Development of carbon-filled gas diffusion layer for polymer electrolyte fuel cells

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Abstract

The fabrication and electrochemical performance of polymer electrolyte fuel cells based on a carbon-filled gas diffusion layer (CFGDL) were studied in detail. The CFGDL consists of a PE-704 carbon electrode backing filled with a mixture of carbon powder and PTFE. The results obtained from the performance evaluation and cyclic voltammetry (CV) analyses indicate that the loading of the carbon powder in the CFGDL plays a critical role in the performance of the fuel cell and utilization of Pt, but the presence of PTFE in the CFGDL has less influence. The carbon content in the CFGDL not only affects the area specific resistance of the CFGDL but also affects the Pt utilization of the catalyst layer, the total cell resistance and thus the cell performance. The optimal performance of the PEFC was obtained when the CFGDL was filled with carbon to $6\,mg\,cm^{-2}$ and PTFE of 40%. The relationship between the surface morphology and microstructure of the CFGDL and the electrocatalytic activity of the cell is also discussed.
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Keywords: PEM fuel cell; Carbon-filled gas diffusion layer; Carbon loading; PTFE content

1. Introduction

Polymer electrolyte fuel cells (PEFC) have been successfully demonstrated in automotive, stationary and portable power applications, but the high cost of the PEFC at present is a major barrier for its commercialization. The gas diffusion electrode (GDE) in a PEFC is a key component that affects the performance and cost of the fuel cell due to its noble metal Pt content. Improvement in the properties of electrode is the most practical way to increase fuel cell performance and decrease the cost of fuel cell. Typically, a GDE in a PEFC structurally comprises a gas diffusion layer (GDL) and a catalyst layer (CL). The GDL in the electrode is constructed from either a sheet of electrically conductive macro-porous substrate, such as a non-woven carbon paper or a woven carbon cloth, or with an added thin micro-porous layer (MPL) of carbon black mixed with polytetrafluoroethylene (PTFE). The macro-porous substrate, also called an electrode backing, as a GDL mainly offers a conductive path between the CL and the current collectors (such as graphite plates), and provides a physical support for depositing the CL. However, with a MPL inserted between the catalyst layer and the electrode backing, the GDL has additional functions: (1) to provide a physical micro-porous support for the catalyst layer while allowing transport of reactant gases to the catalyst layer, (2) to minimize electrical contact resistance with the adjacent catalyst layer, (3) to achieve a proper hydrophobicity for better water management, and (4) to prevent the catalyst layer ink from dropping into the electrode backing, thereby increasing the catalyst utilization. Numerous studies on the GDL focused on the physical properties (electrical conductivity and hydrophobicity), structural morphology (porosity and thickness) and the optimization of compositions (carbon loading and PTFE content) in the MPL and have been discussed in the literature [1–12]. For example, Lufrano et al. [2] investigated the fuel cell performance with two different GDL structures using carbon paper as the electrode backing. In comparison with the GDL without a MPL, the GDL with MPL has shown a significant improvement in fuel cell performance. They believed that the intermediate hydrophobic carbon layer, i.e. MPL could improve the gas and water management. They found that the optimal PTFE content

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in the hydrophobic carbon layer was 20 wt.% for low Pt loading (0.1 mg cm^{-2}). Jordan et al. [3] studied the effect of carbon loading in an MPL inserted between the carbon paper and CL on the fuel cell performance. In their study, the optimal loading of acetylene black carbon in the MPL was found to be 1.9 mg cm^{-2} with a PTFE content of 10 wt.%. They summarized that the carbon loading in GDL could significantly affect the fuel cell performance. The increase in the carbon loading in the GDL not only could improve the microstructure of the diffusion layer for catalyst deposition; but it also decreases the electrical resistance between the catalyst layer and the electrode backing. Qi and Kaufman [10] reported a study on the GDL where a MPL was inserted between the carbon paper and the CL. In the study, they found that the MPL could reduce the differences among different carbon paper types made by the same or different manufacturers. They also investigated the effect of carbon loading and PTFE content in the MPL on the cell performance. The optimal composition of the MPL consisted of 35% PTFE and 65% Vulcan XC-72 carbon with a carbon loading of 2.0 mg cm^{-2} was obtained.

Campbell et al. [6] proposed a different type of GDL, which consisted of macro-porous substrates (which can be any poor electrically conductive or insulating materials) as the electrode backing and filled it with a mixture of an electrically conductive carbon powder and a hydrophobic polymer binder. In their study, a poor electrical conducting non-woven carbon fibre mat with 2.27 Ω cm of through-plane resistivity (compared with 0.17 Ω cm for conventional carbon fibre papers), a non-conductive glass fibre mat and an expanded PTFE mesh filled with a mixture of Shawinigan carbon and PTFE/FEP120 binder were used. The cell performance with this type of GDL was comparable with the conventional GDLs as mentioned above. The results revealed that the electrically conductive material, such as carbon, filled inside the macro-porous electrode backing is critical to the conductivity of the gas diffusion electrode, and this appears to provide the flexibility in the selection of various porous sheet materials for the electrode backing. Unfortunately, only a handful of studies on this type of GDL have been carried out since then.

Our objective in this study is to understand fundamentally, in detail, the properties of a carbon-filled gas diffusion layer (CFGDL) based on the GDL invented by Campbell et al., and to develop a CFGDL with high performance using the lower density and more porous carbon paper filled with the mixture of carbon powder and hydrophobic binder. This was achieved through proper control of the CFGDL's structure and composition (carbon loading and PTFE content), in conjunction with evaluation of properties such as electrical resistance, structural morphology, catalyst utilization and fuel cell performance of the gas diffusion electrode.

2. Experimental

2.1. Electrode preparation

PE-704 carbon paper (SGL, SIGRATHERM® paper with density of 0.14 g cm^{-3} compared to 0.49 g cm^{-3} of Toray car-

bon papers) with more macro-porous structure was chosen as the electrode backing. Vulcan XC-72R carbon powder (Cabot Co.) was used as the electrically conductive filler and PTFE (60 wt.%, Aldrich) was used as the binder. The carbon paper was first impregnated with PTFE emulsion followed by drying until the mass of the carbon paper increased by 40%; it was then sintered at 240–340 °C for 0.5 h to strengthen the structure of carbon paper. A paste composed of PTFE and carbon powder was pressed into the PTFE treated carbon paper to form the CFGDL by brushing. The thickness of the composite structure was maintained the same as that of the carbon paper. The composite structure was finally dried and sintered at 340 °C for 1 h to make the catalyst layer. To study the effect of carbon content in the CFGDL on the electrode performance, a set of CFGDLs with a fixed PTFE content (40%) was prepared by varying the carbon loadings from 2 to 8 mg cm^{-2}. Another set of CFGDLs with different PTFE contents (10–60%) and a fixed carbon loading (6 mg cm^{-2}) were prepared in the same manner.

To prepare the catalyst layer, a homogeneous dispersion of catalyst in anhydrous ethanol (i.e., catalyst ink) was prepared using the E-TEK 20 wt.% Pt/C catalyst and 60% PTFE emulsion. The mass ratio of the catalyst to PTFE was 2:1. The catalyst ink, which is equivalent to a platinum mass of 0.4 mg cm^{-2}, was applied onto one side of CFGDL by painting. A 5% Nafion solution (DuPont) was first diluted 3–5 times with isopropanol as the solvent and then sprayed onto the surface of the catalyst layer of the electrodes with the CFGDL to form a protonated electrode. The Nafion loading was 1 mg cm^{-2} for all the electrodes in this study. The CFGDL with 6 mg cm^{-2} of carbon loading and a 40% PTFE content was used as a standard anode in all MEAs investigated in this study. A Nafion 112 membrane was used as the electrolyte. A pair of protonated electrodes (anode and cathode) were bonded onto both sides of the Nafion proton exchange membrane by hot-pressing at 130–140 °C and 50 kg cm^{-2} for 2 min.

2.2. Characterization and performance evaluation

The through-plane resistivity of the CFGDL was measured by using a single cell fixture [13] as shown in Fig. 1. A CFGDL with an area of 5 cm^2 was assembled in the single cell fixture instead of an MEA. A current was passed through the cell and the voltage drop across the CFGDL sample was measured. The area specific resistance can be obtained from the linear slope of the V–I curves and the through-plane resistivity, ρ, can thus be calculated using following equation:

$$\rho = \frac{R_{ASR}}{L}, \tag{1}$$

where R_{ASR} is the area specific resistance measured and L is the thickness of the sample. The measurement was carried out at room temperature (25 °C). In comparison, the resistivity of the PTFE treated PE-704 carbon paper without carbon filler was also measured.

A single cell with electrode area of 5 cm^2 and mesh flow field was used in the evaluation of the electrode performance. Steady state polarization and cyclic voltammetry (CV) were con-
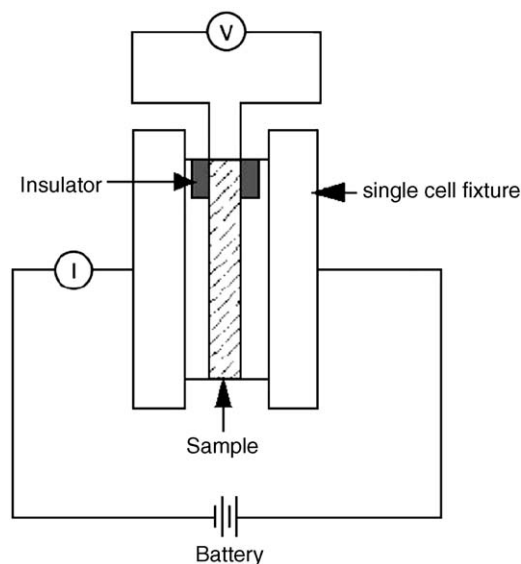
Fig. 1. Schematic diagram for the measurement of the through-plane resistivity of the CFGDL using a standard single cell fixture.
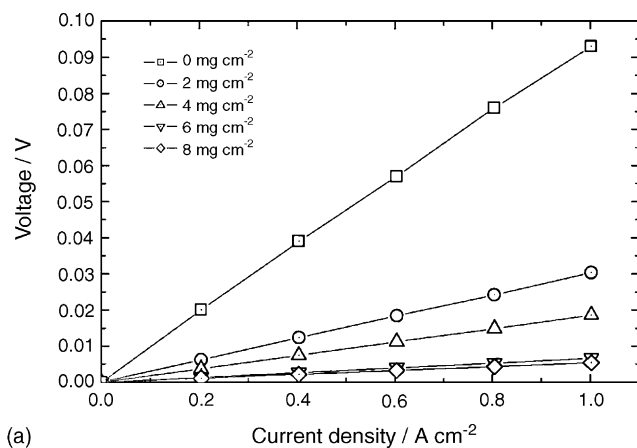

Fig. 2. V–I curves of the CFGDL made (a) with different carbon contents and a fixed 40% PTFE and (b) with different PTFE contents and a fixed 6 mg cm^{-2} carbon. The curves were measured in a single cell fixture at 25 °C.

ducted on each sample. In the polarization measurements, the single cell was operated at 80 °C and 1.5 bars on both anode and cathode using humidified H$_2$/air as reactants. The anode gas humidification was set at 5 °C higher than the cell temperature, while the cathode air humidification was set at 5 °C lower than the cell temperature. For reactant flows arranged in a co-flow manner, the gas flow rates were kept at different stoichiometric values (1.15 times for H$_2$ and 2.5 times for air at 1 A cm^{-2} current density). The testing was carried out using Arbin electronic load system. In the CV measurements, the cell was operated at 70 °C under ambient pressure. Humidified argon (Ar) was fed to the working electrode compartment (cathode), while humidified hydrogen (H$_2$) was fed to the counter electrode compartment (anode). Because of the negligible over-potential at the counter electrode for H$_2$ oxidation, the counter electrode serves as the reference electrode. The sweep rate in the measurements was 50 mV s^{-1} with a potential range of 0.0–1.5 V. The CV measurements were performed using Princeton Applied Research Potentiostat/Galvanostat (Model/263A).

The microstructure of the CFGDL was examined using scanning electron microscopy (JEOL JSM-5600). The cross-section surface of CFGDL was mechanically fractured after immersion in liquid nitrogen for observation.

3. Results and discussion

3.1. Resistance of the CFGDL

Fig. 2 shows the V–I curves of the CFGDL fabricated using different carbon contents with a fixed 40% PTFE and using different PTFE contents with a fixed 6 mg cm^{-2} carbon. The curves appear to be in straight lines, indicating the pure ohmic nature of the V–I curves with little polarization contribution from the CFGDL and the current collector interface. Thus the slope of the curves would be the area resistance of the CFGDL. The V–I
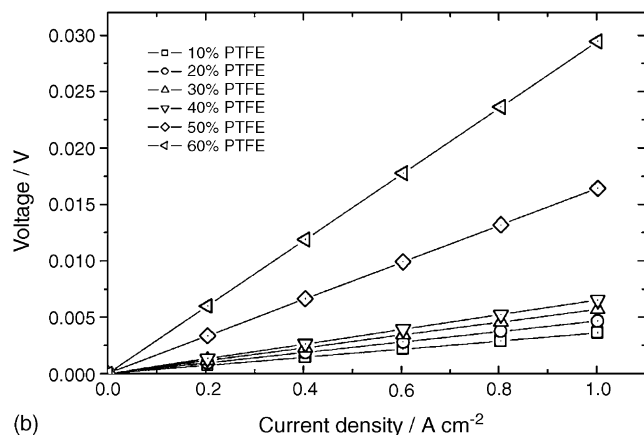
curves indicate that both carbon and PTFE contents have significant effect on the resistivity of the carbon-filled gas diffusion layer.

Fig. 3 shows the dependence of the resistivity, ρ, of the CFGDL on the carbon and PTFE loading. The resistivity of the PTFE treated carbon paper was 3.1 Ω cm. With the addition of carbon filler, the resistivity of the CFGDL drops sharply with the increase of carbon loading from 0 to 2 mg cm^{-2} and then decreases almost linearly with the carbon loading until the carbon content reached ∼6 mg cm^{-2} (Fig. 3a). Further increase in the carbon content has little effect on the resistivity of the CFGDL. As the same single cell fixture was used for all the CFGDL measurements, the difference in the measured resistivity must be related to the carbon content in the CFGDL. This clearly shows that the carbon fillers in the CFGDL play an important role in the electrical conductivity of the CFGDL. In fact, the electrical system of the CFGDL can be assumed to be two conducting networks, macro-porous substrate (carbon paper) and conductive filler (carbon and PTFE mixture). The network chains act as parallel conductors through the CFGDL [14]. Hence,

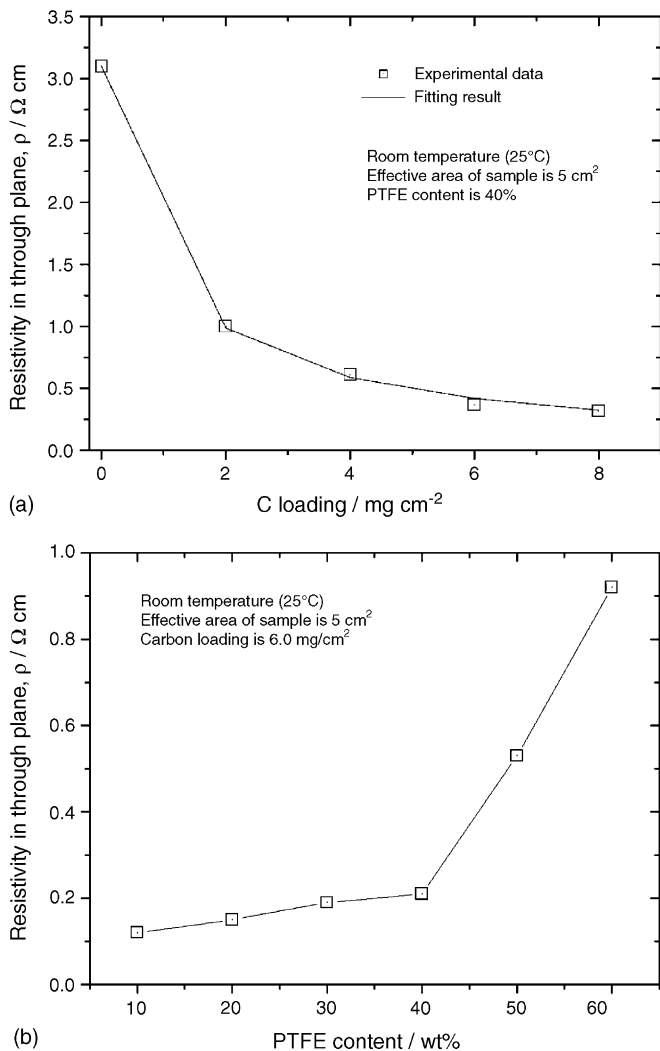$$\frac{1}{\rho} = \frac{V_m}{\rho_m} + \frac{V_f}{\rho_f}, \tag{2}$$

(a)

(b)

Fig. 3. Dependence of the resistivity, ρ, of the CFGDL on (a) the carbon content in the case of a fixed 40% PTFE and the line in the figure was fitted result and (b) the PTFE content in the case of a fixed $6\,\mathrm{mg\,cm^{-2}}$ carbon loading.

where subscripts m and f refer to macro-porous substrate and conducting filler, respectively. The V_m and V_f are the volume fractions of each. ρ_m and ρ_f are the resistivities of the macro-porous substrate and conducting filler, respectively. Note that the volume fraction of conducting filler V_f can be expressed as:

$$V_\mathrm{f} = \frac{m_\mathrm{f}}{d_\mathrm{f}l}, \tag{3}$$

where m_f and d_f are the loading and density of the conducting filler in the macro-porous substrate, respectively, and l is the thickness of the macro-porous substrate. The loading of the conducting filler m_f can be given by the sum of the loading of conductive particle (carbon powder) m_c and the loading of polymer binder (PTFE) m_p,

$$m_\mathrm{f} = m_\mathrm{c} + m_\mathrm{p} = \left(\frac{1+\xi}{\xi}\right)m_\mathrm{c}, \tag{4}$$

where ξ is the loading ratio of conducting particle to polymer binder. Rewriting Eq. (2), the resistivity of CFGDL becomes

$$\frac{1}{\rho} = \frac{V_\mathrm{m}}{\rho_\mathrm{m}} + km_\mathrm{c}, \tag{5}$$

where

$$k = \left(\frac{\xi+1}{\xi}\right)\frac{1}{\rho_\mathrm{f}d_\mathrm{f}l}. \tag{6}$$

If the loading ratio of conducting particle to polymer binder ξ is constant, then ρ_f and d_f will be fixed. For a given system, the thickness of macro-porous substrate l is known, and thus k becomes a constant. Hence, ρ as a function of m_c can be established using Eq. (5).

The result of the fitting of the experimental data ρ versus m_c to Eq. (5) is presented in Fig. 3a. Good agreement between the experimental data points and the simulated ρ versus m_c relation from the curve fitting indicates that Eq. (5) describing the relation of the resistivity to carbon powder loading for CFGDL in this experiment is valid. The assumption of two parallel conducting networks of electrical systems in the CFGDL structure is reasonable.

The same can also be said of the effect of the PTFE content in the CFGDL on the resistivity of the gas diffusion layer. As mentioned above, the CFGDL can be considered to be two parallel conducting networks, macro-porous substrate (carbon paper) and conductive filler (carbon and PTFE mixture). The resistivity of the conductive filler is dependent on the loading ratio of the carbon powder to the PTFE. When the carbon loading in the filler is fixed, the resistivity must be a function of the PTFE content. Basically, the resistivity of the carbon/polymer conductive filler does not increase linearly with increasing polymer content. Instead, the resistivity increases sharply over a narrow range of polymer content. This increase in resistivity is due to the formation of barriers to conductive paths by the PTFE, which is an insulating material, at the critical PTFE content. Below the critical PTFE content the conductive filler in the CFGDL has sufficient continuous conductive networks and shows a high electrical conductivity. Above the critical PTFE content, the conductive filler exhibits a lower conductivity. In the case of CFGDL with a carbon content of $6\,\mathrm{mg\,cm^{-2}}$, the resistivity of the CFGDL is more or less the same for different PTFE contents up to 40%. Above a PTFE content of 40%, the resistivity of the CFGDL increased abruptly with PTFE (Fig. 3b). It is evident that a PTFE content of 40% is the optimal PTFE content and the conductive filler network contributes more to the resistivity of the CFGDL than the macro-porous substrate (carbon paper) network in the CFGDL.

Thus, from the conductivity measurements and theoretical analysis above, it was found that a carbon content of $6\,\mathrm{mg\,cm^{-2}}$ and 40% PTFE was the optimum composition for the CFGDL to achieve the best electrical properties.

3.2. Cycle voltammetry measurement

Fig. 4 shows the cyclic voltammograms of the CFGDL with different carbon and PTFE contents measured at $70\,^{\circ}\mathrm{C}$ under a
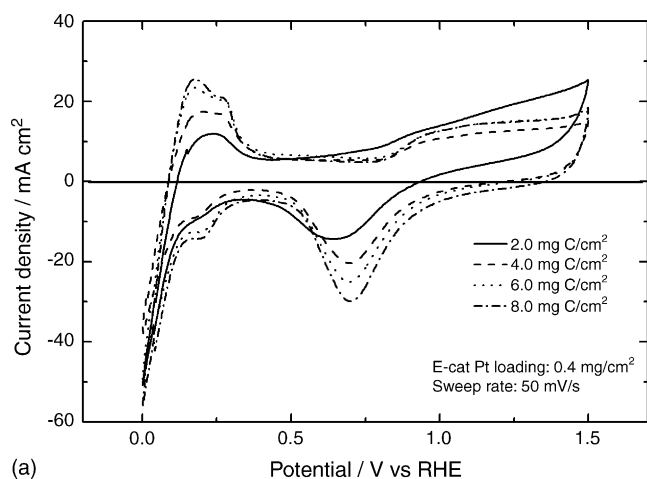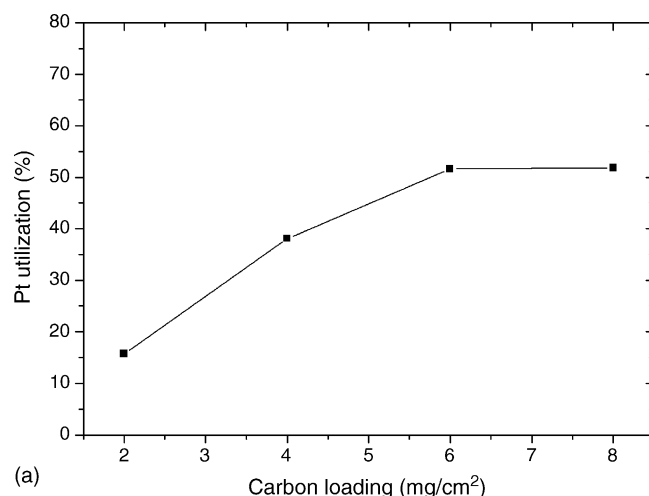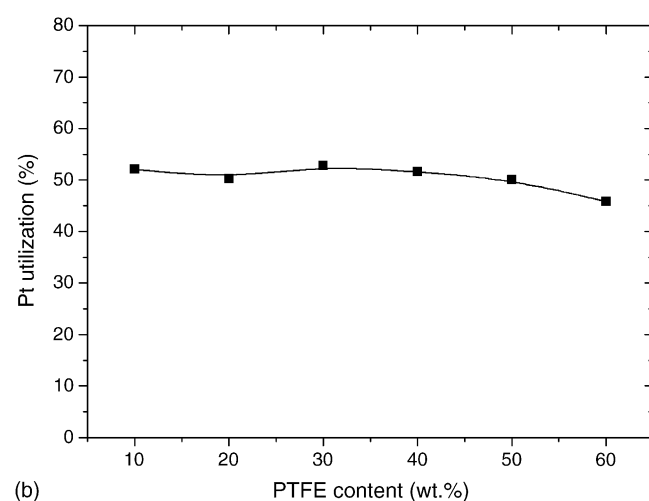
(a)
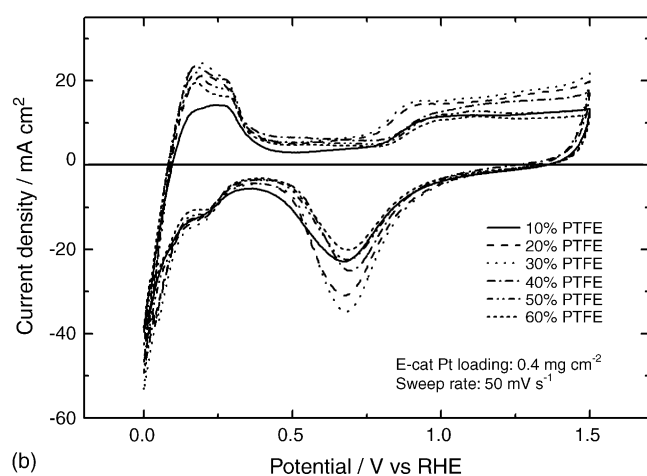
(b)

Fig. 4. Cyclic voltammograms of the CFGDL with (a) different carbon contents and (b) different PTFE contents. The voltammograms were measured at 70 °C and scanning rate of 50 mV s^{-1}. The Pt loading of the cathode was 0.4 mg cm^{-2}.

(a)

(b)

Fig. 5. Pt utilizations of the cells with (a) different carbon and (b) different PTFE contents in the CFGDL of the cathodes, estimated from the cyclic voltammograms of Fig. 4. The Pt loading of the cathode was 0.4 mg cm^{-2}.

scanning rate of 50 mV s^{-1}. The peak associated with the hydrogen desorption at 0.17–0.22 V is clearly affected by both the carbon and PTFE content in the CFGDL. In the case of the CFGDL with a fixed 40% PTFE, the peak height at 0.177 V (i.e., the hydrogen desorption peak) increased with the increase in the carbon content (Fig. 4a), implying the electrochemically active area (ESA) of electrodes and Pt utilization (the ratio of the ESA to SA, the Pt surface area of catalyst) increased with the increase in the carbon content in the CFGDL. Similarly, in the case of CFGDL with a fixed carbon content of 6 mg cm^{-2}, the height of the hydrogen desorption peak at 0.182 V increased with increase in the PTFE content (Fig. 4b). The ESA of electrodes and Pt utilization can be estimated from the cyclic voltammograms assuming the value of 0.21 mC cm^{-2} for the hydrogen desorption charge on the smooth Pt electrode [15,16] and Pt surface area of 140 m^2 g^{-1} for E-TEK 20 wt.% Pt/C catalyst [17].

Fig. 5 is a plot of the Pt utilization of the CFGDL as a function of carbon and PTFE content, estimated from the cyclic voltammetry curves. In the case of the CFGDL with 40% PTFE content, the Pt utilization increases with the increase of carbon loading in the CFGDL (Fig. 5a) from 15.7% (carbon loading:

2 mg cm^{-2}) to 51.8% (carbon loading: 8 mg cm^{-2}). It can be explained that, at low carbon loadings, the macro-pore structure of electrode backing will be inadequately filled with carbon black filler, thus offering a poor physical support for the catalyst layer. This would probably result in, when preparing the catalyst layer, some catalyst particles dropping into the electrode backing. Thus, the catalyst layer will not attach perfectly to the Nafion membrane causing poor ionic contact and a reduced ESA. It was also observed that there is no significant effect of PTFE content in the carbon filler of CFGDL on the Pt utilization, except for the case with 60% of PTFE content (Fig. 5b). This is likely due to a covering of PTFE agglomerates on some reactive sites with excessive PTFE in the carbon filler. This implicitly means that with a reasonable amount of carbon content, the PTFE content in CFGDL is unlikely to be the key factor affecting Pt utilization in the catalyst layer.

3.3. Cell performance

The performance of fuel cells operating at 80 °C under H$_2$/air with different carbon loadings and PTFE content in the CFGDL
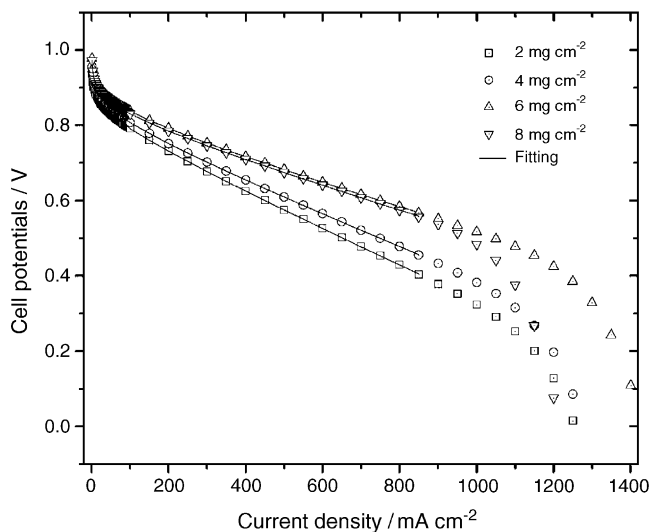
Fig. 6. Polarization curves of the cells with different carbon loadings in the CFGDL of cathodes operating at 80 °C under H$_2$/air. The PTFE content in the CFGDL was 40% and the lines in the figure were fitted results.

of cathodes are shown in Figs. 6 and 7, respectively. The curves in the figures were fitted results according to the empirical equation proposed by Srinivasan et al. [18]. The results show that the fits between the experimental and the predicted data were quite reasonable at low to intermediate current densities.

3.3.1. Effect of carbon loading

Fig. 6 reveals clearly that increasing the carbon loading in the CFGDL has a significant improvement in performance up to 6 mg cm^{-2} in all three polarization regions, i.e., activation (mainly at the cathode), mass transport, and ohmic controlled, but further increasing of the carbon loading produced a constant level of performance in the activation and ohmic controlled regions but a noticeable deterioration in the mass transport region. An analysis of the results above is presented as follows.

In the activation polarization region, the reduced current density with decreasing the carbon loading is due to the loss of a
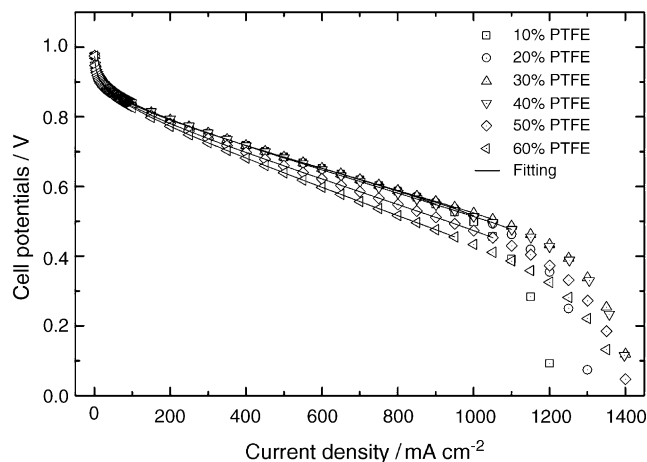

Fig. 7. Polarization curves of the cells with different PTFE contents in the CFGDL of cathodes operating at 80 °C under H$_2$/air. The carbon content in the CFGDL was 6 mg cm^{-2} and the lines in the figure were fitted results.

number of active sites for the oxygen reduction reaction (ORR) inside the catalyst layer. At a lower carbon loading, insufficient conductive filler (carbon powder with PTFE) in the structure of macro-porous substrate (carbon paper) results in the catalyst particles dropping into the structure of CFGDL during the fabrication stage of catalyst layer. The catalyst particles dispersed in the structure of the GDL became inactive for ORR. In other words, this effectively lowers the Pt loading in the electrode. This is proven by the increase in the ESA/Pt utilization of electrodes with the increase of the carbon loading (Fig. 5a).

In the ohmic controlled polarization region, the cell overpotential results from the internal resistances (i.e., the value of R_i produced by fitting of the empirical equation proposed by Srinivasan et al. to experimental data in Fig. 6) of the cell including the resistances of the membrane and various electrode layers, mass transport resistance, and the contact resistances both between the membrane and electrodes and between the electrodes and the bipolar plates. In this experiment, the main contribution to the internal resistance is from the effect of carbon loading in the CFGDL when the PTFE content is fixed at 40%, since the resistance of the membrane, which is strongly dependent on the water content inside, may not change, assuming the membrane is fully hydrated under the humidifying conditions [19]. The decrease in the internal resistance or ohmic over-potential with increase in carbon loading up to 6 mg cm^{-2} in the ohmic controlled region is dependent upon decreasing the area specific resistance (R_{ASR}) of the CFGDL and contact resistance (between the electrode and membrane). The decrease in R_{ASR} of the CFGDL with increasing carbon loading has been mentioned in Section 3.1. In comparison, R_{ASR} of the CFGDL is two orders of magnitude smaller than that of the R_i of the cell as seen in Fig. 8a. The major contribution of the carbon loading in the CFGDL to the R_i is due to the electrical contact resistance between the CFGDL and the catalyst layer and ionic contact resistance between the electrode and the membrane [1]. In other words, if there is insufficient carbon black filler in the macro-structure of the gas diffusion layer, it may not be able to give a good support to the catalyst layer. This could give rise to an increase in the internal resistance of the cell with increasing contact resistance.

The increase in the carbon loading from 2 to 6 mg cm^{-2} in the CFGDL also increases the mass transport limiting current densities in the mass transport control polarization region as seen in Fig. 6. These results contradict those reported by Jordan et al. [3] and Kong et al. [9]. These contradictory results might be due to the different structure of the CFGDL to GDL's in the conventional three-layer electrode. In the CFGDL, the conductive filler (carbon powder with PTFE) is filled into the whole structure of the macro-porous substrate (carbon paper) to form a homogeneous porous structure in the CFGDL, whose thickness remains unchanged under varying carbon loading. The low carbon loading in the CFGDL would increase the amount of macro pores in the carbon paper and retain larger water droplets in the macro pores of CFGDL, leading to increased mass transport resistance to oxygen diffusion [20]. Thus, the electrode with a lower carbon loading in the CFGDL showed a larger mass transport over-potential. For the GDL used in the three-layer electrode, however, a micro-porous layer of carbon black with
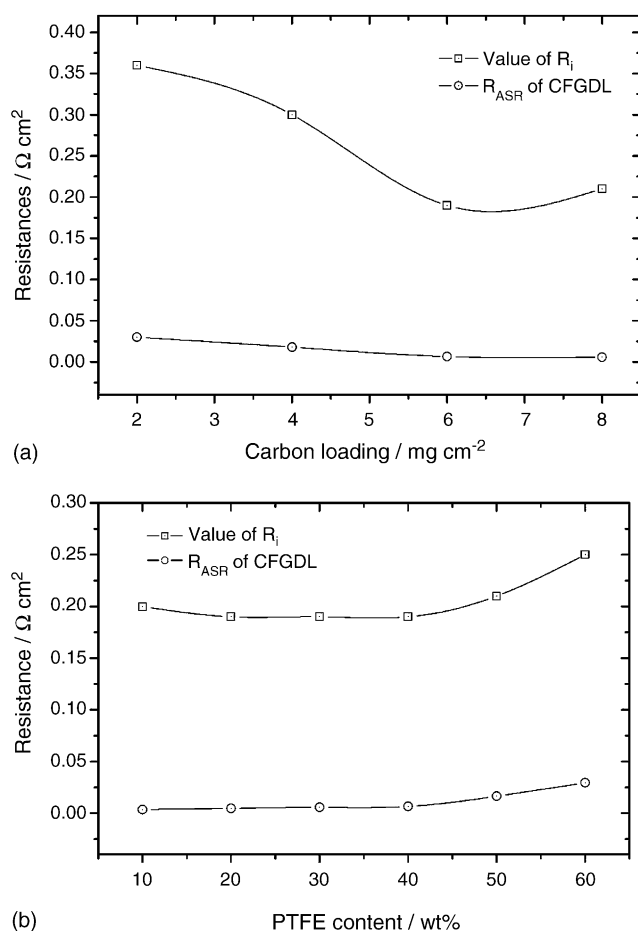
(a)

(b)

Fig. 8. Plots of the cell internal resistance, R_i, against the (a) carbon and (b) PTFE contents of the CFGDL. R_i was evaluated from the polarization curves of Figs. 6 and 7. In comparison, the area specific resistance, R_{ASR} of the CFGDL measured in the single cell fixture was also given in the figure.

PTFE is coated onto a macro-porous substrate (carbon paper or carbon cloth). The extra carbon layer on the macro-porous substrate will increase the thickness of the GDL in the electrode with increasing the carbon loading. The increase in GDL thickness would reduce the gas access to the catalyst layer and thus increase the mass transport over-potential. Similar behaviour can be observed in the case of carbon loading with $8\,mg\,cm^{-2}$ in CFGDL seen in Fig. 6. This is likely due to excessive use of carbon filler, thus decreasing the porosity of the CFGDL. This would cause an increase in the gas diffusion resistance of the CFGDL, as indicated by the relatively low limiting current density of the CFGDL with carbon loading of $8\,mg\,cm^{-2}$ as compared to that of $6\,mg\,cm^{-2}$ (Fig. 6).

3.3.2. Effect of PTFE content

Fig. 7 is the polarization curves of the cells with different PTFE loadings in the CFGDL of cathodes operating at 80 °C under H_2/air. The carbon content in the CFGDL was $6\,mg\,cm^{-2}$ and the curves in the figure were the fitted results. Unlike the effect of carbon loading, the PTFE content of the CFGDL affects the polarization performance of the cell only in the ohmic and mass transport control polarization regions. Less impact of the

PTFE content on the performance in activation control region is observed. The best results were obtained on the cells with CFGDLs having PTFE contents of 30–40%. A low PTFE content of 10% or a high PTFE content of 60% leads to reduced cell performance.

As mentioned earlier, the variation of the PTFE content in the CFGDL with a carbon loading of $6.0\,mg\,cm^{-2}$ has less effect on the ESA/Pt utilization of electrode (Fig. 5b) due to an insignificant loss of catalyst particles from the catalyst layer. This might be the reason that the PTFE content has a lower effect on the performance of the cell in the activation controlled polarization region.

The effect of the PTFE content in the CFGDL with a fixed carbon loading of $6\,mg\,cm^{-2}$ on the cell internal resistances (the value of R_i is produced by fitting of the empirical equation proposed by Srinivasan et al. to experimental data in Fig. 7) in ohmic controlled polarization region can be seen in Fig. 8b. R_i does not change significantly with the PTFE content for the CFGDL with PTFE contents lower than 40%. This is also consistent with the dependence of the area specific resistance (R_{ASR}) of the CFGDL on the PTFE contents as shown in Fig. 3b. With the PTFE content higher than 40%, the total cell resistance begins to increase, which is also consistent with that of the area specific resistance of the CFGDL. In comparison, the R_{ASR} of the CFGDL is still two orders of magnitude smaller than that of the R_i of the cell with a
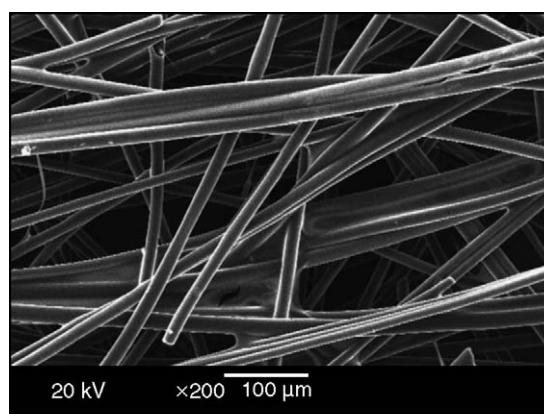
(a)
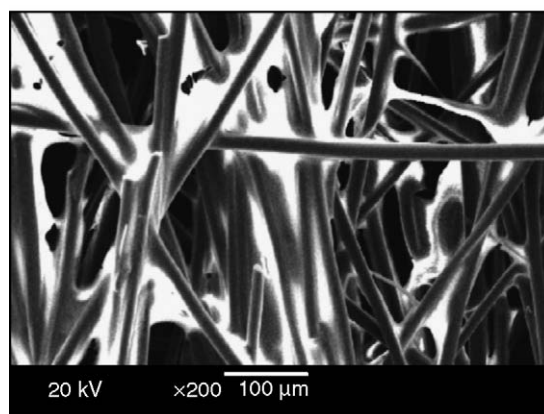
(b)

Fig. 9. SEM micrographs of the SGL704E carbon paper (a) before and (b) after the hydrophobic treatment (PTFE content: 40%).

varying PTFE content in the CFGDL (Fig. 8b). It is believed that the major contribution of the PTFE content in the CFGDL on the R_i is the electrical contact resistance between the CFGDL and the catalyst layer and the resistance associated with mass transport limitation. Below a PTFE content of 40%, the electrical contact resistance would play a significant role in the R_i. Above a PTFE content of 40%, both the electrical contact resistance and the resistance of mass transport would contribute equally to R_i.

Mass transport losses in the GDL come from the resistance to gas diffusion and the transport loss due to water flooding in an operating fuel cell. The gas diffusion rate in GDL is related to the porosity and the thickness of the GDL. The high porosity and thin GDL are helpful for reactants to access the catalyst sites through the GDL. Water flooding of the GDL can be alleviated by introducing the hydrophobic agent, PTFE, inside the GDL structure. It is because water may not be able to form stable droplets inside of hydrophobic micro-pores in the GDL that the GDL is less likely to be flooded. This implies that the catalyst layer is in direct contact with the GDL and will be less likely

to flood [10]. However, the hydrophobic property of the GDL is dependent on the PTFE content in the GDL. The higher the content of PTFE contained in the GDL, the more hydrophobic the surface and micro-pores in GDL will be, and the less the electrode will be flooded. Thus, the mass transport losses due to water flooding will be decreased. On the other hand, the increase of PTFE content in the GDL also decreases the porosity/gas permeation of the GDL [12]. In the case of the CFGDL with an optimum carbon loading of 6 mg cm^{-2}, the primary function of the PTFE contents in the CFGDL is to improve the hydrophobic properties of the porous structure of the gas diffusion layer, which is critical to the gas diffusion and water removal through the GDL. It is evident that the polarization curve of the fuel cell with a PTFE content of 10%, exhibits the lowest mass transport limiting current density due to a serious degree flooding problem in the CFGDL, and the mass transport limiting current density increases to a maximum value when the PTFE content reaches 30%, and then decreases with further increase in PTFE content due to decreasing of the porosity of the CFGDL at higher PTFE contents (Fig. 7).
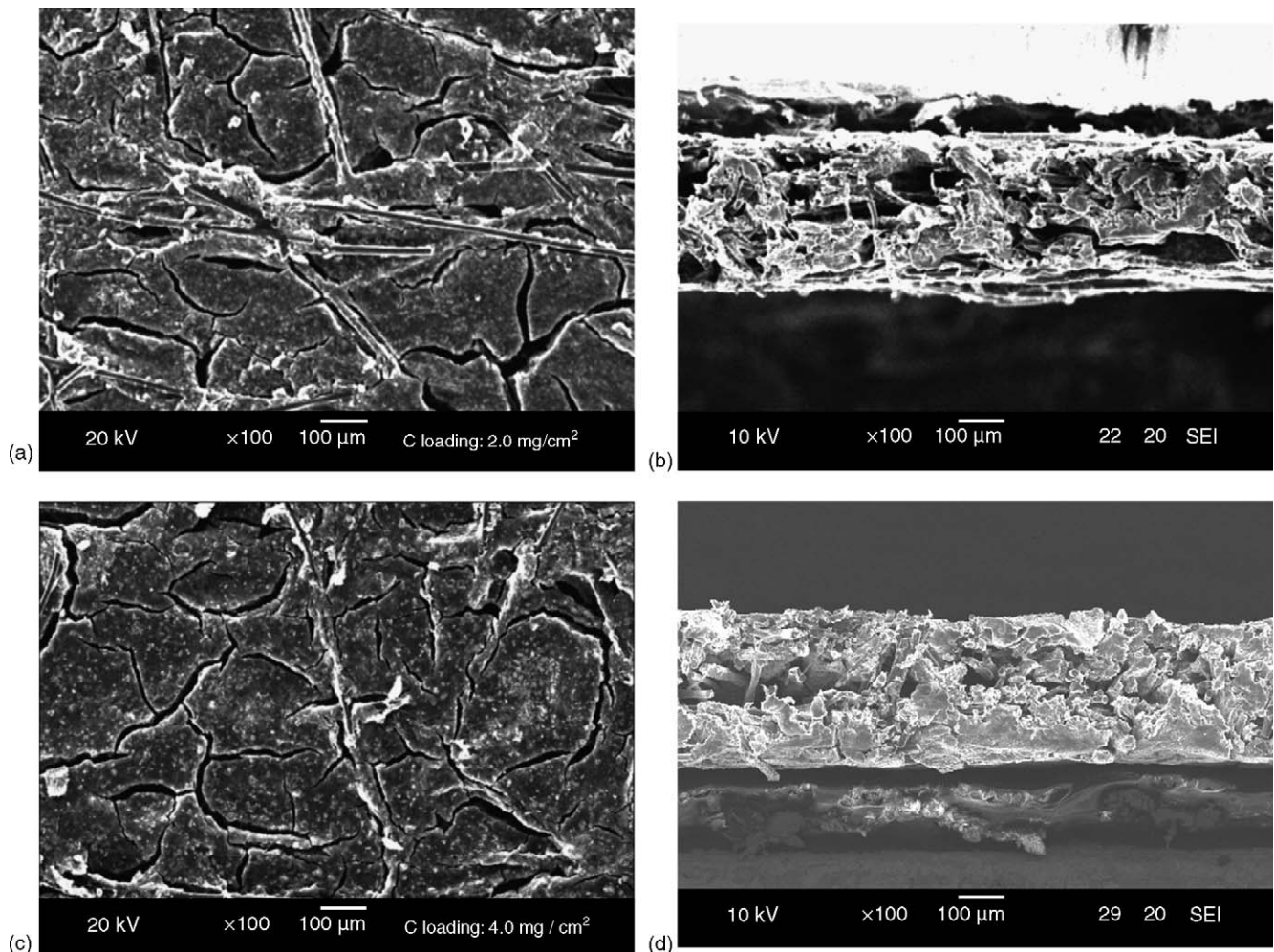

Fig. 10. SEM micrographs of the top-view and cross-section images of the CFGDL with carbon loading of (a) and (b) 2 mg cm^{-2}, (c) and (d) 4 mg cm^{-2}, (e) and (f) 6 mg cm^{-2}, and (g) and (h) 8 mg cm^{-2}. The PTFE content of the CFGDL was 40%.
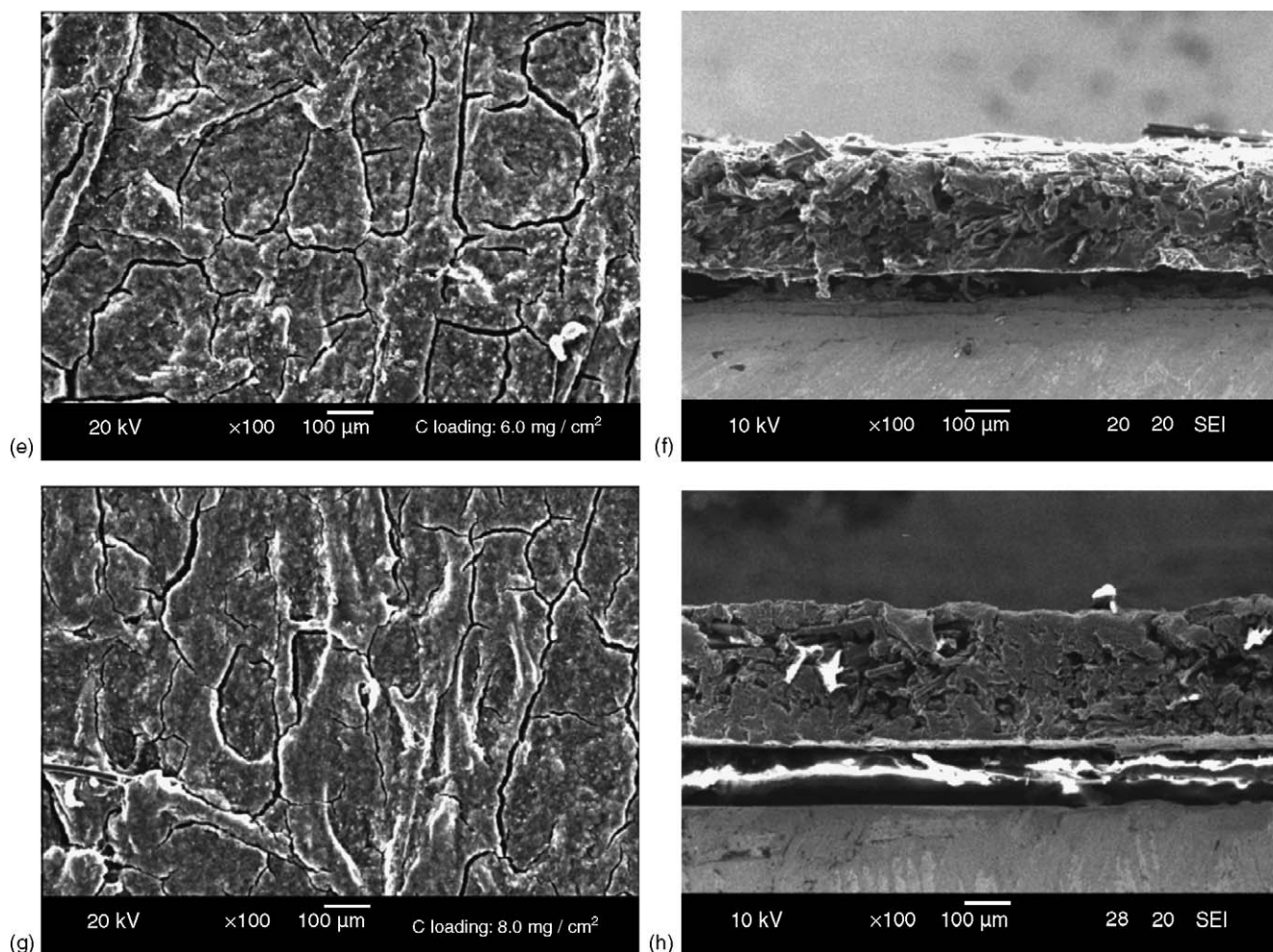
Fig. 10. (*Continued*).

3.4. Microstructure

Fig. 9 shows SEM micrographs of the SGL704E carbon paper before and after the hydrophobic treatment (PTFE immersion). SGL704E carbon paper has a non-woven structure with many open and large pores (Fig. 9a). After the hydrophobic treatment by immersion in PTFE emulsion, SGL704E becomes much stronger due to its fibres being bonded by PTFE. In addition, the fibre surfaces of carbon papers have become hydrophobic, which is helpful for water management in the electrode. There are still a lot of open spaces and large pores in SGL704E carbon paper structure although the porosity is reduced slightly by the PTFE treatment as can be seen in Fig. 9b.

Fig. 10 shows the SEM micrographs of the top-view and cross-section images of the CFGDL with carbon loading of 2–8 mg cm^{-2}. The microstructure of the CFGDL with a carbon loading of 2 mg cm^{-2} was characterized by formation of a large number of coarse cracks on the surfaces and large pores (Fig. 10a and b). The large cracks and open space and pores in the CFGDL would lead to poor electrical conductivity of the CFGDL as shown by the high area specific resistance (Fig. 3a). The large cracks could also increase the contact resistance between CFGDL and catalyst particles and reduce the

support for the catalyst as the Pt catalyst particles may have fallen into the open pores of the gas diffusion electrode. This explanation is supported by the relatively low Pt utilization for the CFGDL with a low carbon content (Fig. 5a). Increase in the carbon loading reduced the number of cracks and the size of the cracks. From the cross-section images, the large pores and open spaces of the CFGDL were also significantly reduced with increase in the carbon content. In the case of a CFGDL with a carbon loading of 6 mg cm^{-2}, the microstructure of the diffusion layer was characterized by micro-pores uniformly distributed across the whole layer (Fig. 10e and f). Such a microstructure appears to be beneficial not only to the electrical conductivity (Fig. 3a) but also to the support of the Pt catalyst (high Pt utilization as shown in Fig. 5a). The high cell performance observed on the CFGDL with a carbon loading of 6 mg cm^{-2} can also be explained by the right microstructure combined with proper hydrophobicity. However, further increase of the carbon loading to 8 mg cm^{-2} led to the formation of a dense microstructure, as shown in Fig. 10h. The dense microstructure would increase the gas diffusion resistance and this explains the reduced cell performance and relatively low limiting current density as compared to the cell with CFGDL having carbon content of 6 mg cm^{-2} (Fig. 6). The present results clearly demonstrate that there is

a close relationship between the microstructure, electrical conductivity of the gas diffusion layer and the cell performance.

4. Conclusions

This paper investigated the fabrication and performance of the carbon-filled gas diffusion layer (CFGDL) and the effect of the carbon loading and PTFE content in the electrode backing on the electrical conductivity, Pt utilization, microstructure and cell performance. The important findings are:

(1) Based on the proposed concept of two parallel conducting networks, macro-porous substrate (carbon paper) and conductive filler (carbon and PTFE mixture), in the CFGDL electrical system, a model for describing the relationship between the resistivity and carbon loading of CFGDL has been developed. Good agreement between the experimental results and the fitted results using the model was observed. This indicates that the assumption of two parallel conducting networks of an electrical system in the CFGDL structure is reasonable. This model might provide useful insight into the electrical conducting mechanism in the CFGDL for prediction of electrical properties of the CFGDL and the design of new kinds of GDLs with new materials.

(2) The loading of the carbon powder in the CFGDL significantly affects the performance of the fuel cell in all three polarization regions, i.e., activation (mainly at the cathode), mass transport, and ohmic control regions. Poor support of the CFGDL for the catalyst layer at low carbon loadings will cause the loss of Pt loading in the catalyst layer and thus an increase in the activation over-potential. Increasing the carbon loading in the CFGDL can also reduce the internal resistance of the cell and hence improve the fuel cell performance mainly due to the decrease in the contact resistance between the interfaces of both GDL/CL and CL/electrolyte membrane. Increasing the carbon loading in the CFGDL can also reduce the mass transport limitation due to the improvement of water management. However, excessive carbon loading in CFGDL decreases the porosity and thus increases the concentration over-potential, in particular for the H_2/air fed fuel cell, which is due to an increased diffusion path in the CFGDL.

(3) Unlike the effect of carbon loading, the PTFE content of the CFGDL at the optimal carbon loading affects only the polarization performance of the cell only in the ohmic and mass transport control polarization regions. It is believed that the major contribution of the PTFE in the CFGDL on the ohmic polarization is from the electrical contact resistance between the interface of CFGDL/CL. The mass transport polarization caused by the PTFE content comes from the

resistance to gas diffusion due to the changed porosity and diffusion path in the CFGDL and water flooding due to the changed hydrophobicity of CFGDL.

(4) The significant effect of the carbon loading in CFGDL on the utilization of Pt is confirmed. With a fixed PTFE content of 40%, increasing the carbon loading from 2 to 8 mg cm^{-2} in CFGDL would increase the Pt utilization from 16% to 52%. This is most likely due to the reduction of the surface cracks, thus providing better support for the Pt catalysts. A rather insignificant effect of the PTFE content on the utilization of Pt is found, except for excessively an high PTFE content of 60%.

(5) With an optimal carbon loading of 6 mg cm^{-2} and a PTFE content of 40% in the CFGDL, the best fuel cell performance and highest utilization of Pt in the electrode have been achieved.

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