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Short communication

Effect of diffusion-layer morphology on the performance of solid-polymer-electrolyte direct methanol fuel cells

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Abstract

The performance of solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs) is substantially influenced by the morphology of the gas diffusion-layer in the catalytic electrodes. Cells utilising gas diffusion-layers made with high surface-area Ketjen Black carbon, at an optimised thickness, show better performance compared with cells utilising Vulcan XC-72 carbon or 'acetylene black' carbon in the diffusion-layer. The cells with a hydrophilic diffusion-layer on the anodes and a hydrophobic diffusion-layer on the cathodes yield better performance. The cells with oxygen or air as the oxidant gave power density of 250 or 105 mW cm^{-2}, respectively, at an operational temperature of 90 °C and 2 bar pressure.

Keywords: Direct methanol fuel cells; Diffusion-layer morphology; High surface-area carbon

1. Introduction

A solid-polymer-electrolyte direct methanol fuel cell (SPE-DMFC) comprises an anode to which methanol is supplied, a cathode to which oxygen is supplied, and a perfluorosulfonic acid membrane (Nafion®) electrolyte that permits the flow of protons from the anode to the cathode [1,2]. The assembly consisting of the anode, the cathode and a Nafion membrane is called the 'membrane electrode assembly' (MEA). The electrodes (anode and cathode) are supported on macroporous carbon paper (thickness ca. 0.3 mm), often called the diffusion-layer backing. The carbon paper is coated on one side with a carbon black/polymer suspension which forms a thin microporous hydrophobic diffusion-layer on to which a catalyst ink is coated. In the absence of the diffusion-layer, the catalyst ink is absorbed directly on to the macroporous carbon paper and this hinders the catalytic reactions in the fuel cell. Consequently, optimisation of the diffusion-layer morphology is seminal to the performance of SPE-DMFCs [3–5].

In recent years, several improvements in the performance of polymer-electrolyte fuel cells have been obtained by optimising the diffusion-layer parameters such as the hydrophobicity and the carbon surface-area [6–13]. Unlike polymer electrolyte fuel cells, however, there are few reports of such studies on SPE-DMFCs. More explicitly, investigations have been restricted to Vulcan XC-72 carbon which has a surface area of 250 $m^2\ g^{-1}$. This is unfortunate as the nature and loadings of carbon blacks of varying surface areas could be considerably important in achieving optimum SPE-DMFC performance. In this communication, therefore, we report a study on the performance of SPE-DMFCs containing MEAs with electrode diffusion-layers made separately from 'acetylene black' with a surface area of 50 $m^2\ g^{-1}$, Vulcan XC-72 carbon with a surface area of 250 $m^2\ g^{-1}$ and Ketjen Black carbon with a surface area of 650 $m^2\ g^{-1}$. The best performance of about 250 mW cm^{-2} is obtained for a SPE-DMFC with a MEA that comprises a hydrophobic diffusion-layer with 0.8 mg cm^{-2} of Ketjen Black carbon with 10 wt.% of Teflon at the cathode and a hydrophilic diffusion-layer with 0.8 mg cm^{-2} Ketjen Black carbon with 10 wt.% of Nafion at the anode.

2. Experimental

2.1. Preparation of carbon-supported Pt and Pt-Ru electrocatalysts

$Na_6Pt(SO_3)_4$ and $Na_6Ru(SO_3)_4$ are used as precursors for catalyst preparation. The $Na_6Pt(SO_3)_4$ precursor was obtained from chloroplatinic acid. Chloroplatinic acid was dissolved in distilled water and the pH of the solution was adjusted to 7 by adding Na_2CO_3. Subsequently, the pH of the solution was lowered to 3 by adding $NaHSO_3$. The

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solution was then gently warmed until it became colourless. The pH of the solution was then raised to 6 by adding Na_2CO_3. This resulted in a white precipitate of $Na_6Pt(SO_3)_4$ which was filtered, washed copiously with hot distilled water, and dried in an air oven at 80 °C. The $Na_6Ru(SO_3)_4$ precursor was prepared by dissolving 207 mg of anhydrous $RuCl_3$ in 50 ml of 0.1 m HCl. The pH of the solution was adjusted to 7 by adding Na_2CO_3. Then the pH of the solution was lowered to 3 by adding $NaHSO_3$. After heating the solution at 80 °C for 30 min, the pH of the solution was raised to 6 by adding Na_2CO_3 when a greyish blue precipitate is obtained which is filtered, washed copiously with distilled water, and dried in air oven at 80 °C for 2 h.

A total of 60 wt.% platinised carbon was prepared by the sulfito-complex route [14,15]. The required amount of Ketjen Black carbon was suspended in distilled water and agitated in an ultrasonic water bath at about 80 °C to form a slurry. The required amount of $Na_6Pt(SO_3)_4$ was dissolved in 1 M H_2SO_4 and diluted with distilled water. This solution was added drop-wise to the carbon slurry with constant stirring at 80 °C. Next, 30% H_2O_2 was added with the temperature maintained at 80 °C. This resulted in vigorous gas evolution and the solution was stirred further for 1 h. Subsequently, an appropriate amount of 1 wt.% formic acid solution was added. Carbon-supported platinum thus obtained was filtered, washed copiously with hot distilled water, and dried in an air oven at 80 °C for 2 h.

The Pt-Ru/C catalyst was prepared in the following manner. The required amount of Ketjen Black carbon (33 mg) was suspended in water (50 ml) and agitated in an ultrasonic water bath to form a thick carbon slurry. A total of 653 mg of $Na_6Pt(SO_3)_4$ was dissolved in 50 ml of 1 N H_2SO_4 and diluted to 750 ml with distilled water. The pH of the solution was adjusted to 5 by adding 10% NaOH solution. A total of 100 ml of H_2O_2 (30%) was added drop-wise with constant stirring. The pH of the solution was adjusted to 5. To this solution, 560 mg of $Na_6Ru(SO_3)_4$ dissolved in 150 ml of 1 N H_2SO_4 was added drop by drop. The pH of the solution was adjusted to 5 after gas evolution ceased. The carbon slurry was then slowly added under constant stirring. Hydrogen gas was bubbled through this admixture for 1 h, and the suspension was allowed to settle, filtered, washed copiously with hot water, and dried in an air oven at 80 °C for 2 h [16].

2.2. Preparation of MEAs

Both the anode and cathode consist of a backing layer, a gas diffusion-layer and catalyst reaction-layer. A Teflonised (20 wt.% Teflon) carbon paper (Kureha) of 0.3 mm thickness was employed as the backing layer in these electrodes. The paper was sintered at 340 °C for 30 min. To prepare the gas diffusion-layer, activated carbon (acetylene black carbon, Vulcan XC-72 carbon, or Ketjen Black carbon) was suspended in water and agitated in an ultrasonic water bath. To this, 10 wt.% of Teflon (Fluon GP-2) suspension or 10 wt.% Nafion (5 wt.% Aldrich solution) was added as desired. The required amount of cyclohexane was then added with continuous agitation. The resultant slurry was spread on to a Teflonised carbon paper and dried in an air oven at 80 °C for 2 h to obtain diffusion-layers with different (0.4, 0.8 and 1.2 mg cm^{-2}) loadings.

To prepare the catalyst reaction-layer, the required amount of the catalyst (60 wt.% Pt/C for the cathode or 60 wt.% Pt-Ru/C for the anode) was mixed with 10 wt.% of Teflon suspension and 15 wt.% Nafion (5 wt.% Aldrich solution). The mixture was suspended in water and agitated in an ultrasonic water bath with continuous stirring. The catalyst ink thus obtained was spread on to the gas diffusion-layer of the electrode, and pressed with a pressure of 75 kg cm^{-2} for 5 min. The anode contained Pt-Ru/C catalyst with a platinum loading of 4 mg cm^{-2} which was kept constant in all the MEAs. The platinum content at the cathode in all the MEAs was maintained at 5 mg cm^{-2} and was also kept constant for all the MEAs.

A thin layer of 5 wt.% Nafion solution was spread (0.5 mg cm^{-2}) on to the surface of each electrode. The MEA was obtained by pressing the cathode and anode on either side of a pre-treated Nafion-117 proton exchange membrane by hot compaction with a pressure of 50 kg cm^{-2} at 127 °C for 3 min.

Table 1
Details of diffusion-layers with power densities of various SPE-DMFCs at 90 °C and 2 bar oxygen pressure

Cell type	Details of the diffusion-layer		Power density (mW cm^{-2})
	Cathode	Anode	
SPE-DMFC 1	0.4 mg cm^{-2} acetylene black carbon with 10 wt.% Teflon	0.4 mg cm^{-2} acetylene black carbon with 10 wt.% Nafion	196
SPE-DMFC 2	0.8 mg cm^{-2} acetylene black carbon with 10 wt.% Teflon	0.8 mg cm^{-2} acetylene black carbon with 10 wt.% Nafion	216
SPE-DMFC 3	1.2 mg cm^{-2} acetylene black carbon with 10 wt.% Teflon	1.2 mg cm^{-2} acetylene black carbon with 10 wt.% Nafion	185
SPE-DMFC 4	0.4 mg cm^{-2} Vulcan XC-72 Carbon with 10 wt.% Teflon	0.4 mg cm^{-2} Vulcan XC-72 Carbon with 10 wt.% Nafion	231
SPE-DMFC 5	0.8 mg cm^{-2} Vulcan XC-72 carbon with 10 wt.% Teflon	0.8 mg cm^{-2} Vulcan XC-72 carbon with 10 wt.% Nafion	242
SPE-DMFC 6	1.2 mg cm^{-2} Vulcan XC-72 carbon with 10 wt.% Teflon	1.2 mg cm^{-2} Vulcan XC-72 carbon with 10 wt.% Nafion	204
SPE-DMFC 7	0.4 mg cm^{-2} Ketjen Black carbon with 10 wt.% Teflon	0.4 mg cm^{-2} Ketjen Black carbon with 10 wt.% Nafion	238
SPE-DMFC 8	0.8 mg cm^{-2} Ketjen Black carbon with 10 wt.% Teflon	0.8 mg cm^{-2} Ketjen Black carbon with 10 wt.% Nafion	247
SPE-DMFC 9	1.2 mg cm^{-2} Ketjen Black carbon with 10 wt.% Teflon	1.2 mg cm^{-2} Ketjen Black carbon with 10 wt.% Nafion	198
SPE-DMFC 10	Without the diffusion-layer	Without the diffusion-layer	196
SPE-DMFC 11	0.8 mg cm^{-2} Ketjen Black carbon with 10 wt.% Teflon	0.8 mg cm^{-2} Ketjen Black carbon with 10 wt.% Teflon	227

2.3. Electrochemical studies on various SPE-DMFCs

Liquid-feed SPE-DMFCs were constructed with various MEAs as described in Table 1. The anode and cathode of the SPE-DMFCs were contacted on their rear with gas/fluid-flow field plates machined from high-density graphite blocks in which channels had been formed. The channels were machined to achieve minimum mass-transport effects in the SPE-DMFCs. The ridges between the channels make electrical contact with the back of the electrode and conduct the current to the external circuit. The channels supply methanol to the anode and oxygen to the cathode. Electrical heaters were placed behind each of the graphite blocks in order to heat the cell to the desired temperature. The methanol solution was pumped to the anode chamber by means of a peristaltic pump and the unreacted solution was collected in the reservoir. Oxygen gas at about 2 bar pressure was introduced to the cathode chamber. The graphite blocks were also provided with collectors for electrical contact and tiny holes to accommodate thermocouples. Galvanostatic

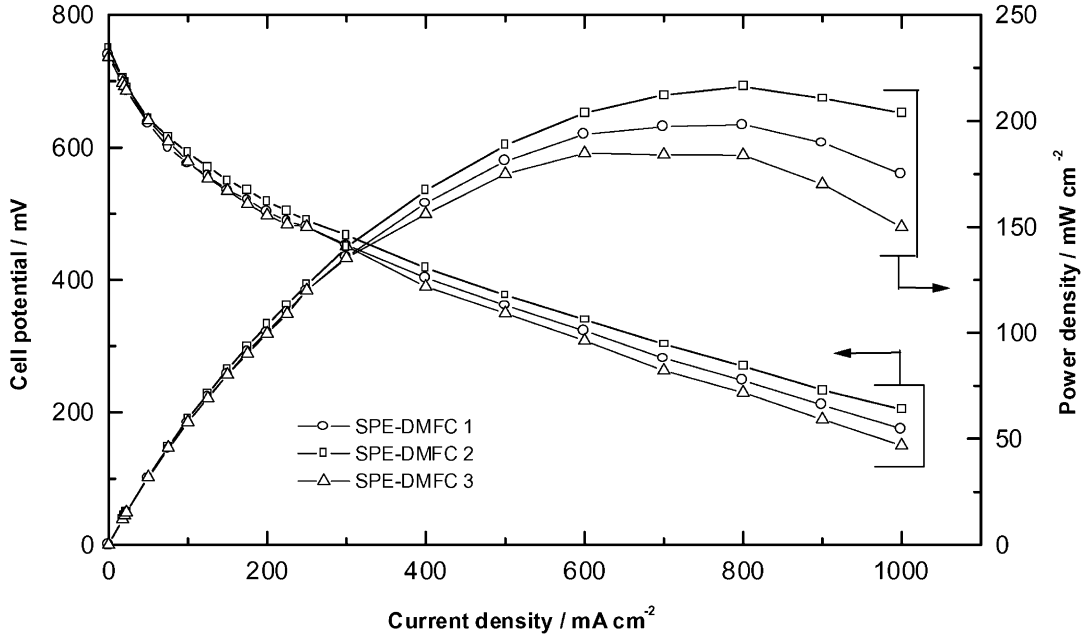

Fig. 1. Effect of varying diffusion-layer thickness with acetylene black carbon on performance of SPE-DMFCs at 90 °C and 2 bar oxygen pressure.

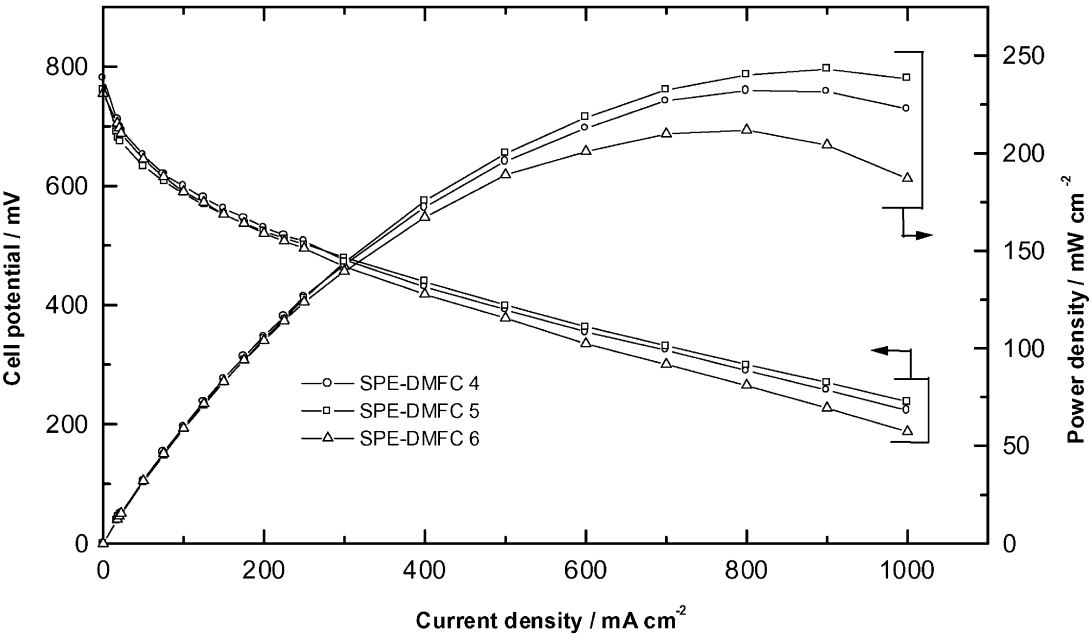

Fig. 2. Effect of varying diffusion-layer thickness on performance of SPE-DMFCs with Vulcan XC-72 carbon at 90 °C and 2 bar oxygen pressure.

current–voltage data on the activated SPE-DMFCs were obtained at various pressures and temperatures. The active geometrical-area of the electrodes was 4 cm^2. The current densities were calculated from the active geometrical area of the electrodes.

3. Results and discussion

The details of various types of SPE-DMFCs studied here are given in Table 1. The effect of varying the diffusion-layer thickness separately with acetylene black, Vulcan XC-72, and Ketjen Black carbon are shown in Figs. 1–3, respectively. From these data, it is clear that the performance of SPE-DMFC varies with the nature of carbon black used and the loading of the diffusion-layer. The SPE-DMFC 8 exhibits the best performance with a maximum power denisity of 247 mW cm^{-2}, while the maximum power density values achieved with acetylene black and Vulcan XC-72 under identical operating conditions were 216 and 242 mW cm^{-2}, respectively. The SPE-DMFC 10 with a MEA without the diffusion-layer exhibits the poorest performance of

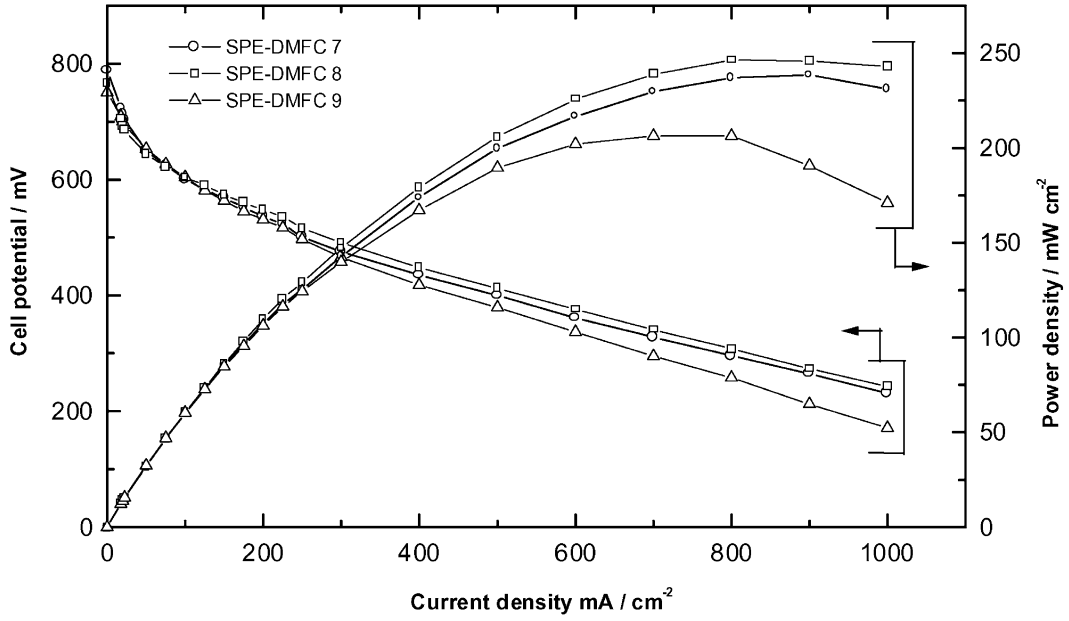

Fig. 3. Effect of varying diffusion-layer thickness with Ketjen Black carbon on performance of SPE-DMFCs at 90 °C and 2 bar oxygen pressure.

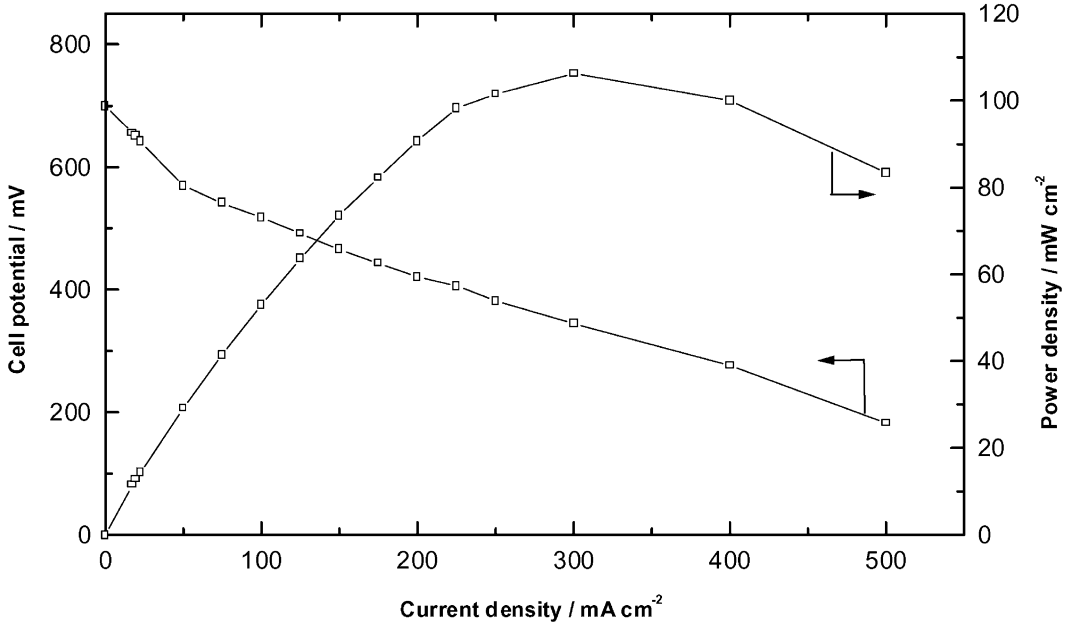

Fig. 4. Performance of SPE-DMFC 8 at 90 °C and 2 bar air pressure.

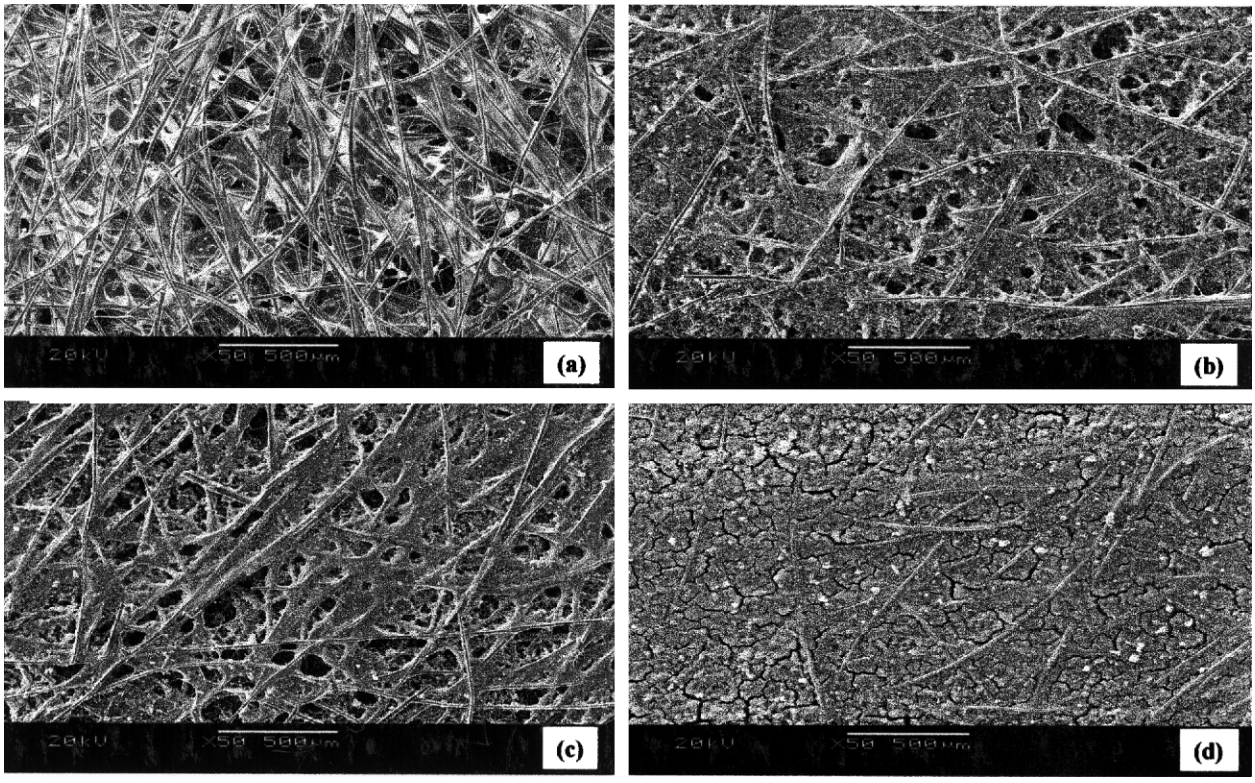

Fig. 5. Scanning electron micrographs of diffusion-layers: (a) bare Kureha carbon paper; (b) acetylene black with 0.8 mg cm^{-2} loading; (c) Vulcan XC-72 with 0.8 mg cm^{-2} loading; (d) Ketjen Black with 0.8 mg cm^{-2} loading.

$\sim$196 mW cm^{-2}. The SPE-DMFC 11 that has a MEA with hydrophobic diffusion-layers with 10 wt.% Teflon on both anode and cathode sides gives a power density of 227 mW cm^{-2}, which is lower than the power density obtained from the SPE-DMFC 8. The galvanostatic data were also obtained with air at 2 bar pressure and 90 °C using the SPE-DMFC 8 (Fig. 4). A maximum power density of 105 mW cm^{-2} was achieved at a current density of 300 mA cm^{-2} with this cell.

We have also examined the morphologies of the backing paper and diffusion-layers with a loading of 0.8 mg cm^{-2} of acetylene black carbon, Vulcan XC-72 carbon and Ketjen Black carbon under a scanning electron microscope. These micrographs are shown in Fig. 5. The diffusion-layers made of Ketjen Black carbon are quiet different from the diffusion-layers made of acetylene black or Vulcan XC-72 carbon. Indeed, the pore structure of the diffusion-layer made of Ketjen Black appears to be more uniform and has finer pores.

4. Conclusions

This study demonstrates that, in general, the performance of SPE-DMFCs containing MEAs with diffusion-layers of Ketjen Black carbon are superior to those of acetylene black and Vulcan XC-72. It should be pointed out, however, that the diffusion-layer morphologies presented here are not necessarily fully optimised and further improvements in performance are highly likely.

Acknowledgements

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