

Short communication

# Investigation of polyaniline impregnation on the performance of gas diffusion electrode (GDE) in PEMFC using binary of Nafion and polyaniline nanofiber

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## Abstract

In this work, a gas diffusion electrode (GDE) with a catalyst layer containing a mixture of Nafion and polyaniline (PANI) nanofiber was prepared by a simple method. The resulting GDE had good mechanical properties and acceptable electrochemical activity. This type of modified electrode could potentially be applied in the development of membrane–electrode assembly. The surface morphologies of the Nafion–PANI-modified GDE and the corresponding GDE modified with Nafion alone were characterized by scanning electron microscopy. The electrochemical properties of the electrodes were characterized using cyclic voltammetry, *I*–*V* polarization curves, AC impedance spectroscopy and chronoamperometry. The results indicated that, compared to the electrode with Nafion alone, the electrode containing PANI nanofiber in the catalyst layer had higher catalyst utilization for the oxygen reduction reaction. The improvement in electrode performance on introduction of PANI can be related to the increasing of good electronic conductance between agglomerations in parallel to ionic conductivity in the reaction layer due to the presence of homogeneously dispersed PANI nanofibular and Nafion.

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## 1. Introduction

A key aspect of recent intensive efforts aimed at developing proton exchange membrane fuel cells (PEMFCs) has been minimizing catalyst loading and maximizing catalyst utilization. Methods for increasing catalyst utilization include using platinum supported on high surface area carbon, impregnation of a proton conductor into the catalyst layer of the gas diffusion electrode (GDE), depositing a thin layer of platinum on the front side of the electrode, using thinner membranes, applying different electrode preparation procedures [1–8] and depositing a thin layer of supported electrocatalyst and a proton conductor on the

proton-conducting membrane or on the catalyst-free electrode [9,10]. The fuel cell performance has been increased still further by adding a proton-conducting polymer (such as Nafion) into the catalyst layer. In Nafion-modified electrodes, the Pt catalyst near or directly in contact with the Nafion membrane is utilized most efficiently. However, the utilization drops off on moving deeper into the catalyst layer, largely due to the limited proton conductivity of the catalyst layer. Nafion solution can be applied onto preformed electrodes or directly mixed with the catalyst during ink preparation [11–13]. The presence of Nafion in the catalyst layer increases the proton conductivity of layer.

Many studies have explored methods for introducing the ionomer into the catalyst layer and optimizing the amount of Nafion incorporated into the electrode structure [14–18]. At low Nafion content, not all the catalyst particles are connected to the membrane by a Nafion bridge. If the Nafion content is too

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high, however, not all the catalyst particles are electronically connected to the diffusion layer. At the optimal Nafion content, all the catalyst particles have good connections for ionic and electronic conduction. Previous results have indicated that if the procedure for adding Nafion solution to the catalyst layer and then drying the layer is carried out in a proper manner, the Nafion loading and method used to introduce the ionomer to the catalyst layer have the greatest influence on the ionic resistance of the catalyst layer and the performance of the electrode. When designing electrodes based on a mixture of carbon-supported catalyst and Nafion, the proportions of the components must be chosen such that a stable “three-phase” boundary is formed, in which the gas, ion conductor and catalytically active electronically conducting phase are all present. This requirement limits the amount of Nafion that can be added because the morphology, low gas permeability and poor electronic conductivity of Nafion disrupt this boundary, adversely affecting cell performance [19–21]. This limitation, along with the high cost of Nafion, has led to interest in finding alternative methods for providing proton and electron conductivity in the catalyst layer.

One alternative to constructing electrodes from Nafion alone is to use Nafion in conjunction with an electron-conducting polymer (ECP). The main advantage of using a mixture of a ECP and Nafion that, when used together, they give good electronic conductance in parallel with ionic conductivity between particles [22]. The catalytic activities of ECP/Pt composites for various reactions has been intensively studied [23–27]. From an application viewpoint, polyaniline (PANI) is considered one of the best organic-conducting materials, and is the ECP that has received the most attention to date. PANI is usually synthesized in aqueous acid solution, either chemically or electrochemically, and generally forms good-quality nanofibers [28].

The aim of the present work was to prepare a catalyst layer containing a PANI–Nafion composite. Since Nafion is not an electronic conductor, it was not possible to prepare the film by direct electrosynthesis. Therefore, Nafion solution was introduced into the catalyst layer by the brushing method which gives an inhomogeneous dispersion of Nafion in the catalyst layer. PANI nanofiber was synthesized by electropolymerization of aniline and trifluoromethanesulfonic acid (TFMSA). The electropolymerization procedure produced a homogenous dispersion of PANI nanofibular in the active sites for polymerization in the Nafion-modified catalyst layer and formed a homogenous dispersion across the catalyst layer. The proton-conductive monomer used in the polymerization, TFMSA, has an excellent ability to dissolve and diffuse oxygen and improved the proton conductivity of the PANI nanofiber in the reaction layer [29,31]. Here, we show that the presence of PANI and Nafion in the catalyst layer increases the utilization of the catalyst and reduces resistant polarization of the GDE related to the electron and proton conductivity of PANI and Nafion. Fig. 1a and b shows schematic diagrams of the homemade PEMFC electrode structure before and after modification with PANI, respectively.

Examination of the morphology of the prepared composite using scanning electron microscopy (SEM) confirmed that the PANI nanofibers formed on the catalyst layer. The present work describes a relatively simple method for preparing a

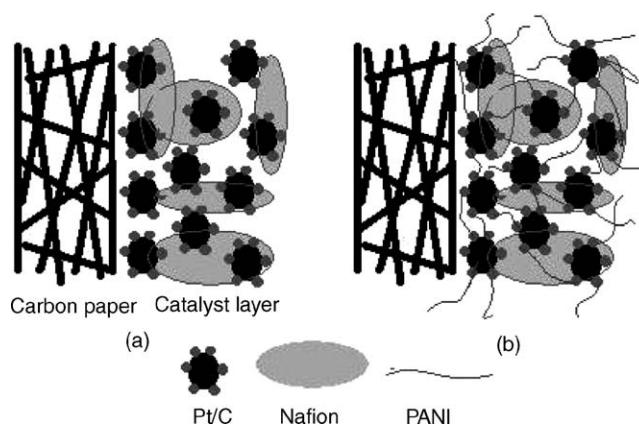


Fig. 1. Schematic diagrams of the homemade PEMFC electrode structure: (a) before modification with PANI and (b) after modification with PANI.

PANI-modified GDE with good properties and sufficient electrochemical activity. This modified GDE could potentially be used as a base for the further development of PEMFC membrane–electrode assembly (MEA) based on ECPs.

## 2. Experimental

### 2.1. Gas diffusion electrode fabrication

The process of electrode fabrication and modification consisted of two steps: (1) a porous GDE was constructed according to a previously described procedure [30] and (2) the GDE was modified with PANI.

To prepare the PTFE-bonded porous GDE, a commercially available electrocatalyst (20% Pt/C powder from Electrochem Inc.) and 30% PTFE emulsion were used. The PTFE was used as a binder and had the required hydrophobicity in the catalyst layer. To prepare the catalyst layer, a mixture comprised of a homogeneous suspension of PTFE, Pt/C catalyst, glycerol (Merck), isopropanol (Merck) and water was homogenized using a sonicator (Misonix model S-3000) for 20 min and then painted onto carbon paper TGPH-0120T (Toray). The resulting composite structure was dried in air at 120 °C for 1 h, then maintained at 280 °C for 30 min to remove the dispersion agent contained in the PTFE, and finally sintered in air at 350 °C for 30 min. The amount of PTFE in the catalyst layer was 30 wt.% and Pt loading was 0.2 mg cm<sup>-2</sup>. Nafion solution (5% from Aldrich) was then brushed onto the surface of the Teflon-bonded GDE, and the resulting composite was dried at 80 °C for 30 min. The amount of Nafion in the GDE was 0.7 mg cm<sup>-2</sup>.

Two Nafion-containing GDEs, denoted GDE<sub>1</sub> and GDE<sub>2</sub>, were prepared using the above method. One of these GDEs (GDE<sub>1</sub>) was used as is, and the other (GDE<sub>2</sub>) was modified with PANI by electrochemical polymerization of aniline and TFMSA. The electrode substrate was placed as the working electrode together with a counter electrode in an electrolytic cell containing an electrolytic polymerization solution containing 0.1 M aniline (Merck) and 0.2 M TFMSA (Merck) [31]. The temperature of the electrolytic polymerization solution was maintained at 0 °C. An electric current was passed between the

electrodes at a fixed amperage of  $2 \text{ mA cm}^{-2}$  for 5 min and then at a fixed amperage of  $20 \text{ mA cm}^{-2}$  for 10 min to effect the electrolytic polymerization, where a potentiostat–galvanostat (EG&G Princeton Applied Research Model 273A) was used to control the electropolymerization. This process led to the formation of a thin film having TFMSA retained within a PANI network on the surface of the catalyst, to produce a cathode.

## 2.2. Electrochemical investigation of the GDEs

Cyclic voltammetry (CV) was performed to determine the electrochemical surface area (ESA) and catalyst utilization. The ESA of the Pt catalyst was evaluated from the voltammogram by dividing the charge (in  $\mu\text{C}$ ) that corresponded to the area under the hydrogen desorption region by  $210 \mu\text{C}$ . The roughness factor (RF) was calculated by dividing the ESA by the geometric area ( $4 \text{ cm}^2$ ) of the electrode. The utilization of the Pt catalyst was evaluated by dividing the RF of the electrode by the theoretical RF (250) [1] for 20% Pt/C, which had a surface area of  $100 \text{ m}^2 \text{ g}^{-1}$  and was used in the present study.

The reduction of oxygen was investigated at the porous GDE (geometric exposed area  $4 \text{ cm}^2$ ) in  $0.5 \text{ M H}_2\text{SO}_4$ . All measurements were carried out at  $25^\circ\text{C}$ , in a conventional three-electrode cell, with  $\text{O}_2$  flowing at  $50 \text{ ml min}^{-1}$ . The GDEs were mounted into a Teflon holder containing a high pyrolytic graphite disk as a current collector and which had provision for oxygen feeding from the back of the electrode. A large-area platinum flat electrode was used as the counter electrode. An Ag/AgCl reference electrode was placed close to the working electrode surface. The electrochemical cell was connected to a potentiostat–galvanostat (EG&G Princeton Applied Research Model 273A), for the  $I$ – $V$  polarization curve and CV, and also to a frequency response detector (model 1025) for electrochemical impedance spectroscopy. In this work, the AC potential altitude was  $5 \text{ mV}$  and its frequency range was from  $0.1 \text{ Hz}$  to  $100 \text{ kHz}$ .

## 2.3. SEM characterization

The surface of the modified PTFE-bonded electrode was investigated by SEM (Philips model XL30).

## 3. Results and discussion

### 3.1. Electrochemical activity evaluation

CV is the technique most commonly used to characterize electrochemical surface areas of electrodes. The ESA of each electrode was calculated using the coulombic charge for hydrogen desorption, assuming a value of  $210 \mu\text{C cm}^{-2}$  for the oxidation of adsorbed atomic hydrogen on a smooth Pt surface [32].

Fig. 2 shows cyclic voltammograms for the electrodes without and with PANI (GDE<sub>1</sub> and GDE<sub>2</sub>, respectively) in  $0.5 \text{ M H}_2\text{SO}_4$  (aq). The ESA of GDE<sub>2</sub> calculated from the voltammogram is higher than that of GDE<sub>1</sub>. This figure indicates that in the GDE containing Nafion and PANI nonofiber (GDE<sub>2</sub>), a large fraction of the modified catalyst layer was electroactive,

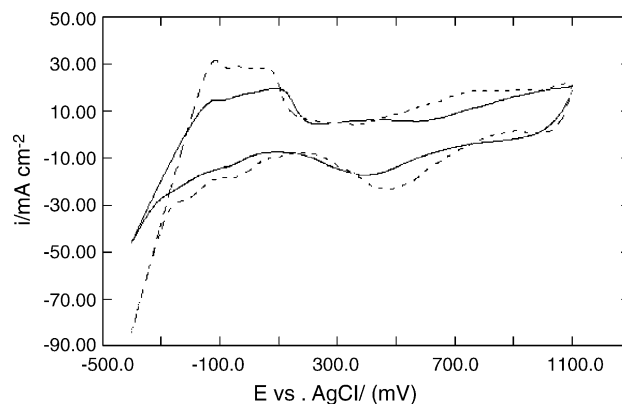


Fig. 2. Cyclic voltammograms of electrodes GDE<sub>1</sub> (—) and GDE<sub>2</sub> (---) in the potential range 1.1 to  $-0.4 \text{ V}$  vs. Ag/AgCl with scan rate  $50 \text{ mV s}^{-1}$ , in  $0.5 \text{ M H}_2\text{SO}_4$  at  $25^\circ\text{C}$ .

Table 1

ESA, roughness factor (RF) and percentage Pt utilization of electrodes with a Pt loading of  $0.2 \text{ mg cm}^{-2}$

Electrodes	ESA ( $\text{cm}^2$ )	Roughness factor	Percentage Pt utilization
GDE <sub>1</sub>	570	142	57
GDE <sub>2</sub>	847	212	85

presumably due to a PANI-related increase in ionic and especially electronic conductivity across the reaction layer [14]. The utilization of platinum in the catalyst layer is 57% for GDE<sub>1</sub> and 84% for GDE<sub>2</sub>. Inclusion of PANI nonofiber in the electrode improved the active surface area, RF and utilization of catalyst, as can be seen in the comparison of the calculated values for GDE<sub>1</sub> and GDE<sub>2</sub> in Table 1.

The CV results for GDE<sub>1</sub> and GDE<sub>2</sub> also show that the inclusion of PANI into the catalyst layer causes a considerable shift toward positive potentials of the region corresponding to reduction of oxide-formation species ( $500 \text{ mV}$ ). This indicates that addition of PANI to the catalyst layer improves catalysis of the oxygen reduction reaction (ORR) at the GDE.

Fig. 3 shows the polarization curves for GDE<sub>1</sub> and GDE<sub>2</sub> in a conventional three-electrode cell. The current density is considerably higher for GDE<sub>2</sub> than for GDE<sub>1</sub>, indicating that the electrode containing Nafion and PANI performs much better

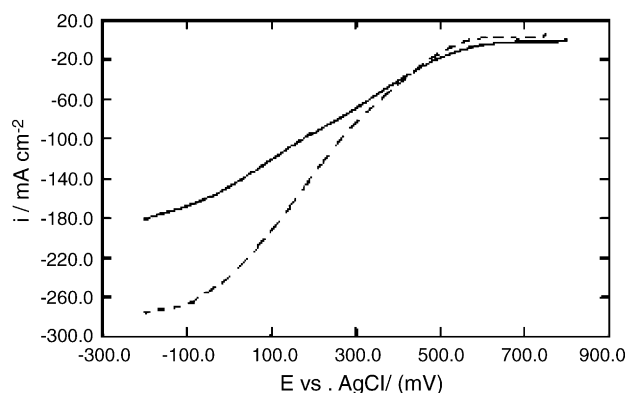


Fig. 3. Polarization curves of electrodes GDE<sub>1</sub> (—) and GDE<sub>2</sub> (---) for ORR in  $0.5 \text{ M H}_2\text{SO}_4$ , at  $25^\circ\text{C}$ .

Table 2  
Electrode kinetic parameters for the ORR at 25 °C on GDE<sub>1</sub> and GDE<sub>2</sub>

Electrodes	$E_r$ (mV)	$b$ (mV dec <sup>-1</sup> )	$R$ ( $\Omega$ cm <sup>-2</sup> )
GDE <sub>1</sub>	729 ± 11	130 ± 6	0.835 ± 0.02
GDE <sub>2</sub>	704 ± 13	58 ± 4	0.61 ± 0.01

than that containing Nafion alone. It is an acceptable result where the ESA and utilization of catalyst increased in GDE<sub>2</sub> according to homogenous dispersion of PANI in catalyst layer and good connection between catalyst particles in this layer. In addition, the high fluorine content of the proton conductive thin film, due to the presence of TFMSA (the dopant of PANI), enhances the solubility and diffusion of oxygen in the reaction layer [31]. This property creates a new role for PANI, whereby it assists both the platinum and acid polymer electrolyte to obtain a better result. For this reason, means that, near the catalyst surface, the concentrations of reactants are increased and hence the ORR is promoted. It should be emphasized that the surface of the electrode and also the full depth of the catalyst layer are activated.

### 3.2. Determination of kinetic parameters

The current density–voltage dependency can be expressed in the following general form [33]:

$$E = E_0 - b \log i - Ri \quad (1)$$

where  $E_0$  is the open-circuit voltage,  $b$  the Tafel slope,  $i$  the current density and  $R$  represents the total contributions of polarization components, which include the charge-transfer resistance ( $R_{ct}$ ), the electrolyte resistance ( $R_e$ ) and the mass-transfer resistance ( $R_d$ ) due to the gas crossing through the diffusion and catalyst layers.  $E_0$  is defined as:

$$E_0 = E_r + b \log i_0 \quad (2)$$

where  $E_r$  and  $i_0$  are the reversible potential for the electrode and exchange current density for the ORR, respectively.

The kinetics parameters of the ORR for GDE<sub>1</sub> and GDE<sub>2</sub> can be obtained from Eqs. (1) and (2).

Table 2 lists the electrode kinetics parameters for GDE<sub>1</sub> and GDE<sub>2</sub>, which were estimated by a non-linear least squares fitting procedure. GDE<sub>2</sub> shows a lower Tafel slope  $b$  and a higher exchange current density, which can be attributed to an enhanced electrocatalytic effect resulting from the presence of PANI in the catalyst layer.

### 3.3. AC impedance spectroscopy

Further information on the electrochemical behavior of GDE<sub>1</sub> and GDE<sub>2</sub> was obtained using electrochemical impedance spectroscopy (EIS). The impedance spectra measured at the open circuit potential for GDE<sub>1</sub> and GDE<sub>2</sub> are shown as Nyquist plots in Fig. 4. The spectrum of each electrode takes the form of a single semi-circular curve. As seen, there is a small difference in linear resistances ( $R_S$ ) between two type's electrodes. This means that resulted linear resistance due to PANI in electrode is

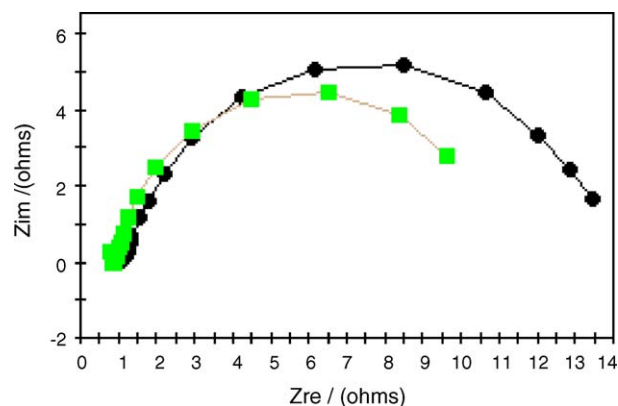


Fig. 4. Impedance response in the Nyquist form 100 kHz to 100 mHz of the porous gas diffusion electrodes: (●) GDE<sub>1</sub> and (■) GDE<sub>2</sub>, at OCV, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

not valuable. Thus, GDE<sub>2</sub> shows slightly better performance in regard to the ORR than GDE<sub>1</sub>. The obtained result would lead to a less homogenous and more resistive catalyst layer due to the improper connection of agglomerations in GDE<sub>1</sub>.

### 3.4. Chronoamperometry

Chronoamperometry is the usual method for determining the diffusion coefficients of electroactive species at electrode surfaces. This method was used to evaluate the quantitative diffusibility of GDE<sub>1</sub> and GDE<sub>2</sub> according to the following equation [34]:

$$i = nFA \left( \frac{D}{\pi t} \right)^{1/2} C^* \quad (3)$$

where  $i$  is the limited current (mA),  $n$  the number of electrons,  $F$  the Coulombic charge (96,485 C mol<sup>-1</sup>),  $A$  the surface area of the electrode (cm<sup>2</sup>),  $D$  the diffusion coefficient (cm<sup>2</sup> S<sup>-1</sup>),  $t$  the time (s) and  $C^*$  is the concentration of reactant (mM). Fig. 5 shows the chronoamperograms of GDE<sub>1</sub> and GDE<sub>2</sub>. It can be seen that the square root of the diffusion coefficient of oxygen ( $D^{1/2}$ ) in GDE<sub>2</sub> is almost 1.5 times that in GDE<sub>1</sub>. This result is consistent with the presence of both TFMSA (the dopant of PANI) and Nafion in the reaction layer, rather than Nafion alone,

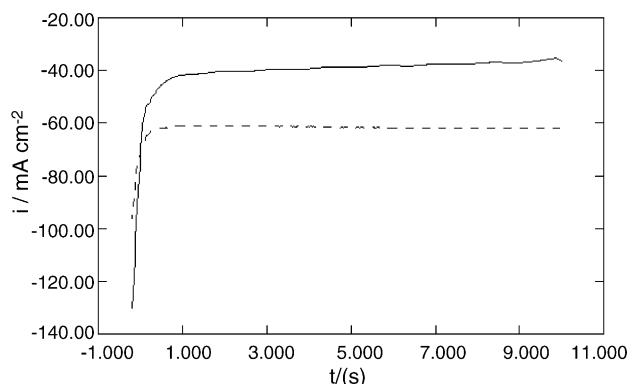


Fig. 5. Chronoamperograms of the electrodes GDE<sub>1</sub> (—) and GDE<sub>2</sub> (---) in the presence of O<sub>2</sub>,  $E_{app} = 0.2$  V vs. Ag/AgCl, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.



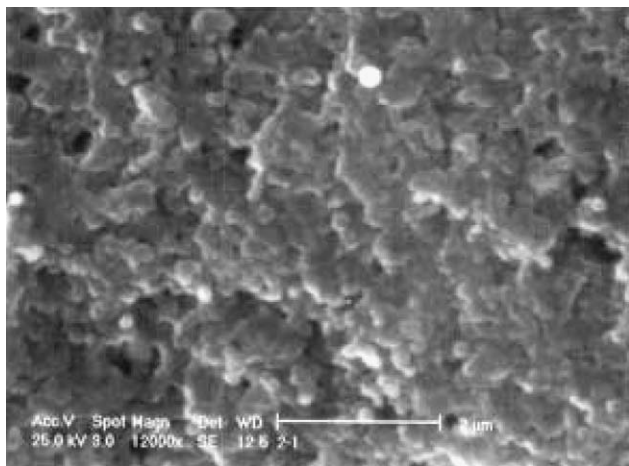


Fig. 6. SEM micrograph of the surface of the GDE modified with Nafion solution (GDE<sub>1</sub>) recorded at 12,000× magnification.

enhancing the solubility and diffusion of oxygen in the reaction layer due to the high fluorine content.

### 3.5. SEM characterization

Typical SEM micrographs of GDE<sub>1</sub> and GDE<sub>2</sub> are shown in Figs. 6 and 7. In general, the surfaces of both electrodes are rough and porous. Comparison of the micrographs indicates that the morphology of the GDE is not significantly influenced by the inclusion of PANI. When PANI was loaded on the electrode, the surface of the electrode was covered with PANI nanofibers, although no obvious difference is observed in the morphologies of GDE<sub>1</sub> and GDE<sub>2</sub> at a magnification of 12,000× (Figs. 6 and 7). At the higher magnification of 30,000× (Figs. 8 and 9), however, nanofibers of PANI can be seen on the platinum particles on the surface of GDE<sub>2</sub>. The fibrous nature of the PANI provides a large surface area and good connections between catalytic particles in the reaction layer. Comparison of GDE<sub>2</sub> with the corresponding electrode modified with PANI alone [35] revealed that the latter electrode had a higher density of PANI nanofibers. The electrochemical activity and morphol-

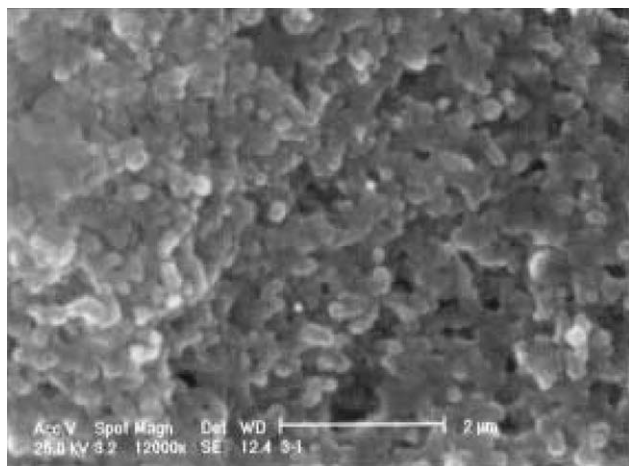


Fig. 7. SEM micrograph of the surface of the GDE modified with Nafion and PANI (GDE<sub>2</sub>) recorded at 12,000× magnification.

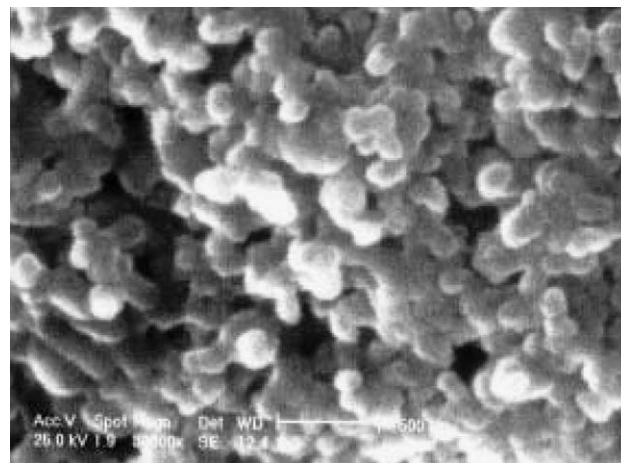


Fig. 8. SEM micrograph of the surface of the GDE modified with Nafion solution (GDE<sub>1</sub>) recorded at 30,000× magnification.



Fig. 9. SEM micrograph of the surface of the GDE modified with Nafion and PANI (GDE<sub>2</sub>) recorded at 30,000× magnification.

ogy of the electrode with PANI alone are reported in our previous paper [35].

## 4. Conclusions

The main goal of the present work was to reproducibly prepare an electrocatalyst containing a mixture of Nafion and PANI in the catalyst layer of a GDE. Our results on the preparation and behavior of these cathodes for application in PEMFCs can be summarized as follows:

- I. Modification of the electrode catalyst layer using PANI increases the Pt utilization in the ORR (from 57 to 84%), meaning that less Pt can be used to achieve the same performance.
- II. The presence of PANI in addition to Nafion in the catalyst layer reduces the polarization resistance of the electrode compared to that of the electrode containing Nafion alone; hence fuel cells using PANI–Nafion electrodes are expected to give superior performance.

III. Inclusion of PANI into the electrocatalyst changes the morphology of the GDE. The fibrous nature of PANI provides good connections between catalytic particles. The introduction of PANI into the electrode enhances the performance (i.e., lowers the overpotential) by minimizing ohmic resistance, charge-transfer and mass transport limitations.

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