDE preparation

A commercial carbon-supported Pt catalyst was used for the electrode construction utilizing the method of brushing the catalyst suspension onto a commercial gas diffusion layer (GDL). The main constituents of the suspension are dispersed catalyst, polymeric binder and solvent. As the polymeric binder Teflon (PTFE) or PBI was employed. As the solvent demineralized water mixed with propan-2-ol was used in the case of PTFE as a binder. Dimethylformamid (DMFA) was used in the case of PBI binder.

Before brushing, the suspension was treated in an ultrasound bath for 30 min at ambient temperature. Prepared, slightly viscous ink was applied to the GDL. Between each layer the electrode was dried at 80°C under nitrogen atmosphere. The amount of catalyst deposited was determined using an analytical balance. A platinum load of 0.5 mg/cm^2 was used. After the last layer had been brushed, in the case of PBI binder the electrode was dried at 120°C under nitrogen atmosphere to remove the solvents completely. In the case of PTFE binder, the electrode was finally thermally treated at 350°C for 30 min under argon atmosphere.

2.3. Fuel cell experiments

Testing in the laboratory single fuel cell consisted of recording load curves and long-term constant voltage load at given temperatures (in the range of 95–160°C). To accomplish this task a DC Electronic Load (Iotech, CHINA) was used. The laboratory set up made it possible to control the temperature of the fuel cell, input gases and gas humidifiers. The flow of hydrogen was set at 30 ml/min and oxygen at 20 ml/min. The temperature of the humidifiers was kept at 50°C during all experiments.

The resistance of the fuel cell system was determined by impedance measurements in a two-electrode arrangement using the same instrumentation as in the case of the conductivity measurements of the membranes (see section 3.1).

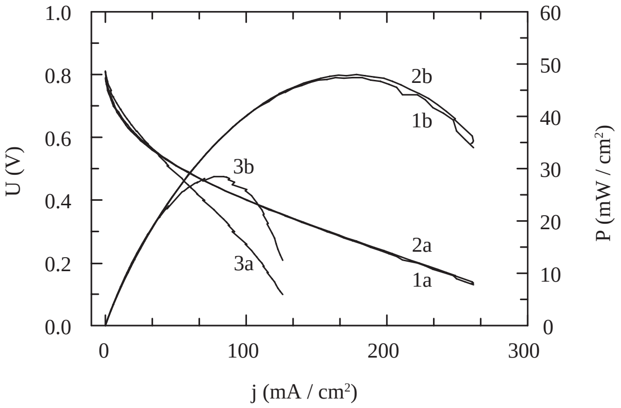

Fig. 1. U/j (marked by letter *a*) and P/j (marked by letter *b*) curves of MEA using GDEs with PTFE binder in CL (28 wt.%) in H_2/O_2 fuel cell, 6.25 cm^2 active area, PBI-based membrane doped by 400% of H_3PO_4, 20 ml/min O_2 and H_2 30 ml/min flow rate, temperature of humidifier 50°C, operating temperature: 1–95°C, 2–120°C, 3–140°C.

For the initial optimization, the electrodes were firstly tested employing a PBI-based commercial membrane doped by 400 wt.% of H_3PO_4. In the next step, the optimized electrodes were tested with Nafion-supported [BMIM][Tf]. The active electrode area comprised 6.25 cm^2 and the constriction moment of force was set at 2 Nm during the cell completion.

2.4. Chemicals and materials used

For the preparation of the GDEs and IL-based membranes, the following chemicals and materials were used. Carbon-supported Pt catalyst (30 wt.% of Pt) and carbon gas diffusion layer (GDL) by E-TEK (USA), 60 wt.% PTFE dispersion in water and HPLC quality propan-2-ol by Aldrich (FRG), PBI solution in N,N-dimethylacetamide by Celanese (F), Liquion 1100 (5 wt.% Nafion solution in propan-2-ol) by Ion Power (USA), N,N-dimethylformamide by Penta (CZ), [BMIM][Tf] 99% purity by Solvent Innovation (FRG). For the fuel cell experiments, hydrogen was used as the fuel (5.5 purity) and oxygen (2.5 purity) as the oxidant, both by SIAD (CZ).

3. Results and discussion

3.1. Optimization of electrodes with phosphoric acid-based membranes

3.1.1. PTFE as a binder

In the case of polytetraflourethylene as an inert polymeric material the proton conductivity can be supplied to the CL just by partial occupation of the pores (formed in CL by the evaporation of the solvent) by a liquid proton conductor, e.g. phosphoric acid or IL. Penetration of one of these media into the CL structure thus represents a direct prerequisite for the occurrence of three-phase contact in the bulk of CL and thus for sufficient catalyst utilization. Using PBI-based membranes with a high H_3PO_4 doping level of 400 wt.%, the acid squeezed from the membrane after the constriction of the fuel cell assembly typically impregnates the CL sufficiently.

In the present case, electrodes employing PTFE as a CL binder (28 wt.% of CL) showed a relatively good performance at temperatures up to 120°C. Above this temperature the performance of the fuel cell dramatically decreased. At 140°C the power density reached half of the value obtained at 120°C (see Fig. 1). This decrease in performance was reversible. After the temperature decrease to 120°C the performance of the fuel cell regained the original level. An explanation for such behavior is the insufficient penetration of the CL by phosphoric acid. Moreover, at elevated temperatures the membrane dimensions contracted due to the loss of traces of water. This resulted in the partial loss of contact on the electrode–membrane interface.

3.1.2. PBI as a binder

PBI was used as a binder in order to improve CL impregnation by phosphoric acid and thus to further increase catalyst utilization. An attempt was also made to impregnate CL by the IL used. The three-phase contact formation probability increase is expected to be a first effect. An improvement of the ionic contact between the CL and the polymer electrolyte membrane is also anticipated.

The different amounts of PBI in the catalyst ink had an important impact on the morphology of the CL. Exceeding a certain PBI concentration level, namely 15 wt.%, resulted in an irregular formation of the CL which was damaged by numerous cracks. Below this level, the surface of the GDE was relatively smooth. The formation of the cracks was caused by the dimensional instability of PBI during drying. This value is 20% lower than that recommended by other authors [5]. The reason is the thickness of the CL. In the current case, a catalyst with a lower Pt concentration on the catalyst support was used. This made it necessary to apply a thicker CL in order to obtain an identical Pt load compared to the more concentrated catalysts used in other studies. Such a CL is then more sensitive to the PBI content.

The results of the fuel cell experiments proved that the optimum concentration of PBI in CL is 15 wt.%.

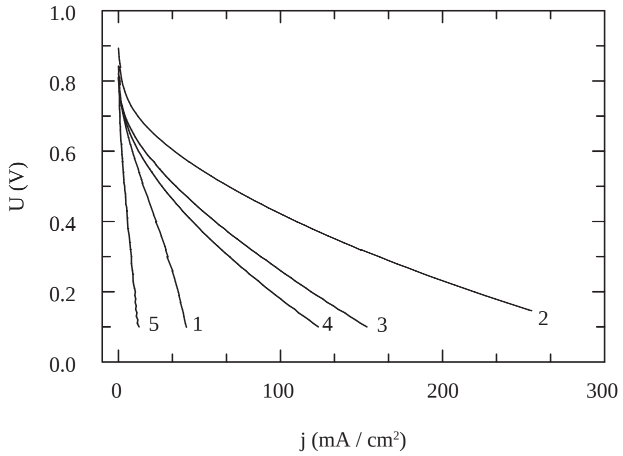

Fig. 2. U/j curves of MEA utilising GDEs with PBI as a binder in CL at 120°C, 6.25 cm^2 active area, PBI-based membrane doped by 400% of H_3PO_4, 20 ml/min O_2 and 30 ml/min H_2 flow rate, temperature of the humidifier 50°C, PBI content in CL: 1–10 wt.%, 2–15 wt.%, 3–20 wt.%, 4–22wt.%, 5–30 wt.%.

This is documented by Fig. 2. A lower content of PBI led to a low doping of the layer with phosphoric acid, resulting in insufficient three-phase contact. At the same time, the amount of polymer binder was not sufficient to maintain the integrity of the layer. At higher concentrations of PBI the layer was not effective because of the numerous cracks.

The GDE containing 15 wt.% of PBI in CL as the binder exhibited an increasing fuel cell performance with increasing operational temperature in the tested temperature range of 95–140°C, see Fig. 3. Electrodes prepared in this way were subsequently used for testing the selected polymer-supported IL-based membranes.

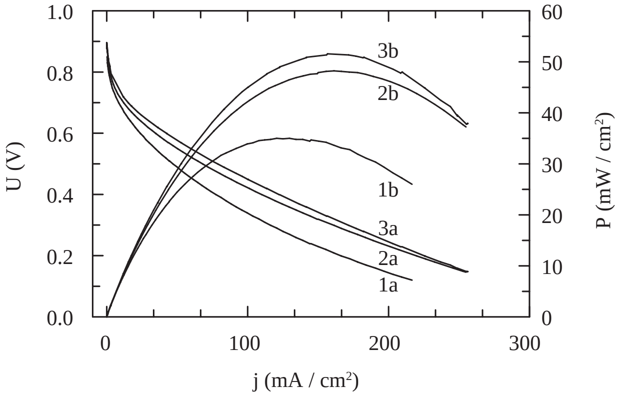

Fig. 3. U/j (marked by letter *a*) and P/j (marked by letter *b*) curves of MEA utilising GDEs with 15 wt.% of PBI in CL, 6.25 cm^2 active area, PBI-based membrane doped by 400% of H_3PO_4, 20 ml/min O_2 and 30 ml/min H_2 flow rate, temperature of the humidifier 50°C, operating temperature: 1–95°C, 2–120°C, 3–140°C.

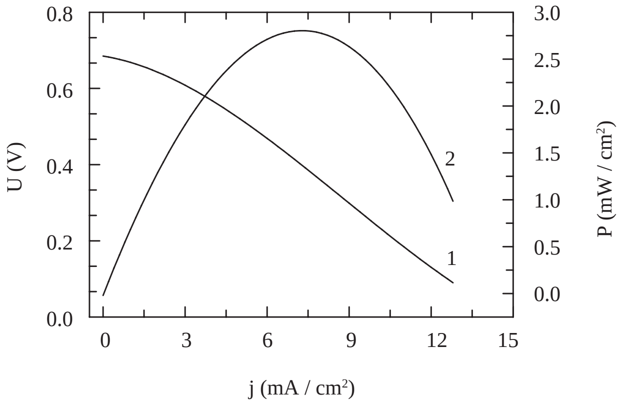

Fig. 4. U/j (marked by letter 1) and P/j (marked by letter 2) curves of MEA utilising GDEs with 15 wt.% PBI in CL and [BMIM][Tf]-based Nafion-supported membrane, membrane–electrode interface treated by 85 wt.% H_3PO_4, 6.25 cm^2 active area, 20 ml/min O_2 and 30 ml/min H_2 flow rate, temperature of the humidifier 50°C, operating temperature 130°C.

3.2. *Nafion-supported [BMIM][Tf]-based membrane in fuel cell*

The results obtained in the fuel cell utilizing Nafion-supported [BMIM][Tf] composite membranes were nearly 30 times lower compared with the results

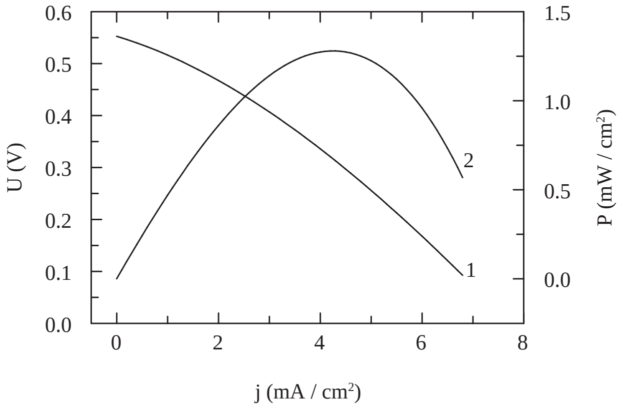

Fig. 5. U/j (marked by letter 1) and P/j (marked by letter 2) curves of MEA utilising GDEs with 15 wt.% PBI in CL and [BMIM][Tf]–based Nafion-supported membranes, membrane–electrode interface treated with 50 μl of [BMIM][Tf], 6.25 cm^2 active area, 20 ml/min O_2 and 30 ml/min H_2 flow rate, temperature of the humidifier 50°C, operating temperature 130°C.

obtained with a PBI-based membrane, see Fig. 4, although the membrane exhibited relatively high ionic conductivity (16.2 mS/cm at 140°C under dry atmosphere). An explanation for this fact can be found in:

a) the permeation of the gases through the membrane, resulting in ineffective utilization of the fuel and in the formation of mixed potential. The value of the open circuit voltage was below 0.7 V. (see Fig. 4 and Fig. 5.) This value is more than 0.2 V lower compared with PBI-based commercial membranes. This observation indicates the possibility of the appearance of permeation. The reason for such behavior may be that the membrane is perforated due to its insufficient mechanical properties. Another explanation is the enhanced permeability of the membrane filled, to a great extent, by IL. The application of supported IL membranes for gas separation is reported in the literature [10]. H_2 was found to be the most permeable gas in this type of materials.
b) insufficient proton conductive connection between the membrane and the GDE due to the low content of IL in the membrane (50% of total membrane weight compared with the PBI-based membrane doped by 400 wt.% of H_3PO_4). The amount of IL squeezed from the membrane by the constriction of the fuel cell assembly is not sufficient to provide satisfactory proton conductivity across the interface. This theory was supported by the results of the electrochemical impedance measurements. The resistance of the fuel cell system utilizing the IL-based membrane was as high as 2 Ω at 160°C. A comparison of this value with a value found for the PBI phosphoric acid-doped membrane under identical conditions, *i.e.* 0.06 Ω, clearly indicates insufficient proton conductivity of the IL-based system. Doping the CL of electrodes by immersion in 85% H_3PO_4 for 15 min brought about only a small improvement (25%). More extensive CL doping did not have a more positive effect. Treatment of the membrane–CL interface by 50 µl of [BMIM][Tf] also had a slightly positive influence on the resistance of the system (the resistance decreased from 2 Ω to1 Ω). Nevertheless, this is still an unacceptably high value. However, after this treatment the performance of the fuel cell did not improve. In fact, it decreased, see Fig. 5. Such behavior can be attributed to flooding of the CL pores by IL.
c) limited proton conductivity of IL, although it exhibited sufficient ionic conductivity during the ex-situ experimental tests.

4. Conclusion

The method of preparation of GDEs for application in a high temperature PEM FC employing the brushing of catalyst suspension onto a commercial gas diffusion layer was investigated. For this purpose, a commercial catalyst (30 wt.% Pt supported by carbon) was used. PBI proved to be a more appropriate material as a binder in the CL than polytetraflourethylene at operational temperatures above 120°C. The optimum content of PBI in the CL was found to be 15 wt.%. Employing commercial PBI-based membranes, the performance of the fuel cell was 50 mW/cm^2 at 0.4 V and 140°C.

The electrodes were tested with a 1-butyl-3-methylimidazolium triflouromethanesulfonate-based Nafion-supported membrane to prove their compatibility with a novel type of polymer-supported membrane based on ionic liquids. The fuel cell performance observed was approx. 30 times lower. Treating the membrane–electrode interface with phosphoric acid or IL did not improve cell performance significantly. The most probable explanation for the low performance of the fuel cell is the low proton conductivity or high hydrogen/oxygen permeability of the membrane.

Acknowledgement

This work was supported by the European Commission within the framework of the APOLLON B project under contract No. 033228 and by the Grant Agency of the Czech Republic within the framework of project No. 203/08/0465.

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