New Porous Carbon Materials as Gas Diffusion Layer for Polymer Electrolyte Fuel Cells

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ABSTRACT

New porous carbon materials are proposed in which washi, the Japanese paper as well as cotton and other cellulose materials are carbonized by new method, retaining their original fibrous structures. Porous carbon sheets thus fabricated are used as gas diffusion layer in fuel cells. Fuel cell testing is conducted and the optimum conditions of fabrication are investigated. Low cost and superior characteristics of new carbon structure are demonstrated based on morphological study and fuel cell polarization data.

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Keywords : Porous Carbon, Morphology Retaining Carbonization, Gas Diffusion Layer, Polymer Electrolyte Fuel Cell

1. Introduction

Because of its natural abundance and good manufacturing and handling properties, carbon materials possess important position in material science and technology. Nobel laureate Hideki Shirakawa delivered in his lecture that the element carbon shows “many faces” with different electronic properties (conductive, semi-conductive and insulating), due to its diverse phase and bonding states (SP, SP2, SP3). New materials like graphene, fullerene, nanotube, as deformed two dimensional SP2 derivatives, are intensely studied since their discovery in recent decades. Especially carbon fibers find very important applications as high-strength, light-weight bulk materials. This is also true in fuel cell technology, and carbon materials are used in such areas as catalyst support, gas diffusion layer (GDL) and bipolar plates. Yet the cost reduction for the market penetration of fuel cells is one of challenges, and economic supply of carbon materials should also be pursued to this end. There have been many articles published on GDL, including structural modification, simulation of porous media, but very few are reported on new GDL materials.

In this work, new porous carbon sheets are proposed, which are to be used as GDL in anodes and cathodes of polymer electrolyte fuel cells (PEFCs). So far only a few researches on cellulose-derived carbon fibers and application to GDL materials are reported, and this work would be a unique proposal of this key material for PEFC. The porous carbon structure is realized by morphology-retaining carbonization technology applied to “washi”, the Japanese traditional paper, and other cellulose materials. This cellulose material has a specific long fibrous structure, which achieves a strong and flexible porous sheet.

When this material is carbonized in special atmosphere, it gives porous carbon sheets retaining its original fibrous structure and textural properties with high carbon yield. This technology could be applied also to other cellulose materials like cotton cloth, and be able to replace commercial GDL made from artificial carbon fibers and cloths. Pre-treatment and fabrication are optimized, and fuel cell testings based on this future candidate of GDL are conducted in this report.

2. Experimental

Materials and procedure for preparation of porous carbon sheets are described in S1 of the Supporting Information section. The morphology-retaining carbonization process consists of an iodine (I2) treatment of washi in a vessel for ca. 10 days. The impregnated I2 in cellulose fibrils makes lateral interaction between glucose molecules, which results in least fragmentation and high content of graphitic structure during carbonization at 800 °C in Ar atmosphere for 1 h. To improve the electric conductivity, porous carbon sheets were further heat-treated in Ar for 30 min at 1400–2600 °C, in a tube furnace (Asahi-rika). Another carbonization process was furtherly pursued in which sisal paper and cotton fabrics were pre-treated in organic sulfonic acid solution (1 M CH3SO3H or C6H5SO3H) for 5 min and dried in atmosphere. This process was effective in facilitating dehydration reaction during carbonization at 800 °C, and final carbon yield of samples increased to ca. 38%, close to theoretical carbon content of cellulose 44.4%. The carbonized samples were further heat-treated in 5% CH4/N2 for 30 min at 1000–1600 °C. The latter process was essential to cause graphitization and improve electric conductivity of samples. To facilitate the process and lower the temperature to 1000 °C, samples were subjected to chemical treatment before the heat-treatment. Samples were immersed in (i) 0.25 M citric acid aqueous solution (abbreviated as CA), (ii) 0.6 M glutaraldehyde in acetic acid (abbreviated as GA), or (iii) 0.45 M terephthalaldehyde in acetic acid (abbreviated as PA) overnight, and dried in atmosphere. In this chemical treatment, –CHO or –COOH groups were assumed to form functional groups on carbon fabrics, and promoted graphitization by curing defects in C–C bonds during heat-treatment.

Porous carbon sheets thus obtained were used as GDL to fabricate a membrane electrode assembly (MEA), and tested in fuel cell mode. Porous carbon sheets were made hydrophobic by immersing in polytetrafluoroethylene (PTFE) colloid and then dried in an oven at 350 °C for 30 min (ca. 3 mg(PTEF) cm−2). Catalyst ink was a mixture of 20 wt% Pt/Ketjen black catalyst (Ishifuku UNPC20-II), 5 wt% Nafion solution (Aldrich), and ethanol in 3:50:3 mass ratio. The ink was stirred ultrasonically for 15 min, then
for 2–3 days with a magnetic stirrer, and smeared >10 times on the surface of carbon sheets with a stainless-steel roll. MEA was prepared from catalyst-coated carbon sheet GDLs with 0.5 mg cm\(^{-2}\) Pt loading both for the anode and cathode and Nafion 115 membrane, by hot-pressing at 135 °C, 100 kg cm\(^{-2}\) for 3 min. As a reference, commercial carbon paper (Toray TGP-H-090) was also used.

MEA was incorporated in a single fuel cell with electrode area 4 cm\(^2\) (ElectroChem, Inc., MA, USA), and tested using a fuel cell test station and software (Sokken, Inc., TFC-2000). The cell temperature was 70 °C, and operated with H\(_2\) and O\(_2\) or Air, both humidified at 60 °C. Polarization curves and power density vs. current density curves were obtained with Ohmic drop correction using a current interrupter.

For morphological analysis of carbon paper GDLs, a laser microscope (KEYENCE VK9700 microscope) was used for the microscopic observation and 3D and surface roughness measurements.

3. Results and Discussion

3.1 Iodine pre-treated porous carbon sheets

The obtained porous carbon papers were composed of carbonized micro- and nano-fibrils, and showed an electric conductivity increasing with increasing the heat-treatment temperature. During carbonization, washi shrunk by about 20%, but its structure was retained (Fig. 1). The specimen showed about 0.2–0.4 g cm\(^{-3}\) bulk density, 75% porosity, with 20–40 S cm\(^{-1}\) surface conductivity.

Potential-current and power density-current relations revealed that some washi derived GDL exhibit very promising results as compared with commercial GDL. Sisal hemp after carbonization at 800 °C gave the peak power 0.19 W cm\(^{-2}\), about 43% of the commercial one (0.44 W cm\(^{-2}\)). But the performance increased steeply when heat-treated at high temperatures. For the sample heat-treated at 2600 °C, peak power increased to 0.51 W cm\(^{-2}\). Examples of potential-current and power density-current relations of some samples are shown as Fig. S1–Fig. S7 in the Supporting Information section.

Table 1 summarizes characteristics and fuel cell performances of several kinds of washi carbon paper GDLs prepared at several heat-treatment temperatures. Data on commercial sample are also cited for comparison. Apparent bulk density and conductivity increased with the increase in heat-treatment temperature. Cell performance (peak power, maximum current and the current at 0.7 V) improved with heat-treatment temperature. Sisal hemp carbon paper heat-treated above 1400 °C proved equal to or better cell performances than commercial carbon paper. Gasen and gampi were comparative to commercial carbon paper above 1800 °C and 2200 °C, respectively. Data on sisal hemp heat-treated at 1600 °C are also reported as Table S1 and Table S2, and Fig. S8, in Supporting Information section.

3.2 Factors affecting the performance of fuel cells

Comparing different original washi in Table 1, it appears that fuel cell performance is not directly related to physical properties of GDLs. In order to understand which factor of the washi GDL is important, some considerations are necessary.

| Washi samples | H.T. temp. | Conductivity S cm\(^{-1}\) | App. density /g cm\(^{-3}\) | Peak power /W cm\(^{-2}\) | I at 0.7 V /A cm\(^{-2}\) |
|---------------|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sisal hemp    |            |                             |                             |                             |                             |
| 1400 °C       | 18         | 0.28                        | 0.30                        | 0.185                       | 0.188                       |
| 2200 °C       | 23         | 0.31                        | 0.36                        | 0.44                        |                             |
| 2600 °C       | 22         | 0.33                        | 0.36                        | 0.48                        |                             |
| Gasen         |            |                             |                             |                             |                             |
| 1400 °C       | 7          | 0.61                        | 0.61                        | 0.22                        |                             |
| 1800 °C       | 42.5       | 0.52                        | 0.52                        | 0.26                        |                             |
| 2200 °C       | 45         | 0.52                        | 0.37                        | 0.32                        |                             |
| 2600 °C       | 49         | 0.56                        | 0.33                        | 0.21                        |                             |
| 2600 °C       | 43         | 0.53                        | 0.35                        | 0.31                        |                             |
| Gampi         |            |                             |                             |                             |                             |
| 1400 °C       | 26         | 0.39                        | 0.39                        | 0.30                        | 0.20                        |
| 1800 °C       | 30         | 0.36                        | 0.36                        | 0.28                        | 0.22                        |
| 2200 °C       | 34         | 0.38                        | 0.38                        | 0.32                        | 0.37                        |
| 2600 °C       | 37         | 0.35                        | 0.35                        | 0.39                        | 0.34                        |
| Commercial PAN | 100        | 0.45                        | 0.45                        | 0.44                        | 0.37                        |

Table 1. Characteristics and fuel cell performances of washi carbon paper after heat-treatment. Single cell operated at 70 °C with H\(_2\) and O\(_2\) humidified at 60 °C. Ohmic drop corrected.

Figure 1. Original washi and carbon paper after carbonization (top photos), and scanning electron microscope images (bottom photos).
most effective, peak power is plotted against carbon paper thickness, conductivity and PTFE amount in the carbon paper (Fig. 2). Some optimum values are found for the geometric parameters of carbon paper, and it appears that these are related to the Ohmic loss and water flooding in the carbon paper GDLs. However, because of the scattering in these plots, we can imagine that other factors are also working in addition to these parameters.

Figure 2. Relations between peak power density (Ohmic drop corrected) of a fuel cell operated at 70 °C, and characteristics of porous carbon GDLs. ◆: H₂ and O₂ humidified at 60 °C; ■: H₂ and Air humidified at 60 °C.

| Profile   | Horizontal distance | Height difference | Average height |
|-----------|---------------------|-------------------|----------------|
| Whole     | 705.8/10um          | 35.149um          | 170.184um      |
| Partial   | 0.000um             | 96.127um          | 159.758um      |

Figure 3. Morphology analysis of commercial carbon paper by laser microscope. From upper left to lower right: surface view; surface morphology; 3-D morphology; roughness line scan.

Surface morphology of carbon papers was measured for several samples using laser microscope. The porosity and surface roughness were also observed. Figure 3 shows morphology of commercial carbon paper which was made from synthesized carbon fibers. Straight carbon fibers made good openings that were good for gas permeation, but the surface showed quite rough structure.
In comparison to the carbon fiber GDL, washi carbon papers showed specific structures depending on the original material. Gasen showed large openings but low porosity, and waving surface resulted in moderate power, as shown in Fig. S9a and Fig. S9b, in Supporting Information section. Gampi was characterized by thin fibers and the porosity was similar to commercial one (Fig. S10a and Fig. S10b). The surface was smooth, and this factor was effective in good contact with the catalyst layer and polymer electrolyte. Although sisal hemp showed the lowest conductivity, it revealed the highest cell performance. This might be due to the large openings with straight fiber structures, and rather smooth surface (Fig. 4a and Fig. 4b).

We can summarize the surface morphology of carbon papers in relation to fuel cell performances as follows. For sisal hemp, large opening structure by straight fibers resulted in high polarization performance. Gasen and gampi showed smooth surface structure, and this was good for the contact of GDL and polymer electrolyte membrane. Commercial carbon paper showed straight fibers and

**Figure 4.** Morphology analysis of sisal hemp carbon paper by laser microscope. a: Sisal hemp after carbonization at 800 °C; b: Sisal hemp after heat-treatment at 2600 °C. Photos arranged in the same way as in Fig. 3.
large opening, but large surface waving might negatively affected the adhesiveness of GDL to membrane.

Figure 5 shows cross-sectional view of carbon papers at the rib of gas flow channel. At the edge of the rib, commercial carbon paper showed a large step, but that of washi was small. This may be due to the flexible structure of washi.

3.3 Sulfonic acid pre-treated porous carbon sheets

The high electric conductivity (30–50 S cm⁻¹ in surface lateral direction) and porous morphology (porosity 70–80%), with soft and smooth surface structure of washi porous carbon, as compared to commercial ones (ca. 100 S cm⁻¹ and 80% respectively, but made with rigid and straight unwoven carbon fabrics), may be the advantage to open its application as GDL in low temperature fuel cells. However, in order to be the candidate of GDL, the cost of fabrication would be the issue, and heat-treatment at high temperatures (1600–2600 °C) for washi GDL is a drawback.

Lowering the heat-treatment temperature is pursued, applying pre-treatment with sulfonic acids and chemicals before carbonization and heat-treatment. Sisal washi and cotton cloth fabrics were used as materials. The merit of cotton cloth would be its low cost and the ease of fabrication, together with compatibility of carbonized surface with the Pt/C catalyst layers and good contact to polymer electrolyte membrane.

Figure 6 compares characteristics of porous carbon fabrics after carbonization at 800 °C, pre-treated either with I₂ or sulfonic acid. There was only little difference between CH₃SO₃H and C₆H₅SO₃H, as long as small molecular weight sulfonic acids were used. It is seen that shrinkage of samples, especially that of thickness after carbonization was larger for those pre-treated with I₂ than for those pre-treated with sulfonic acid. Mass decrease was also larger for the former (70%) than for the latter (60%). Bulk density was smaller for the former (ca. 0.25 g cm⁻³) than for the latter (ca. 0.3 g cm⁻³). Demerit of I₂ pre-treatment was the long time (ca. 10 days) required for penetration into washi fabrics, and lesser carbon yield after carbonization.

After carbonization, sisal hemp and cotton cloth samples were chemically treated with CA, GA or PA, and heat-treated at 1000–1600 °C in CH₄/N₂. MEA was prepared from thus made GDL, and tested for the fuel cell operation. Chemical treatment was effective in lowering the heat-treatment temperature from 1400 °C to 1000 °C. In Fig. 7, characteristics of porous carbon sheets derived from sisal and cotton fabrics are shown without and with chemical treatments. Cotton fabrics appear to be the best material to prepare porous carbon GDL, owing to flexible texture. Comparison of performances of these MEAs with those prepared using commercial GDL revealed equal or even better power generation performances even for heat-treatment at 1000 °C.

Although the porous carbon cloth prepared from cellulose fabrics gave smaller electric conductivity than PAN derived commercial porous carbon paper, the former showed better pore structure and
surface morphology than the latter. This has made compatible substrate as the support of the catalyst layer and enabled good adhesion with proton conducting polymer membranes. It is observed from Table S2 in Supporting Information section that higher cell performance came out with samples of lower Ohmic drop. Since the Ohmic resistance of 4 cm$^2$ polymer electrolyte membrane is calculated to be of less than 10 mΩ for 50 μm thickness,$^{25}$ major part should be from the contact layer between the catalyst and membrane interfaces. It is anticipated that designing this contact layer optimum, not merely the bulk resistance of the carbon layer will be the key factor to fabricate high performance GDLs of fuel cells.

4. Conclusions

Porous carbon paper made from washi and cotton fabrics was used as GDL for the first time in polymer electrolyte fuel cells. Carbonization was conducted based on morphology-retaining carbonization technology. In this method, cellulose fabrics were first treated with iodine or sulfuric acid, and carbonized at 800 °C in an inert atmosphere. This pre-treatment resulted in least fragmentation of original fibril structure of cellulose, and high carbon yield of resultant porous carbon sheet. Specimens were further heat-treated at high temperatures (1400–2600 °C), in order to promote the graphitic structure and improve the electric conductivity.

Porous carbon GDL was used to prepare MEA, and evaluated for fuel cell operation. Results showed that such GDLs revealed promising performances in fuel cell mode, and higher the heat-treatment temperature, better the performances. Required heat-treatment temperature depended on original washi or cotton materials. Morphological analysis showed that specific fiber structure of washi, not merely the conductivity of carbonized material, was the factor to provide good GDL.

In order to lower the heat-treatment temperature, chemical treatment with aldehydes was tested, to form functional groups on carbon materials. This process turned out to be effective in promoting graphitization of carbon fabrics, and heat-treatment temperature as low as 1000 °C was attained. These eco-materials could be applied as candidates for power generation devices, which would play a central role in the future hydrogen energy society (fuel cell vehicles, on-site power generation, etc.).

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-64057.

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Figure 7. (a) Characteristics of porous carbon sheets derived from sisal and cotton fabrics, pre-treated in CH$_3$SO$_3$H and heat-treated at 1000 °C. Bars indicate from left to right: bulk density g cm$^{-3}$; 1/10 times conductivity S cm$^{-1}$; power density W cm$^{-2}$ of a fuel cell operated at 70 °C with H$_2$ and O$_2$ humidified at 60 °C. (b) Effect of chemical treatment with CA, GA or PA, on the power density of a fuel cell operated at 70 °C with H$_2$ and O$_2$ humidified at 60 °C. In each sample, bars indicate from left to right: carbonized at 800 °C after pre-treatment with CH$_3$SO$_3$H; furtherly heat-treated at 1000 °C, without and with chemical treatment. The fourth bars are for samples pre-treated with C$_6$H$_5$SO$_3$H instead of CH$_3$SO$_3$H.

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