Short communication

Optimal microporous layer for proton exchange membrane fuel cell

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ABSTRACT

This study elucidates how fabrication processes (screen-printing and spraying) and constituent materials (carbon paper as backing, Acetylene Black (AB) carbon (42 nm), XC-72R carbon (30 nm) or BP2000 (15 nm) as carbon powders, and 10–50% fluorinated ethylene propylene (FEP) as hydrophobic substances) for microporous layers (MPLs) affect the performance of proton exchange membrane fuel cells. The screen-printing process produces MPLs with smaller surface fractures than does the spraying process. The effect of optimal FEP content on cell performance is noted. The presence of an optimal FEP content is due to the counterbalance between enhanced performance produced with increased gas permeability and decreased performance yielded with small contact area and electrical conductivity with excess FEP. The MPL with large carbon powders is preferred when oxygen supply is limited; otherwise, small carbon powders should be utilized. Optimal MPL design should address negative effects possibly associated with contact resistance, gas permeation resistance, and excess water resistance.

1. Introduction

The gas diffusion layer (GDL) distributes reactant gas uniformly into the catalyst layer and conducts electrons out of a proton exchange membrane fuel cell (PEMFC). Adding a microporous layer (MPL) made of carbon carrier modified with hydrophobic material between the GDL and catalyst layer reduces water flooding and thereby improves cell performance [1–3]. Passalacqua et al. [4] indicated that adding an MPL made of a single carbon layer prevented direct contact between the catalyst layer and carbon paper. Chen et al. [5] improved cell performance at high current density by adding a water management layer (WML) between the conventional gas diffusion layer and catalyst layer.

Coating procedures to deposit an MPL onto a GDL have been developed [6–9]. The hydrophobic coating materials are polytetrafluoroethylene (PTFE) [10] and fluorinated ethylene propylene (FEP) [11]. Carbon carriers, such as oil-furnace carbon Vulcan XC-72R (XC-72R) [6], Acetylene Black (AB) [7] and Black Pearls 2000 (BP2000) [8] were tested. The contents of the hydrophobic agent impact the conductivity and hydrophobicity of the generated GDL. Prasanna et al. [12] determined that optimal cell performance was achieved when PTFE content was 20%, a percentage attributable to the yielded high gas permeation rate. Giorgi et al. [13] noted

decreased cell performance with high PTFE levels in the GDL at high current density, which is attributable to reduced void volume at high PTFE levels. Park et al. [14] proposed that porosity and void diameter of gas diffusion material varied with PTFE content, which impacts cell performance by altering the contact area between a GDL and catalyst layer.

Jordan et al. [15] noted that a cell using Acetylene Black (AB) carbon performed better than a cell using Vulcan XC-72R (XC-72R) carbon. Furthermore, these authors argued that a cell achieves optimal performance with $1.9 \, \mathrm{mg \, cm^{-2}}$ AB carbon when using oxygen as the cathode oxidant. When using air as the cathode oxidant, the optimal cell performance was achieved with $1.25 \, \mathrm{mg \, cm^{-2}}$ AB carbon. Autolini et al. [16] coated Vulcan XC-72R carbon and Shawinigan AB carbon on carbon cloth and carbon paper to form a diffusion layer. Their experimental results indicated that cell performance at partial oxygen pressure of 1 atm was improved with Shawinigan AB carbon. Conversely, when the partial pressure of oxygen was increased to 3 atm, good electrochemical performance was noted when Vulcan XC-72R carbon was deposited on the catalyst layer. Williams et al. [17] demonstrated that gas permeability affected the limiting current density of cells.

Comparative analysis of a PEMFC with a GDL via different techniques provides important information when searching for an appropriate fabrication technique and processing parameters. This study fabricated a GDL using different contents of hydrophobic substances and different carbon species. The performance of single fuel cell assembly was evaluated as polarization curve using oxygen or

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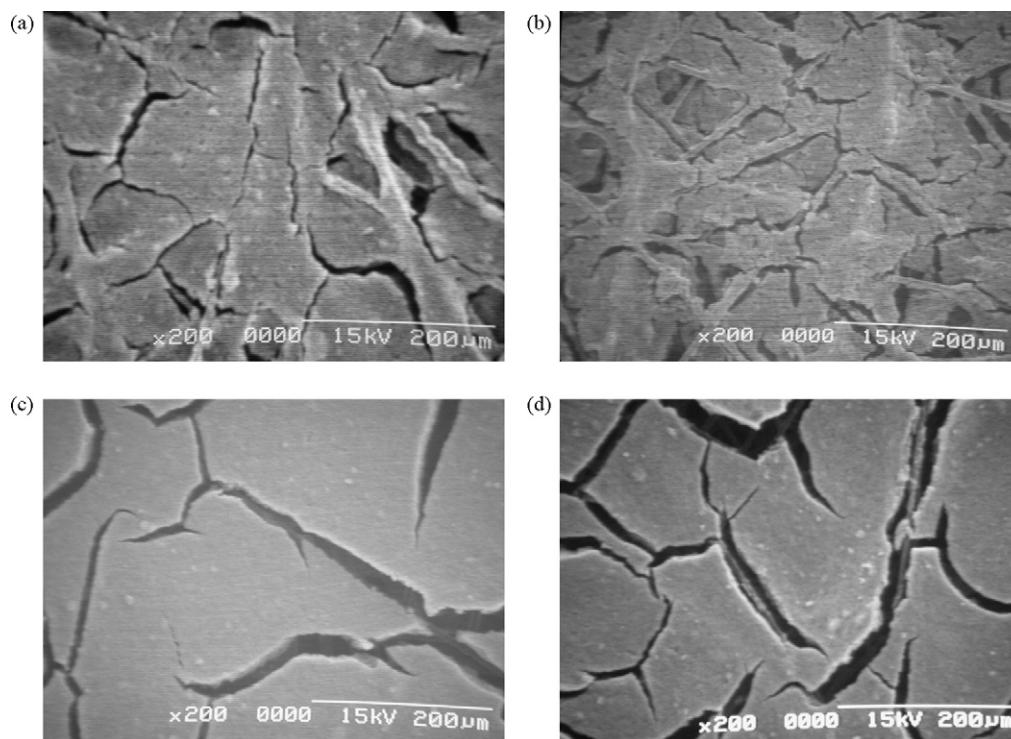*E-mail address:* wangxd99@gmail.com (X.-D. Wang).

Fig. 1. Surface SEM micrographs of the microporous layer with different FEP contents prepared using the screen-printing process and the spraying process. (a) Screen-printing with 20% FEP; (b) screen-printing with 50% FEP; (c) spraying with 20% FEP; (d) spraying with 50% FEP.

air as the cathode oxidant. The aim of this study is not to present a novel design and operational strategy, but rather to experimentally confirm the conclusions of some previous studies.

2. Experimental setup and methodology

2.1. Materials and coating

A two-stage process was adopted in this study to prepare the GDL and MPL for a PEMFC. Carbon paper was utilized as backing due to its low electrical resistance and self-hydrophobicity. Although most MPL studies employed PTFE as the hydrophobic substance, this study coated an FEP layer onto the carbon paper as such studies are rare. A carbon slurry made of a mixture of FEP and carbon powders was then deposited by screen-printing or spraying processes on the FEP-coated carbon paper to form an MPL. The following three carbon powders were used: AB ($42\,nm$, $51\,m^2\,g^{-1}$), Vulcan XC-72R carbon ($30\,nm$, $250\,m^2\,g^{-1}$), and Black Pearls 2000 ($15\,nm$, $475\,m^2\,g^{-1}$). All powders were obtained from E-TEK (NJ, USA). The formed layer comprised an FEP-coated carbon paper layer and the MPL. A Scanning Electron Microscope (SEM) (Hitachi, Tokyo, Japan) was employed to analyze the surface morphology of the MPL. The average Darcy permeability constant was determined at $25\,°C$ by measuring the pressure drop through the MPL corresponding to a given air flux preset by a mass flow device.

2.2. The fuel cell

A membrane electrode assembly (MEA) was constructed with a three-layer structure—an anode catalyst layer (platinum and ruthenium load of $0.45\,mg\,cm^{-2}$), a cathode catalyst layer (platinum load of $0.60\,mg\,cm^{-2}$) and a PEM with a thickness of $35\,\mu m$. The MEA was of the PRIMEA 5621 series with active area of $5\,cm \times 5\,cm$ (W.L. Gore and Associates, Inc., Elkton, USA). The GDL was made in the laboratory with TGP-H-090 carbon paper ($5\,cm \times 5\,cm \times 270\,\mu m$)

(Toray, Tokyo, Japan) as backing. The graphite plate with pattern AXF-5QCF (POCO, Decatur, USA), machined with a serpentine flow field with a width and depth of $1\,mm$, was the flow field bipolar. The collector ($10\,cm \times 10\,cm \times 10\,mm$) was made of copper covered with gold to reduce contact resistance between the plate and flow field and enhance erosion resistance.

2.3. The test rig

The cathode and anode reactants were fed with constant stoichiometric flow rates of 2.0/1.5 on the cathode and anode sides. Cell temperature was set at $65\,°C$; the inlet gases for the cathode and anode were at atmospheric pressure and cathode and anode humidification temperatures were set to $70\,°C$ and $80\,°C$, respectively. Agilent 6060B with the maximum power output of $300\,W$, maximum voltage of $60\,V$, and maximum current of $60\,A$, was the electrical load for the system.

3. Results and discussion

3.1. Surface fractures

The carbon paper impregnated with high FEP content had more fractures on surface than that with low FEP content (Fig. 1). The occurrence was attributable to the relatively less carbon content available to form a uniform MPL. However, the fractures in the MPL made by screen-printing were smaller than those for the sprayed MPL (Fig. 1a–d).

3.2. MEA performance

Different fabrication processes yielded different pore size distributions and average ohmic resistances for the MPL, thereby influencing overall cell performance. High average porosity and large surface fractures on the MPL increased gas permeability to

Table 1
Average gas permeability for different fabrication processes of microporous layer with Vulcan XC-72R carbon powders.

FEP content	Average Darcy permeability constant ($\times 10^{-12}$ m^2)	
	Screen-printing	Spraying
10%	0.68	1.01
20%	0.75	1.53
30%	0.89	1.81
40%	1.01	1.94
50%	1.13	2.00

the catalyst layer. The average Darcy permeability constants for the screen-printed or sprayed MPL with Vulcan XC-72R carbon powders were measured (Table 1). The average gas permeability increased as FEP content increased in the MPL; which was attributable to the surface fractures developed to ease gas flow. Additionally, gas permeability of the sprayed MPL was higher than that screen-printed at the same FEP loading; this finding correlates with SEM observations (Fig. 1).

The MEA performance of the screen-printed MPL and sprayed MPL was tested with Vulcan XC-72R carbon as the carbon powder, 10–50% FEP as the hydrophobic substance, and ethylene glycol as the solvent. Cell tests were conducted using oxygen (Fig. 2) or air as the oxidant (Fig. 3). Cell performance was better with the screen-printed MPL than with the sprayed MPL.

The effects of FEP content in the screen-printed MPL or sprayed MPL on overall MEA performance were compared at a constant with Vulcan XC-72R carbon loading of 1 mg cm^{-2} using oxygen as the oxidant (Fig. 2). Cell performance using oxygen as the oxidant peaked at 30% FEP content for the screen-printed MPL.
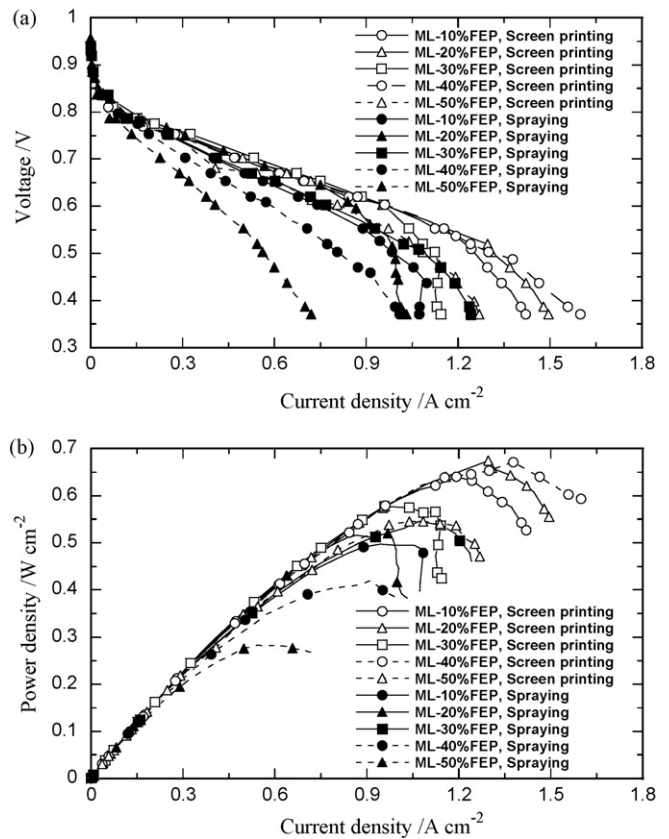
Fig. 3. Effects of different fabrication processes and FEP contents on the cell performance with air as oxidant. (a) *I–V* curve; (b) *I*–power curve.

The effects of using different carbon powders for the screen-printed MPL on overall MEA performance were compared at a constant carbon loading of 1 mg cm^{-2} and 20% FEP (Fig. 4). The cells using BP2000 performed best in pure oxygen tests (Fig. 4a). Conversely, cells using AB carbon performed best when air was the oxidant (Fig. 4b).

3.3. Discussion

Although the large fractures in the sprayed MPL enhanced the gas permeation rate, the contact area between the MPL and catalyst layer was reduced, producing high contact resistance. The worse MEA performance by the sprayed MPL compared with that of the screen-printed MPL (Fig. 2) was likely due to over-competition of increased contact resistance relative to the increased gas permeation rate. The maximum power in air oxidant tests (Fig. 3) indicates that oxygen supply was limited at high current density loadings.

Adding FEP increased gas permeability (Table 1), thereby enhancing cell performance. Conversely, FEP increased the size of fractures and thereby reduced the size of the contact area (Section 3.2) and overall electrical conductivity of the MPL (note: electrical conductivity of FEP is low). The counteraction of these two factors yielded a maximum cell performance at 30% FEP for the screen-printed MPL and at 20% FEP for the sprayed MPL. Excessive amounts of FEP yielded poor cell performance, as in the case with 50% FEP. Detailed comparisons reveal that the MEA of the screen-printed MPL was slightly better than that of the sprayed MPL.

When oxygen supply was limited, as in the air tests, large voids and low surface area generated by AB carbon (42 nm, 51 m^2 g^{-1}) yielded high gas permeation over the MPL, enhancing cell performance. When the oxygen supply was not limited in the pure
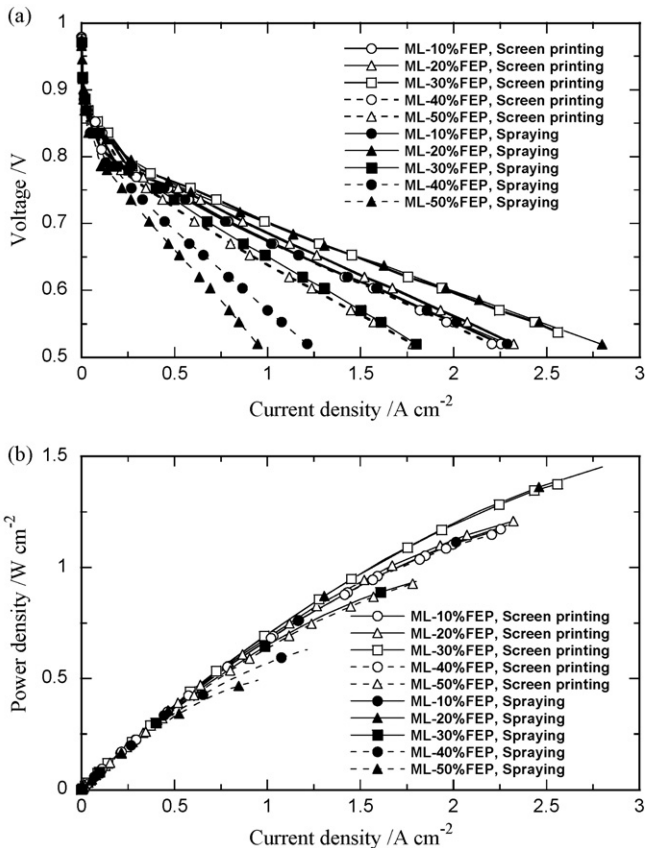
Fig. 2. Effects of different fabrication processes and FEP contents on the cell performance with pure oxygen as oxidant. (a) *I–V* curve; (b) *I*–power curve.
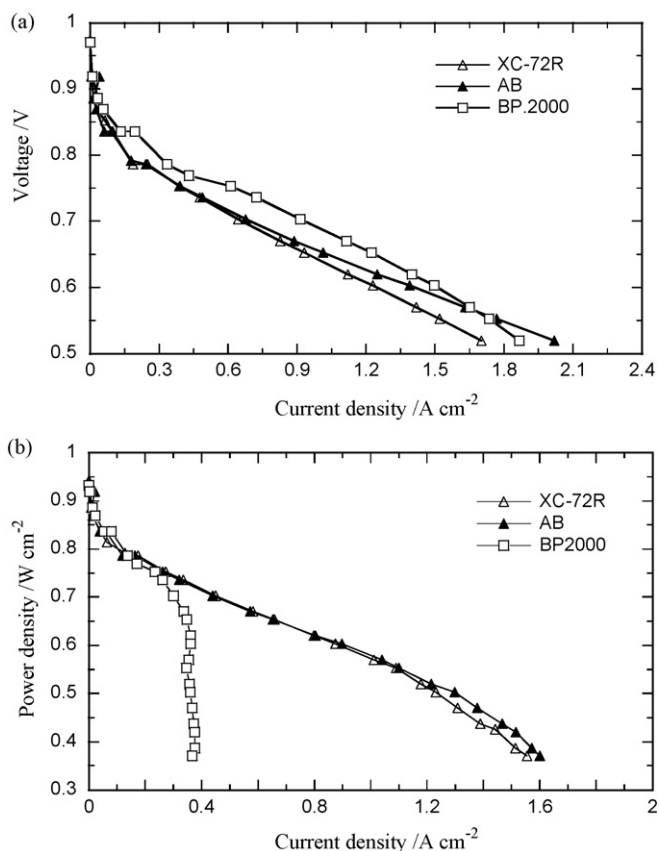
Fig. 4. Effects of carbon black categories on the *I–V* performance. (a) Oxygen as oxidant; (b) air as oxidant.

oxygen test, efficient removal of excess water by BP2000 (15 nm, 475 m² g⁻¹) was essential for enhanced cell performance.

In sum, the optimal MPL design had the best MEA performance presents a compromise between the negative effects by contact resistance between the MPL and catalyst layer, resistance by gas permeation, and excess water removal. Within the experimental conditions in this study, the screen-printed MPL with 30% FEP and 1 mg cm⁻² Vulcan XC-72R carbon powder yielded the best MEA performance (about 1.4 W cm⁻²) with pure oxygen as the oxidant.

4. Conclusions

This study compared cell performance with a screen-printed MPL and sprayed MPL using AB carbon, XC-72R carbon and BP2000 carbon as carbon powders and 10–50% FEP as the hydrophobic substance. The following conclusions were obtained.

1. Fabrication of a MPL by spraying produced larger surface frac-
   tures than screen-printing, particularly when FEP content was
high. Large surface fractures can lead to high gas permeability in an MPL (Table 1).
2. The MEA performance was better with the screen-printed MPL than with the sprayed MPL, due to lower contact resistance of the former between the MPL and catalyst layer.
3. Optimal FEP content maximized MEA power output, due to a compromise between reduced gas permeation resistance and increased contact resistance between the MPL and catalyst layer when FEP content increased.
4. The MPL with carbon powder with large particles yielded the best cell performance with air as the oxidant due to the induced high gas permeability. The MPL with carbon powder with small particles yielded the best cell performance with pure oxygen as the oxidant for easy removal of the excess water produced.
5. The MEA performance was maximized with the MPL design by considering contact resistance, gas permeation resistance, and excess water resistance. In this study, the screen-printed MPL with 30% FEP and 1 mg cm⁻² Vulcan XC-72R carbon powder yielded the best MEA performance (about 1.4 W cm⁻²) with pure oxygen as the oxidant.

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