

# Study of polyaniline doped with trifluoromethane sulfonic acid in gas-diffusion electrodes for proton-exchange membrane fuel cells

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## Abstract

Polytetrafluoroethylene (PTFE)-bonded gas-diffusion electrodes (GDEs), modified with polyaniline as an electron and proton conductor in the catalyst layer, are prepared and evaluated for use in proton-exchange membrane fuel cells (PEMFCs). Polyaniline is coated on the GDE by electropolymerization of aniline and trifluoromethane sulfonic acid as the proton-conductive monomer. The electrodes are characterized by cyclic voltammetry, current–potential measurements, electrochemical impedance spectroscopy, and chronoamperometry. The polyaniline is found to be homogeneously dispersed in the catalyst layer, making it a good candidate proton and electron conductor. Use of polyaniline instead of Nafion in the catalyst layer, increases the utility of the electrocatalyst by 18%. The results are consistent with the presence of polyaniline as a conductive polymer in the reaction layer reducing the polarization resistance of the electrode in comparison with that of a corresponding electrode containing Nafion. Thus, the present results indicate that PEMFCs using polyaniline-containing electrocatalysts should give superior performance to those using catalysts containing traditional ionomers.

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## 1. Introduction

Platinum is the most important catalyst used in gas-diffusion electrodes (GDEs) [1,2] for proton-exchange membrane fuel cells (PEMFCs). The discovery in the 1980s that introducing an ionomer (liquid Nafion) into GDEs [3] extends the three-dimensional reaction zone of the electrode and leads to a significant lowering of the platinum loadings, i.e., from about 4–10 mg cm<sup>-2</sup> (platinum black) to about 0.4 mg cm<sup>-2</sup> or even less (carbon-supported platinum). Nafion may be applied by impregnation, brushing, spraying, or floating/dipping the electrode in a solution of the ionomer.

Several studies have examined the influence of the ionomer content in the catalyst layer on GDE performance. In a review of data from various studies on the optimum Nafion content of the catalyst layer, Antolini [4] concluded that introduction of the ionomer into the catalyst layer by impregnation gave a lower optimum Nafion content than introducing the ionomer by placing it in the catalyst ink.

Matsubayashi et al. [5] reported that the variation in electrode performance with the amount of Nafion depends on the method used to introduce the electrolyte. Hsu et al. [6] studied the effect of Nafion impregnation of a dual electrode by cyclic voltammetry and a.c. impedance measurements. The maximum electroactive surface area (ESA) and the minimum ohmic resistance of the cell occurred at 0.67 mg Nafion per cm<sup>2</sup>.

In all of the methods used to date, the Nafion solution is introduced into the catalyst layer as a physical or chemical

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mixture [7–9]. The use of this approach has the disadvantages that it is difficult to control the amount of Nafion applied and impossible to achieve a homogeneous distribution of the ionomer in the reactive layer. As a result, the mass activity is decreased and hence the cost of fabrication is increased. The ideal catalyst layer for a GDE would be gas- and water-permeable, and would conduct both protons and electrons. Electron–proton conductive polymers, especially polyaniline (PANI) doped with trifluoromethane sulfonic acid as a proton-conducting monomer, are good candidates for resolving the problems outlined above. PANI and its derivatives have been considered promising materials for batteries and the catalysis of electrochemical reactions [10–27].

Several electrocatalytic reactions have been investigated in systems comprised of noble metals dispersed in electron-conducting polymers. These reactions include the reduction of protons [10,11] or oxygen [12–16], and the oxidation of hydrogen [17,18] or small organic molecules such as formic acid [19,20], methanol [21–26], and ethylene glycol [27]. In addition, studies have been carried out on the effect of varying the catalyst composition (PANI or Nafion with Pt) on the oxygen reduction reaction (ORR) [28] and on the modification of GDEs [29]. In most cases, the reaction rate (i.e., the current density) was increased and the overvoltage was greatly reduced by introducing PANI into the electrodes.

For practical applications such as fuel cells, the amount of electrocatalyst must be minimized to decrease material costs. To achieve this, one or both of the following approaches have been used: (i) increasing the platinum utilization in the ORR; (ii) using advanced catalysts.

Electrodeposition of PANI films under potentiodynamic conditions is facile in aqueous solutions and gives rise to homogenous dispersion of the polymer across the catalyst layer [30]. In the polymerization, PANI is used as the polymer network and trifluoromethane sulfonic acid as the proton-conducting monomer contained in the polymer network [31,33].

The presence of PANI in the catalyst layer increases catalyst utilization [32] and reduces the polarization resistance of the GDE due to the electronic conductivity of PANI and the proton conductivity afforded by monomers retained in the PANI network.

In most cases, PANI is used for modification of smooth surfaces such as glassy carbon or platinum foil. In the present study, however, PANI is used in a porous medium (GDE) for the ORR. Specifically, a polytetrafluoroethylene (PTFE)-bonded porous GDE is modified with (i) PANI doped with trifluoromethane sulfonic acid, or (ii) a Nafion solution. The purpose of this work is to obtain more information on the effect of nanofibrous polyaniline on the ORR in a GDE. Furthermore, the electrodes are characterized by steady-state galvanostatic polarization (GP), electrochemical impedance spectroscopy (EIS), chronoamperometry, and cyclic voltammetry (CV). In addition, the morphologies of the prepared composites are studied by scanning electron microscopy (SEM). The kinetic parameters derived from the GP exper-

iments are complemented by polarization resistance data obtained from EIS and by the hydrogen absorption charge obtained from CV measurements.

## 2. Experimental

### 2.1. Gas-diffusion electrode fabrication

The process of electrode fabrication and modification consisted of two steps:

- (i) construction of the PTFE-bonded porous GDE;
- (ii) modification of the GDE using PANI doped with trifluoromethane sulfonic acid (GDE1) or a Nafion solution (GDE2).

To prepare the PTFE-bonded porous GDE, a commercially available electrocatalyst (20 wt.% Pt/C powder from Electrochem Inc.) and 30 wt.% PTFE emulsion were used. The PTFE served as a binder and had the required hydrophobicity in the catalyst layer. To prepare the catalyst layer, a homogeneous suspension of PTFE, Pt/C catalyst, glycerol, isopropanol and water was painted on the carbon paper (TGP-060T). The composite structure was then dried in an oven at 120 °C for 1 h, heated at 280 °C for 30 min to remove the dispersion agent contained in the PTFE emulsion, and finally sintered in air at 350 °C for 30 min. The amount of PTFE in the catalyst layer was 30 wt.% and the Pt loading was 0.2 mg cm<sup>-2</sup>. Finally, the GDE was modified with conductive polymer (GDE1) by electrochemical polymerization of PANI and trifluoromethane sulfonic acid [33]. The electrode substrate was placed as a working electrode together with a counter electrode in an electrolytic cell containing an electrolytic polymerization solution that consisted of 0.1 M aniline (Merck) and 0.2 M trifluoromethane sulfonic acid (Merck). The temperature of the electrolytic polymerization solution was maintained at 0 °C. An electric current was passed between the two electrodes at a fixed level of 2 mA cm<sup>-2</sup> for 5 min and then at 20 mA cm<sup>-2</sup> for 10 min to effect the electrolytic polymerization. An EG&G Princeton Applied Research Model 273A instrument was used for electropolymerization. This procedure resulted in a thin film with trifluoromethane sulfonic acid retained within the PANI network on the surface of the catalyst, for use as a cathode. To prepare the second GDE (GDE2), a Nafion solution (5 wt.%; Aldrich) was brushed on to the surface of the PTFE-bonded GDE. The amount of Nafion in GDE2 was 0.7 mg cm<sup>-2</sup>.

### 2.2. Electrochemical investigation of GDE

Cyclic voltammetric was performed to determine the electrochemical surface area, utilization, and roughness factor of the catalyst. The reduction of oxygen was investigated on a geometric exposed area of the GDE of 4 cm<sup>2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. All measurements were performed at 25 °C, in a conventional three-electrode cell, with O<sub>2</sub> flowing at 50 ml min<sup>-1</sup>. The

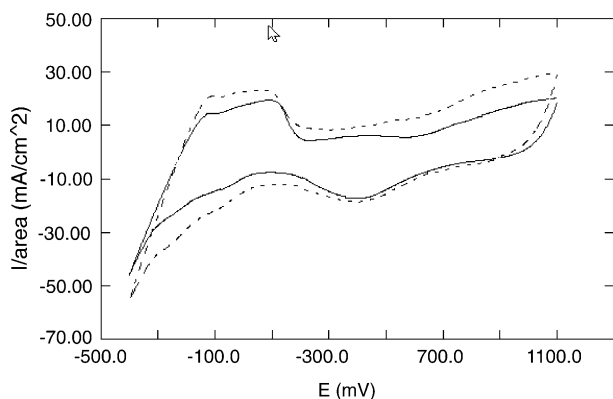


Fig. 1. Cyclic voltammograms for electrodes GDE1 (---) and GDE2 (—) in potential range 1.1 to  $-0.4$  V vs. Ag/AgCl with scan rate  $50 \text{ mV s}^{-1}$ , in  $0.5 \text{ M H}_2\text{SO}_4$  at  $25^\circ\text{C}$ .

GDEs were mounted on a glass holder that contained a platinum disc as the current-collector with provision for oxygen feeding at 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 Model 273A) for  $I$ – $V$  polarization measurements and cyclic voltammetry, and also to a frequency response detector (model 1025) for electrochemical impedance spectroscopy. The a.c. potential amplitude was  $5 \text{ mV}$  and the frequency range was  $0.1$ – $100 \text{ kHz}$ .

### 2.3. Scanning electron microscopy characterization

The surfaces of the modified PTFE-bonded GDEs (GDE1 and GDE2) were investigated by scanning electron microscopy (SEM, Philips model XL 30).

## 3. Results and discussion

### 3.1. Cyclic voltammetry and polarization curve measurements

The cyclic voltammograms for GDE1 and GDE2 in  $0.5 \text{ M H}_2\text{SO}_4$  are shown in Fig. 1. The coulombic charge for hydrogen desorption was used to calculate the active surface area of each electrode [34]. Comparison of the calculated values of the active surface area, roughness factor and utilization for GDE1 and GDE2 (Table 1) reveals that the use of PANI instead of Nafion gives improvements in all of these characteristics.

Table 1

ESA, roughness factor (RF) and percentage Pt utilization of electrodes with  $0.2 \text{ mg cm}^{-2}$  for ORR in  $0.5 \text{ M H}_2\text{SO}_4$  at  $25^\circ\text{C}$

Electrode	ESA ( $\text{cm}^2$ )	Roughness factor	Pt utilization (%)
GDE1	756	189	75
GDE2	570	142	57

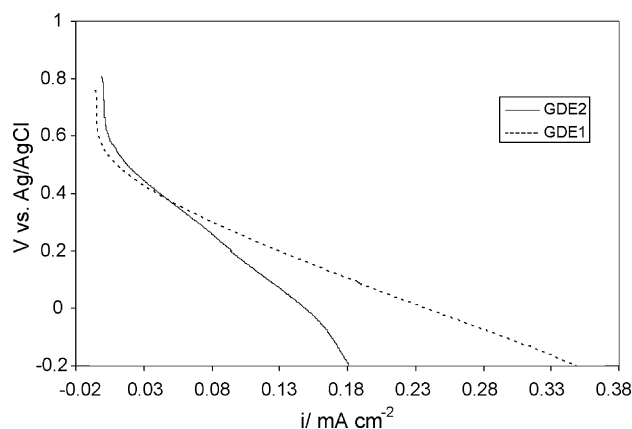


Fig. 2. Polarization curves for electrodes GDE1 (---) and GDE2 (—) for ORR in  $0.5 \text{ M H}_2\text{SO}_4$  at  $25^\circ\text{C}$ .

For example, Pt utilization is increased from 57 to 75%. The polarization curves for GDE1 and GDE2 in a conventional three-electrode cell are presented in Fig. 2. The current density values are considerably greater for GDE1 than for GDE2, which indicates that the performance of the cell is much better than that obtained when using an electrode containing Nafion. The superior performance of GDE1 is attributed to an increase in the three-dimensional reaction zone and to the PANI establishing good connections between the catalytic particles in the reaction layer.

This result is consistent with the increased ESA and utilization of catalyst in GDE1 due to homogenous dispersion of PANI in the catalyst layer. In addition, the proton-conducting thin film on GDE1 has the capability to enhance the solubility and diffusion of oxygen in the reaction layer due to the high fluorine content of trifluoromethane sulfonic acid. For this reason, the concentrations of the reactants near the surfaces of the catalysts are increased, and hence the reaction is enhanced. It should be emphasized that, because of the nature of electrochemical PANI coating, both the electrode surface and the full depth of the reaction layer are activated.

### 3.2. Determination of kinetic parameters

The kinetic parameters of the ORR for a GDE can be obtained from the polarization data. The experimental polarization data is analyzed using the semi-empirical equation [35]:

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

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

where  $E_r$  is the reversible potential for the electrode;  $b$  the Tafel slope;  $i_0$  the exchange current density for the ORR in the Pt/C catalyst;  $R$  represents the total contributions of the 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

Table 2  
Electrode kinetic parameters for ORR in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C

Electrode	$E_r$ (mV)	$b$ (mV per decade)	$R$ ( $\Omega \text{ cm}^{-2}$ )
GDE1	687	102	0.397
GDE2	729	130	0.835

diffusion and catalyst layers. Fitting of the above equation to the experimental data was made by a non-linear least squares NLLS method [36], and the derived kinetic parameters are listed in Table 2.

The higher Tafel slope for GDE1 compared with GDE2 (130 mV versus 102 mV per decade, respectively) can be attributed to differences in the interphase conditions, and is indicative of differences in the rate-determining steps for the ORR on the PANI and Nation structures. The electrode containing PANI shows the best performance (i.e., lowest overpotential), i.e., by minimizing ohmic resistance, charge transfer and mass transport limitations. To achieve maximum efficiency, it is necessary to prepare an environment with a triple interface comprised of Nafion or PANI, platinum and oxygen.

The present results indicate that the main advantages of PANI doped with proton-conductive monomer (trifluoromethane sulfonic acid) are: (i) an increased concentration of oxygen in the catalyst layer; (ii) good dispersion of PANI in the catalyst layer; (iii) increased electron conductance in the catalyst layer. Although PANI has the disadvantage of low ionic conductivity, the increased oxygen solubility that occurs in the presence of PANI should at least partially compensate for this shortcoming. On the other hand, the addition of Nafion has the advantage of increasing the ionic conductance in the catalyst layer. Nevertheless, the addition of Nafion to the reactive layer has the practical disadvantage in that it is impossible to distribute homogeneously the Nafion solution throughout the catalyst layer [4]. An additional disadvantage of using Nafion is that it may block some platinum particles in the catalyst layer.

### 3.3. Impedance spectroscopy

The oxidation structures of PANI have been shown to be strongly dependent on the applied potential and the pH of the electrolyte [36–40]. These two factors also significantly influence the electronic conductivity and the environment at the polymer/electrolyte interface [37–41]. To gain more information on the GDEs (GDE1 and GDE2), the a.c. impedance spectrum of each electrode was obtained at two potentials. The resulting data in the Nyquist representation obtained at 200 mV versus Ag/AgCl, saturated with KCl and OCV (open circuit voltage) are presented in Figs. 3 and 4. The polarization resistance  $R_p$  is lower for GDE1 than for GDE2, as determined from the CV and  $I$ - $V$  polarization curves. Although the impedance spectra have similar semi-circular shapes, the diameters of the semi-circles differ substantially.

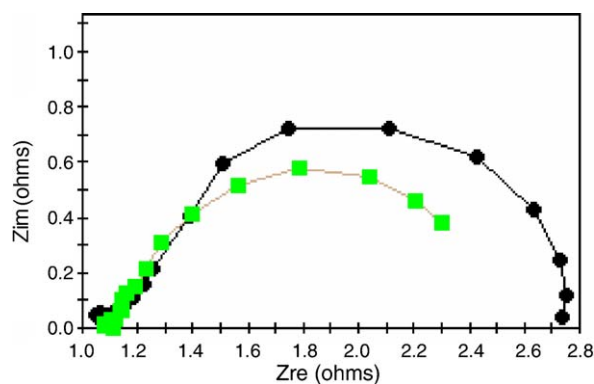


Fig. 3. Nyquist plots of impedance response from 20 kHz to 100 mHz for porous gas-diffusion electrodes: (●) GDE1, (■) GDE2, at 200 mV vs. Ag/AgCl, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

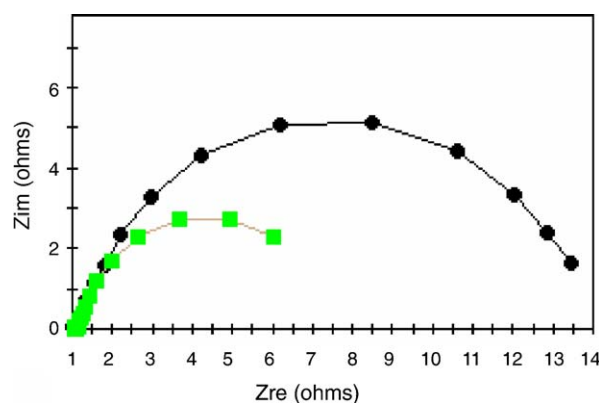


Fig. 4. Nyquist plots of impedance response from 20 kHz to 50 mHz for porous gas-diffusion electrodes: (●) GDE1, (■) GDE2, at OCV, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

### 3.4. Chronoamperometry

Chronoamperometry is the usual method employed to determine the diffusion coefficient of electroactive species at the surface of an electrode. This method was used to compare quantitatively the diffusibility of oxygen in GDE1 and GDE2, according to [42]:

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

where  $i$  is the limiting current (mA);  $n$  the number of electrons;  $F$  the coulombic charge ( $96485 \text{ C mol}^{-1}$ );  $A$  the surface area of the electrode ( $\text{cm}^2$ );  $D$  the diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ );  $t$  the time (s);  $C^*$  the concentration of the reactant (mM). Chronoamperograms for GDE1 and GDE2 are given in Fig. 5. The value of  $D^{1/2}$  for GDE1 is more than double that for GDE2. This result is consistent with the ability of PANI to enhance the solubility and diffusion of oxygen in the reaction layer due to its high fluorine content.

### 3.5. SEM characterization

Scanning electron microscopy has been used to obtain morphological information on both the polyaniline

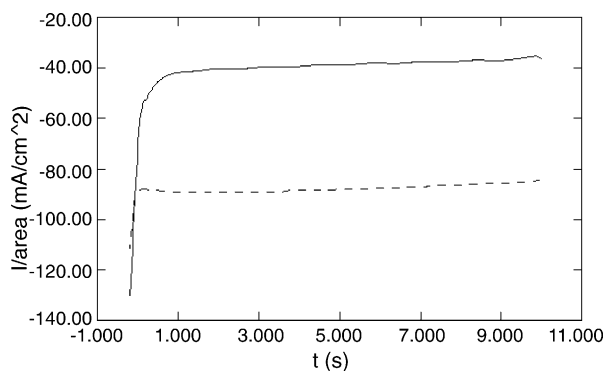


Fig. 5. Chronoamperograms of GDE1 (---) and GDE2 (—) in presence of O<sub>2</sub>.  $E_{app} = 0.2$  V vs. Ag/AgCl, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

nanofibres and dispersed platinum particles, especially their agglomeration distributions. To explain the different electrocatalytic activities of the modified PTFE-bonded GDEs depending on the modifier used (i.e., PANI or Nafion), knowledge of the characteristics of the modifier, in particular the size, real surface area, and distribution of the modifier within the catalyst layer, is of great assistance. As is well known, the specific surface area of the platinum, calculated from the electrochemically active surface area and the platinum loading, is a useful macroscopic quantity for characterizing the effect of PANI and Nafion solution on the conductivity of the catalyst layer, as well as the degree to which the ionomer is homogeneously distributed throughout the reactive layer.

Micrographs of GDE1 and GDE2 recorded at a magnification of 12 000 $\times$  are shown in Figs. 6 and 7. At this magnification, no obvious differences can be discerned between the two electrodes. At a higher magnification of 30 000 $\times$  (Figs. 8 and 9), however, long nanofibres of PANI can be seen on the platinum particles on the surface of GDE1. The fibrous nature of the PANI provides a large surface area and good connections between catalytic particles in the reaction layer. Permeation of the PANI nanofibres through the catalyst layer on GDE1 is evident in Fig. 10, which is a micrograph

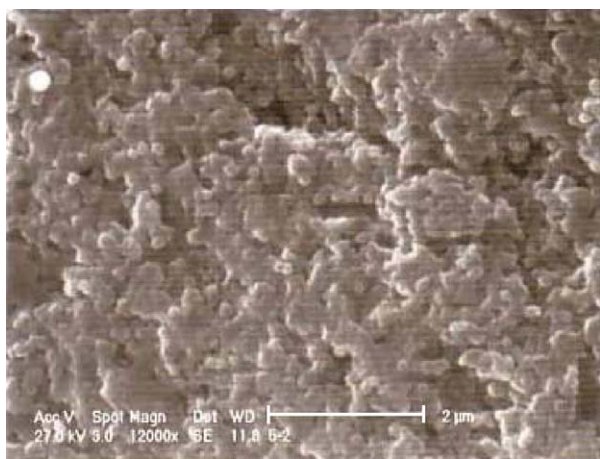


Fig. 6. SEM micrographs of surface of GDE modified with polyaniline (GDE1) recorded at 12 000 $\times$  magnification.

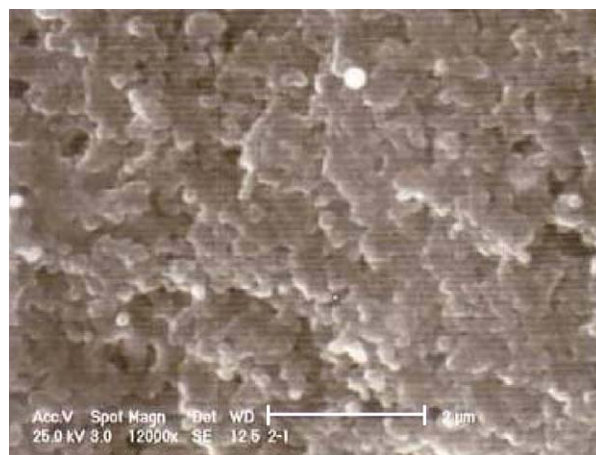


Fig. 7. SEM micrograph of surface of GDE modified with Nafion solution (GDE2) recorded at 12 000 $\times$  magnification.

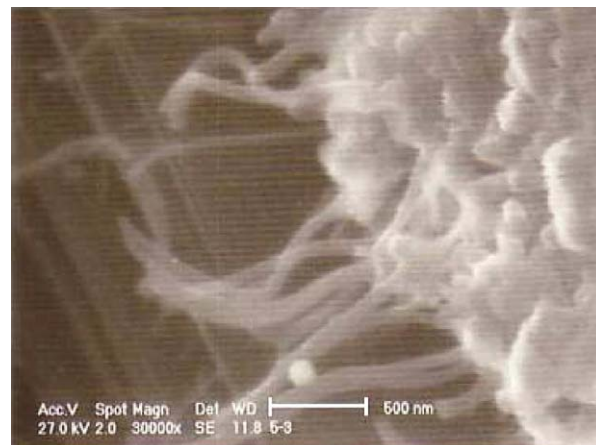


Fig. 8. SEM micrograph of surface of GDE modified with polyaniline (GDE1) recorded at 30 000 $\times$  magnification.

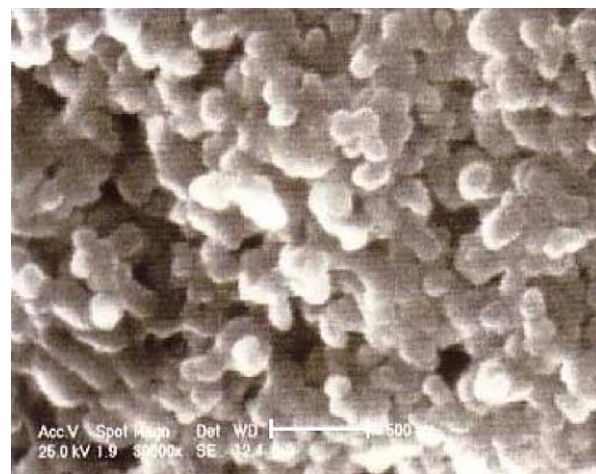


Fig. 9. SEM micrograph of surface of GDE modified with Nafion solution (GDE2) recorded at 30 000 $\times$  magnification.

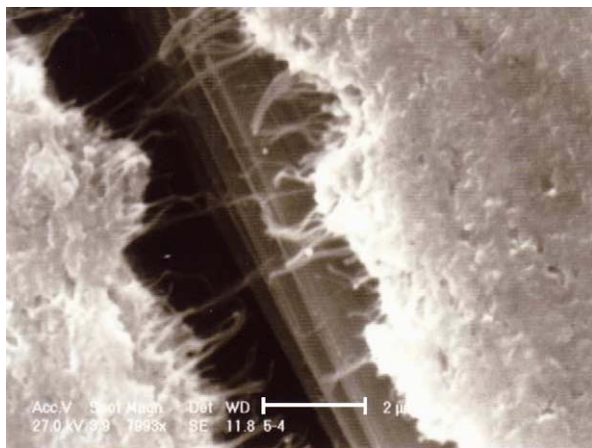


Fig. 10. SEM micrograph of surface of GDE modified with polyaniline (GDEI) after cleaving the electrode.

of a cleaved GDEI electrode. This image clearly shows many polyaniline fibres in the region of the break that would have provided connections between the particles in the intact catalyst layer.

#### 4. Conclusions

The characteristics of GDEs containing PANI and the traditional ionomer Nafion in the catalyst layer have been analyzed with a view to developing a more effective GDE for use as a PEMFC cathode. The results indicate the following:

- (i) Introduction of PANI into the electrode catalyst layer increases the Pt utilization. Thus, less Pt can be used in the modified electrode.
- (ii) The presence of PANI changes the morphology of the GDE. A homogenous distribution of electron-conducting polymer is obtained, and this increases the catalytic properties of the reaction layer.
- (iii) The presence of PANI as a conducting polymer in the reaction layer seems to reduce the polarization resistance of the electrode compared with that of the electrode containing Nafion. Hence, fuel cells using PANI-containing electrodes are expected to give superior performance.
- (iv) The fibrous nature of PANI provides a large surface area and good connections between the catalytic particles. The introduction of PANI into the electrode gives superior performance (i.e., lower overpotential) by minimizing ohmic resistance, charge transfer and mass transport limitations.

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