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Short communication

Effect of carbon black concentration in carbon fiber paper on the performance of low-temperature proton exchange membrane fuel cells

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Abstract

This study uses fuel cell gas diffusion layers (GDLs) made from carbon fiber paper containing carbon black in proton exchange membrane fuel cells (PEMFCs) in order to determine the relationship between carbon black content and fuel cell performance. The connection between fuel cell performance and the carbon black content of the carbon fiber paper is discussed, and the effects of carbon black on the carbon fiber paper's thickness, density, and surface resistivity are investigated. When a carbon fiber paper GDL contains 10 wt% phenolic resin and 2% carbon black, and reaction area was 25 cm^2 and operating temperature 40 °C, tests show that a carbon electrode fuel cell could achieve 1026.4 mA cm^{-2} and maximum power of 612.8 mW cm^{-2} under a 0.5 V load.

Keywords: Fuel cell; Gas diffusion layer; Carbon fiber paper; Carbon fiber felt; Hot pressing; Carbonization

1. Introduction

Because of their high efficiency, high-power density, low-operating temperature, and low noise, proton exchange membrane fuel cells (PEMFCs) are thought to be superior to other fuel cell systems in vehicle applications [1–4]. The focus of this study is on fuel cell gas diffusion layers (GDLs), which provide a channel for the transport of fuel and a medium for the transmission of current. PEMFCs typically use GDLs made of carbon fiber paper or carbon fabric, and GDL composition can play a major role in cell performance [5]. Considerable research attention has been paid to the diffusion layer, which constitutes an important intermediate layer between the bipolar plates and catalyst layers [6]. As Scherer [7] discusses, the properties of the diffusion layer will affect the optimum performance of the catalyst and electrode. Carbon fiber fabric or carbon fiber papers are currently the most common materials used to produce GDLs, and carbon's advantages of high conductivity and corrosion resistance makes it well suited for the special environment inside a fuel cell. A new technique for fabricating GDLs was developed recently [8]. The conductivity of carbon fiber increases and the hydrophobicity of the surface functional group declines with the graphitization temperature [9,10].

While carbon fiber fabric is prone to warping and shrinking in fuel cells, carbon fiber paper offers excellent size stability. This study therefore chose to research carbon fiber paper. Carbon black may be used in polymer electrolyte fuel cell (PEFC) electrodes, both in the catalyst layer, where it serves as a platinum support, and in the GDL, where it is mixed with polytetrafluorethylene (PTFE) [11]. In general, carbon black is most commonly used as a Pt carrier in the catalyst layer. Uchida et al. [12] studied the effect of the morphology of the carbon support for a Pt catalyst on PEFC performance. This study added different amounts of carbon black to carbon fiber paper in an effort to increase the conductivity of the paper and boost fuel cell performance. Most studies have approached the issue of performance from cell design [13–21] and applied products, but have failed to look at the basic materials and process R&D. Research has nevertheless shown that, in theory, the physical and chemical characteristics of a GDL should have a major influence on cell performance. Although there are several compelling reasons for operating at a higher temperature [22], we selected 40 °C as the fuel cell operating temperature. While Chen and Tseung [23] decided to study direct ethyl formate fuel cells at room temperature, we chose to work at 40 °C because in the future we plan to apply fuel cells in electronic products. Although electronic

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products typically operate at room temperature, they often produce enough heat to make the temperature of the fuel cell rise above room temperature and reach roughly 40 °C. We focus on GDL production technology in this study, and our ultimate goal is to boost fuel cell performance through improved GDLs.

In this study, we discuss the relationship between fuel cell performance and the carbon black content of carbon fiber paper GDLs, and investigate the effect of carbon black content on thickness, density, and surface resistivity.

2. Experimental parameters

This study used oxidized fiber felt (from Kuo Tung Felt Co. Ltd.) and phenolic resin (from Chang Chun Plastics Co. Ltd.) as raw materials. The oxidized fiber felt was first carbonized at a temperature of 1000 °C to produce carbon fiber felt. The phenolic resin was mixed so as to constitute 2 and 10 wt% (percentages by weight unless otherwise noted) of the solution, and type N-660 carbon black was added in order to constitute 0, 2, 6, and 10% of overall solution content, and was mixed thoroughly with the phenolic resin. Table 1 shows the experimental parameters in this study. Phenolic resin was selected as the impregnating solution because it is highly sticky but has a hard carbon structure [24], and we added carbon black to the impregnating solution because it has good electrical conductivity and there is little contact resistance between the carbon particles [25]. The carbon fiber felt was impregnated with the phenolic resin mixture, placed in an oven, and baked at a temperature of 70 °C for 15 min. Hot pressing at a temperature of 170 °C and pressure of 10 kg cm^{-2} was performed to change the composite material to the form of carbon fiber paper. Carbonization was then performed at a temperature of 1300 °C.

An AccuPyc 1330 Pycnometer was used to measure the true density. A Japanese Mirage MD-200S electronics hydrometer was used to perform Archimedes density testing. A Teclock SM-114 thickness tester was used to measures the thickness of the carbon fiber paper, and thicknesses were the average of measurements taken at five random points. A Loresta GP MCP-T600 meter was used to measure the surface resistivity. Testing and analysis of surface resistivity was performed in accordance with JIS K 7194 standard testing procedures. A cold field emission scanning electron microscope was used to analyze the cross-section of the carbon fiber paper at 500× and 2500×.

Using the carbon fiber paper as a fuel cell GDLs entailed cutting the paper into 5 cm × 5 cm pieces and then forming three-layer MEAs with catalyst-coated membrane (CCM) from Dupont™ (type NRE-211). We focused on the material used for the GDL in this study, and we plan to study how to spray or coat a microlayer and PTFE on the GDL in the future. A microlayer was not applied to the carbon fiber paper in this study. The CCM and carbon fiber paper were not bonded together by hot pressing, and only 90 kgf cm^{-1} torsion was used to ensure close contact between the layers. The MEA was placed in a fuel cell testing module, which was sealed with Teflon washers before testing. The activated area in each cell was 25 cm^2, and the bipolar plates consisted of serpentine-type grooved graphite plates made of highly compact graphite. Stainless steel plates and PTFE washers were used to seal the module and create a fuel cell. The gas flow rate at the anode (H_2) was 200 cm^3 min^{-1}, and was also 200 cm^3 min^{-1} at the cathode (O_2). All single cell operations were performed without external pressurization, and humidified pure hydrogen and pure oxygen were used. Gas entrance pressure was 1 kg cm^{-2}, and cell temperature was set at 40 °C during testing.

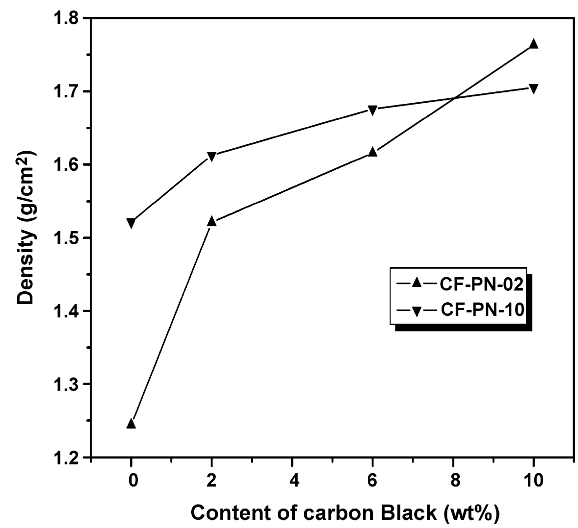

Fig. 1. True density of carbon fiber paper containing various percentages of carbon black and phenolic resin: (▲) 2% resin content and (▼) 10% resin content.

3. Results and discussion

Fig. 1 shows true density curves for carbon fiber paper containing different percentages of carbon black and phenolic resin. It can be seen from Fig. 1 that true density increases with increasing carbon black content. It can also be discovered that the true density of carbon fiber paper with 2% phenolic resin and no carbon black was 1.24 g cm^{-3}, and the true density rose to 1.76 g cm^{-3} when carbon black accounted for 10% of the impregnation mixture. Density thus increased by 40% with rising carbon black content. The true density of carbon fiber paper made with 10% phenolic resin and no carbon black was 1.52 g cm^{-3}, and the true density rose to 1.70 g cm^{-3} when carbon black accounted for 10% of the impregnation mixture. Density thus increased by 10% with rising carbon black content.

Fig. 2 shows Archimedes density (also known as volume density) curves for carbon fiber paper containing different percentages of carbon black and phenolic resin. It can be seen from Fig. 2 that volume density increased with rising carbon black content. While the volume density of carbon fiber paper containing 2% phenolic resin and no carbon black was 0.217 g cm^{-3}, the volume density rose to 0.676 g cm^{-3} when carbon black was 10%. Volume density thus increased by 212% as the carbon black content rose. The volume density of carbon fiber paper containing 10% phenolic resin and no carbon black was 0.43 g cm^{-3}, which rose to 0.728 g cm^{-3} when 10% carbon black was added. Volume density thus increased by 69% as the carbon black content rose.

Table 1
Test plate production parameters in this study

Type	Type of oxidized fiber felt	Phenolic resin content (wt%)	Carbon black content (wt%)
CFPN02CB00	Heat treatment at 1000 °C	2	0
CFPN02CB02		2	2
CFPN02CB06		2	6
CFPN02CB10		2	10
CFPN10CB00	Heat treatment at 1000 °C	10	0
CFPN10CB02		10	2
CFPN10CB06		10	6
CFPN10CB10		10	10

The true density and volume density of carbon fiber paper both increased significantly as the paper's phenolic resin content and carbon black content were increased. This is because phenolic resin increases bonding between the fibers of carbon fiber paper, and increasing carbon black concentration induces the carbon black to enter the voids between fibers, increasing the density of the carbon fiber paper. It can be seen from Figs. 1 and 2 that density rose with carbon black content for carbon fiber paper containing both 2 and 10% phenolic resin, and this effect was particularly evident for carbon fiber paper containing 2% phenolic resin. This is because increasing resin content tends fill most of the voids in the carbon fiber paper, leaving fewer voids to be filled by carbon black particles. As a consequence, the increase in density with carbon black content is not so evident in the case of carbon fiber paper containing 10% phenolic resin.

Fig. 3 shows thickness curves for carbon fiber paper containing different percentages of resin and carbon black. The main factors affecting thickness include the thickness of the material, the hot pressing pressure, and the resin content. Oxidized fiber felt precarbonized at 1000 °C had an original thickness of 0.80 mm. The hot pressing pressure was 10 kg cm^{-2}. The thickness of the carbon fiber paper changed little when it contained 2% phenolic resin—the thickness only fell to 0.70 ± 0.05 mm, a reduction of 12.5%. The thickness fell to 0.50 ± 0.05 mm, however, a reduction of 37.5%, when the phenolic resin content was increased to 10%. The greater the phenolic resin content, the more tightly bound the fibers of carbon fiber felt. Increasing the carbon black content has no major effect on the thickness of carbon fiber paper. This shows that the main factor affecting the thickness of carbon fiber paper is the phenolic resin content, and that the carbon black content does not significantly affect thickness. Phenolic resin is highly sticky, and can cause the fibers of carbon felt to bind together, reducing the thickness of the carbon fiber paper.

Fig. 4 shows the effect of phenolic resin and carbon black content on the surface resistivity of carbon fiber paper. It can be seen that carbon fiber paper with a 2% phenolic resin content has a surface resistivity of 0.75 ± 0.05 Ω sq^{-1}, while carbon fiber paper with a 10% phenolic resin content has a surface resistivity of 0.50 ± 0.05 Ω sq^{-1}. This indicates that the main factor affecting surface resistivity is the phenolic resin content. Increasing phenolic resin content causes the fibers in carbon fiber paper to bind more tightly, which increases the conductivity of the paper. Although carbon black can fill the voids between fibers, it lacks stickiness and therefore cannot significantly increase the conductivity of carbon fiber paper. However, while the effect of carbon black is not significant when the phenolic resin content

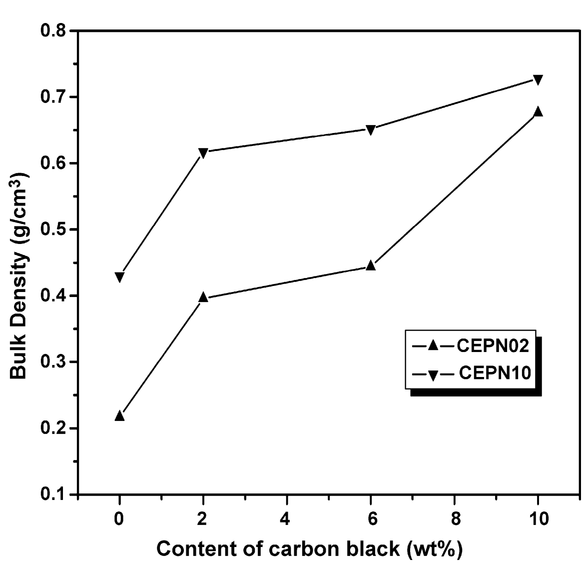

Fig. 2. Archimedes density of carbon fiber paper containing various percentages of carbon black and phenolic resin: (▲) 2% resin content and (▼) 10% resin content.

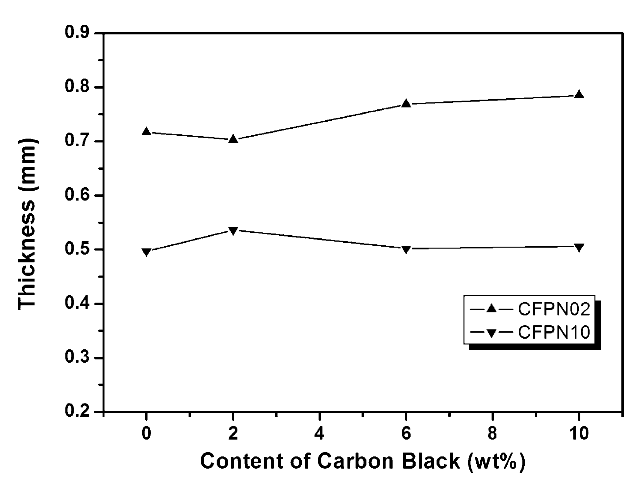

Fig. 3. Thickness of carbon fiber paper containing various percentages of carbon black and phenolic resin: (▲) 2% resin content and (▼) 10% resin content.

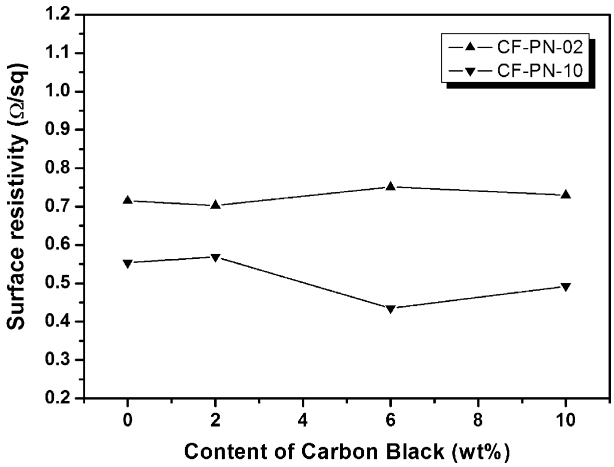

Fig. 4. Surface resistivity of carbon fiber paper containing various percentages of carbon black and phenolic resin: (▲) 2% resin content and (▼) 10% resin content.

is low, a higher phenolic resin content causes the fibers to bind more tightly, trapping relatively large amounts of carbon black; the higher carbon black content will then cause a slight increase in the conductivity of the paper. Although phenolic resin has a hard carbon structure, it can also induce the fibers to bind more tightly and thereby provide more routes for electron transmission. Carbon black was added to increase the conductivity of the carbon fiber paper; its effects are more evident when the phenolic resin content is 10% than when the content is 2%.

SEM observation of carbon fiber paper showed that the methods used in this study caused phenolic resin and carbon black to enter the carbon felt. Following hot pressing, the phenolic resin induced the fibers to bind together, creating the desired carbon fiber paper. Fig. 5 shows the carbon fiber paper produced using oxidized fiber felt precarbonized at 1000 °C and various phenolic resin contents. In Fig. 5(A), when the phenolic resin content is 2%, the fibers of the carbon fiber paper are not bound together in bunches to any noticeable degree. In Fig. 5(B), when the phenolic resin content is 10%, fibers are clearly bound together as bunches. In Fig. 5(C) and (D), it can also be seen that, as carbon black content increases, excess carbon black is not coated by phenolic resin. Fig. 6 shows high-magnification SEM views of the cross-section of the paper. In Fig. 6(B), when the phenolic resin content is 10%, the fiber bunches are coated by phenolic resin, which is in accordance with previous experience. In Fig. 6(C) and (D), we see that after the carbon black content passes a certain value, it can no longer bind effectively with the resin and carbon fiber, which means that cell performance will not improve consistently after this point.

Fig. 7 shows polarization curves obtained at a temperature of 40 °C after the carbon fiber paper GDLs were used in test fuel cells. The carbon fiber paper used for the GDL in this study was not subjected to hydrophobic treatment, and no electrode microlayer was applied. Fig. 7 shows that current density is 346 mA cm^{-2} when the load is 0.5 V and carbon fiber paper containing 2% phenolic resin and no carbon black is used. Current density increases to 1069.6, 864.4, and 946.8 mA cm^{-2}, respectively, when the carbon black content is 2, 6, and 10%.

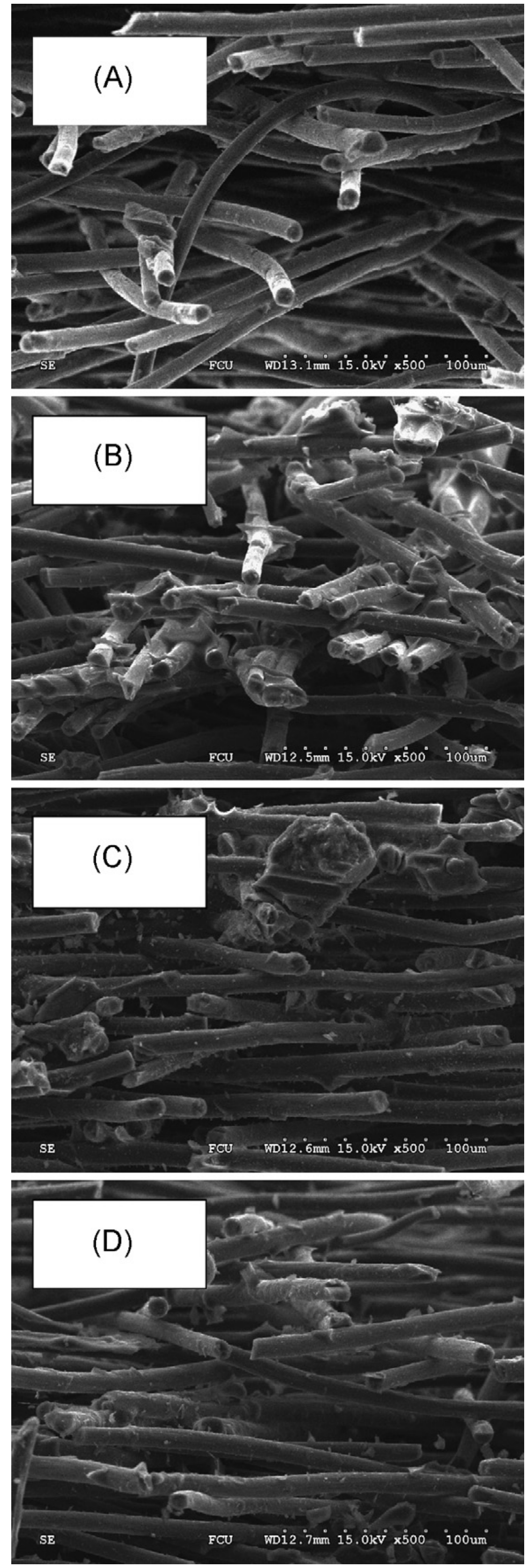

Fig. 5. SEM micrographs (at 500×) of the cross-section of carbon fiber paper containing high- and low-phenolic resin content, cross-section of (A) CFPN02CB02; (B) CFPN10CB02; (C) CFPN10CB06; (D) CFPN10CB10.

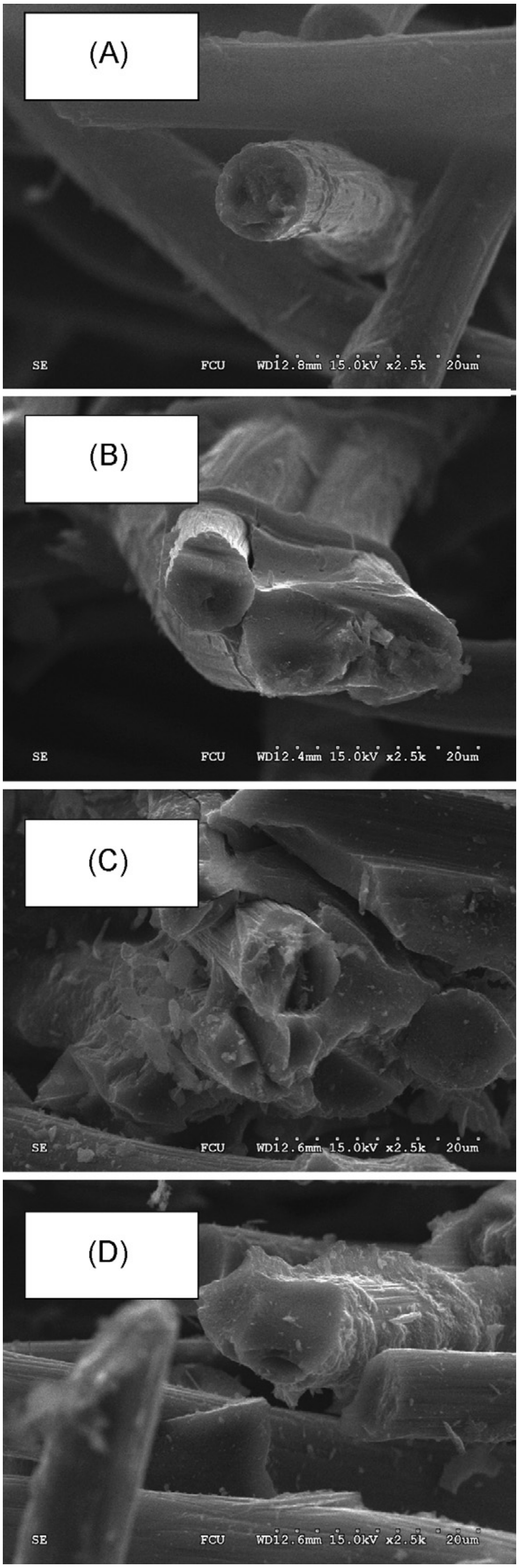

Fig. 6. SEM micrographs (at 2500×) of the cross-section of carbon fiber paper containing high- and low-phenolic resin content, cross-section of (A) CFPN02CB02; (B) CFPN10CB02; (C) CFPN10CB06; (D) CFPN10CB10.

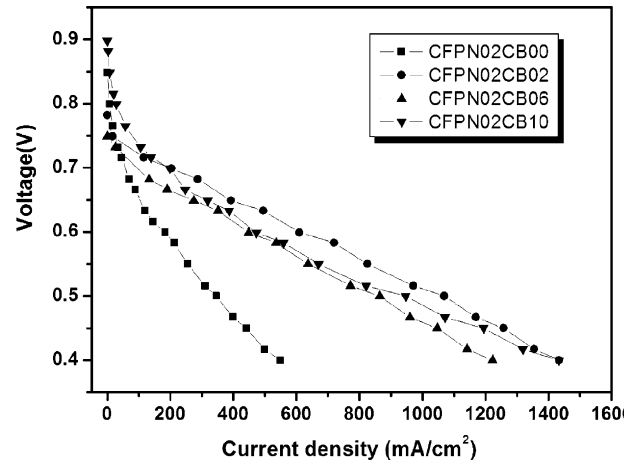

Fig. 7. Current density vs. operating voltage curve at 40 °C when phenolic resin content is 2%.

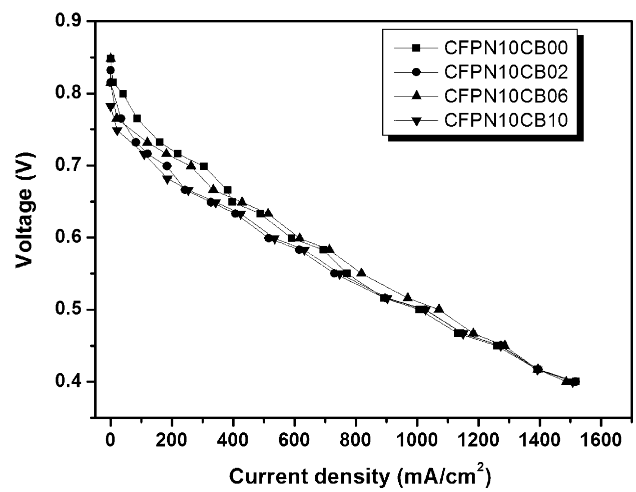

Fig. 8. Current density vs. operating voltage curve at 40 °C when the phenolic resin content is 10%.

It can be seen that cell performance is relatively poor when the carbon fiber paper has a 2% phenolic resin content and contains no carbon black. In addition, cell performance does not continue to improve after the carbon black content reaches a certain level. Fig. 8 shows the current density versus operating voltage curve at 40 °C when the phenolic resin content is 10%. The current density is 1007.2, 1026.4, 1071.2, and 1027.6 mA cm^{-2}, respectively, when the load is 0.5 V, the resin concentration is 10%, and the carbon black content is 0, 2, 6, and 10%. When the phenolic resin content is 10%, increasing carbon black content does not further improve cell performance. It is evident that cell performance does not continue to improve after the resin and carbon black content have reached certain levels, and this is because any excess carbon black will not be able to enter the voids between the fibers in the paper.

4. Conclusions

Oxidized fiber felt precarbonized at 1000 °C was used to produce carbon fiber felt, which was impregnated with 2 and 10% phenolic resin to make carbon fiber paper used as a fuel cell electrode material. In addition, 0, 2, 6, and 10% carbon black was added to the paper, and the carbonization temperature was 1300 °C. The physical characteristics of the resulting material varied as follows: the density of carbon fiber paper carbonized at 1300 °C increased with resin and carbon black content. The phenolic resin content was found to be the main factor determining the thickness of the paper, and an increasing content of phenolic resin reduced the thickness of the carbon fiber paper. When the phenolic resin content was 10%, the CFPN10CB00 carbon fiber paper had a thickness of 0.50 mm. The surface resistivity fell markedly with increasing phenolic resin content and slightly with carbon black content. CFPN10CB00 had a resistivity of 0.5538 $\Omega\,sq^{-1}$, and had a current density of 1007.2 $mA\,cm^{-2}$ when the load was 0.5 V.

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