

Material Processing of Bamboo for Use as a Gas Diffusion Layer in Proton Exchange Membrane Fuel Cells

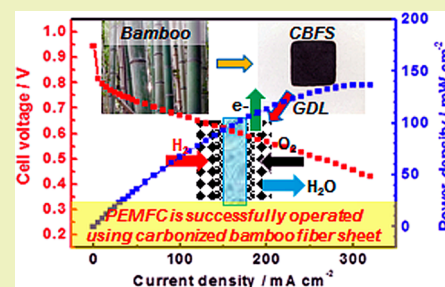
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Supporting Information

ABSTRACT: The material processing procedure of bamboo was investigated for use as a gas diffusion layer (GDL) of proton exchange membrane fuel cells (PEMFC). Bamboo fibers were obtained from bamboo (*Phyllostachys edulis*, moso bamboo) through mechanical treatment, delignification in NaOH solution at 120 °C, and subsequent defibration using an electric blender. The fibers contained cellulose, hemicellulose, and lignin as 70, 20, and 10 wt %, respectively. The fibers were molded into bamboo fiber sheets (BFS) and were subjected to carbonization to give carbonized bamboo fiber sheets (CBFS), in which the fibrous morphology remained. Both the in-plane and the through-plane electrical conductivities were measured after carbonization. For the first time, a single PEMFC operation test was demonstrated using CBFS as a GDL. As current GDLs are based on carbon fiber obtained from fossil fuel resources, the implementation of a plant-based method for GDL production would be beneficial in terms of CO₂ reduction as well as sustainability.

KEYWORDS: Bamboo, Delignification, Carbonization, Proton exchange membrane fuel cell (PEMFC), Gas diffusion layer



INTRODUCTION

Bamboo represents a diverse group of plants that taxonomically belong to the subfamily *Bambusoideae* under the family *Gramineae*, and it is widespread in the subtropics and tropics of Asia, Africa, and Latin America. Ben-Zhi et al. and Zhou et al. reported that the total area of bamboo forests was estimated to be 22.0×10^6 ha around the year 2000, which was thought to be approximately 1.0% of the total global forest area.^{1,2} In addition, bamboo is known to be one of the fastest growing plants, with a growth rate ranging from 30 to 100 cm per day, resulting in the progressive growth of bamboo forests at a rate of 3% per year, while the global forest area in a number of countries has decreased drastically. Thus, bamboo forests are considered to act as large carbon sinks, giving bamboo an advantage over other sustainable bioresources. It is reported that the lower annual yield of bamboo species is estimated as 2.0–5.8 Mg ha⁻¹ year⁻¹.³ However, Yiping and Henley reported that the rapid growth of bamboo may lead to biodiversity loss.⁴ This could be considered a serious disadvantage of bamboo in terms of its environmental impact.

In order to benefit from both the advantages and disadvantages, several application technologies have been developed for bamboo.³ In particular, its use as “biomass,” a potential energy source, has been investigated in terms of its practical application.^{3,5} Our main research focus, however, has been on the use of bamboo in fuel cells without the direct combustion of bamboo.^{6,7}

Bamboo has a fibrous microstructure and is composed mainly of cellulose, lignin, and hemicellulose, which allows the isolation of cellulose fiber with relative ease. We therefore

attempted to employ bamboo as a starting material for the preparation of the gas diffusion layer (GDL) of proton exchange membrane fuel cells (PEMFC). This type of fuel cell has recently attracted a great amount of interest for use as an electric power source for both vehicles and off-grid power sources, as they produce electric power with extremely low emissions of greenhouse and poisonous gases, such as CO₂, NO_x, and SO_x, if pure H₂ is employed as the fuel. Therefore, if a method can be developed to allow the use of bamboo in fuel cells, CO₂ reduction could be magnified thanks to its higher carbon fixation capacity and faster growth rate. At present, GDLs are generally composed of carbon fiber, which is produced from fossil fuels such as coal and petroleum, raising concerns about sustainability. Thus, if bamboo can be utilized as a material for GDLs, these sustainability issues could be resolved, due to both the renewable nature of bamboo and its faster growth rate.

In this study, we prepared bamboo fibers from bamboo (*Phyllostachys edulis*, moso bamboo) via mechanical treatment, delignification in NaOH solution at 120 °C, and subsequent defibration using an electric blender. Indeed, the delignification process is necessary to obtain cellulose and the fibers from bamboo as described in the literatures.^{8,9} Hence, optimization of the delignification process using NaOH was first investigated. The resulting bamboo fibers were then molded into the desired sheet morphology (bamboo fiber sheets; BFS) via a paper-

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making procedure, and finally, the fiber sheets were subjected to carbonization to give carbonized bamboo fiber sheets (CBFS). The physicochemical properties of the CBFS obtained following carbonization were also investigated, and a single PEMFC operation test was demonstrated using CBFS as the material for the GDL for the first time.

MATERIAL AND METHODS

Material. Bamboo (*Phyllostachys edulis*, moso bamboo) cut in Japan in 2013 was employed in this study. Reagents were purchased from Kishida Chemical Co., Ltd., Japan, except where specified otherwise. NaOH (product number: 900-02185) was used for delignification of the bamboo strips. H₂SO₄ (000-74433), and CH₃COOH (014-00266) were used for quantification of lignin and hemicellulose in the resulting bamboo fibers. HNO₃ (000-54483) was used in the identification of the metal contaminants in the products after delignification. Ultrapure water was obtained from Simplicity UV (Merck Millipore Co., Ltd.). The Pt-loaded carbon catalyst (Pt/C, TEC10E50E, Tanaka Kikinzoku Kogyo K. K., Japan), Nafion ionomer (Aldrich, 274704), 2-propanol (000-64785), and Nafion 117 membrane (E. I. DuPont de Nemours and Co.) were used in the single PEMFC operation test.

Preparation and Characterization of Bamboo Fiber. Bamboo was cut into strips approximately 150 mm in length using a metallic chopper. After both the inner and outer skins had been carefully descaled using a cutting machine (Silverlloy Co., Ltd.), the strips were subjected to pressing using a roll press machine (Silverlloy Co., Ltd.) to form a number of defects in the specimen. The above procedure is required to help penetration of the NaOH solution into the specimen during the delignification process.

The resulting strips were then subjected to the delignification process. The specimen (60 g) was treated with aqueous NaOH solution (1 L) using an autoclave (Panasonic, SR-P37) at approximately 120 °C and 200 kPa. The concentrations of NaOH solution used for the optimization were 0.01, 0.05, and 0.10 mol dm⁻³ (M). The treatment time was in the range of 1–3 h. After treatment with NaOH, the products were rinsed with ultrapure water until the filtrate reached a neutral pH. The pH values of the NaOH solutions both before and after the delignification were measured using a HORIBA F-53 pH meter with a HORIBA 9625-10D pH electrode. The products were subsequently subjected to defibration using an electric blender (Iwatani, IFM-650D) at 21,500 rpm for 1 min. The morphologies of the resulting products were observed using an optical microscope (OM, Keyence, VX-500F). The average diameter of the fibers was estimated from an OM image of more than 100 fibers.

The quantities of lignin and hemicellulose in the obtained fibers were determined according to the method described by The Japan Wood Research Society.¹⁰ For lignin content determination, a sample of dried fiber (1 g) was immersed in a solution of H₂SO₄ (15 mL of 72 vol %) for 4 h at room temperature. The fibers were then transferred to a conical flask with ultrapure water (560 mL) and heated under reflux for 4 h. The residue was collected by vacuum filtration with a glass filter (Sibata Scientific Technology Ltd., 1GP16, pore size = 10–16 μm) and rinsed with hot water (500 mL). The mass of the resulting dried residue was recorded after drying at 105 °C. For hemicellulose content determination, a sample of dried fiber (1 g) was immersed in a solution of NaOH (25 mL of 17.5 vol %). After immersion at room temperature for 30 min, the fibers were collected by vacuum filtration using a glass filter (Sibata, 1GP250, pore size = 160–250 μm). The resulting brown-colored residue was ground with a glass rod on the glass filter and was then subjected to immersion in a solution of CH₃COOH (40 mL of 10 wt %) for 5 min. The residue was again collected by vacuum filtration with a glass filter (Sibata, 1GP250) and rinsed with ultrapure water (1 L). Finally, the mass of the resulting dried residue was recorded after drying at 105 °C. Both the lignin and hemicellulose mass ratios in the fibers were calculated from the initial and final masses.

The metal contents of the resulting samples were investigated by means of inductively coupled plasma analysis (ICP, Agilent

Technologies, 700 Series) after immersion in a 1 M HNO₃ solution for 72 h.

Preparation and Carbonization of Bamboo Fiber Sheets (BFS). Bamboo fibers (5 g), which were obtained *via* treatment with a 0.10 M NaOH solution, were dispersed in ultrapure water (500 mL) and then poured into a plastic mold (Gincho Sangyo Co., Ltd., HA-80, mold size = 10 cm × 15 cm). After molding and flattening, the BFS was removed from the mold and dried at 60 °C for 12 h.

The resulting BFS was then cut into squares (5 cm × 5 cm), sandwiched between two alumina plates, and transferred to an electric tube furnace (Asahi Rika Seisakusho, ARF-1150-400-120 KC). The sheet was heated to 1000 °C at a rate of 10 °C/min and maintained at this temperature for 3 h under an Ar atmosphere. For heat treatments requiring temperatures greater than 1500 °C, a high-temperature furnace (Kurata Giken, A43-1094) was used, with a heating rate of 20 °C/min and a holding time of 30 min. The resulting carbonized bamboo fiber sheet will be referred to as “CBFS”.

Characterization of CBFS. The morphologies of the carbonized bamboo fibers in the CBFSs were investigated using field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701F). The average diameter of the carbonized bamboo fibers was estimated using OM observations, as described above. X-ray diffraction (XRD, Rigaku, RINT-Ultima3) and Raman spectroscopy (Raman, Horiba-Jovin Yvon, LabRAM ARAMIS) were used to investigate the carbonization behavior.

Electrical conductivity (κ) in both the in-plane and the through-plane is required for use as a GDL material. Then, the in-plane conductivity of CBFS was measured using a four-probe electrical conductivity meter (Mitsubishi Chemical Analytech, Roresta GP), and the through-plane conductivity was measured using a digital multimeter (Advantest, R6451A) and an electric conductivity cell (Takumi Giken) at a pressing pressure of 40 MPa. The apparatus for the electrical conductivity measurements are found in Figure S1 of the Supporting Information. Furthermore, in order to evaluate hydrophobicity, another important requirement for a GDL material, the contact angle (θ) for a water droplet was measured using a contact angle meter (Excimer Inc., SImage mini).

Single PEMFC Operation Tests. A single PEMFC operation test was also carried out using both the prepared CBFS and a commercially available carbon paper-based GDL (CP, Toray Industries, Inc., TGP-H-120, hydrophobic Teflon treated). The CBFS obtained after carbonization at 3000 °C was employed because of its high electrical conductivity and higher hydrophobicity. A Pt/C catalyst and a Nafion ionomer were mixed at a weight ratio of 1.00:0.39 in 2-propanol (1 mL) at room temperature for 24 h. An aliquot of the prepared catalyst ink was then applied to 1 cm² of both the CP and the CBFS, which had a Pt loading density of 1.0 mg cm⁻². The Nafion 117 membrane was subjected to chemical treatment before use, as detailed by Kinumoto et al.¹¹ The catalyzed CBFS (cathode) and CP (anode) were hot-pressed onto a Nafion 117 membrane at 1.0 MPa and 160 °C for 5 s.¹² The resulting membrane-electrode-assembly (MEA) was employed for the operation test. For comparison, an MEA was also prepared using catalyzed CP at both electrodes.

A single PEMFC (JARI's standard single cell, Japan) using polytetrafluoroethylene (PTFE) sheets for the gasket, along with carbonaceous bipolar plates, was employed for the operation test, with both the cathode and the anode having a geometric surface area of 1 cm² (Figure S2, Supporting Information). The components and configuration of this cell were previously described by Hashimasa et al.¹³ The flow rates of H₂ and O₂ for the operation test were set at 30 sccm at 0.1 MPa, respectively, which were over the equilibrium rates at each operation current density in the present study. The cell temperature and the humidification temperature for gases were set at 80 and 70 °C (relative humidity = 64%), respectively. The operation tests were carried out using a fuel cell operation mode of a multi potentiostat (VMP3, Biologic) until the maximum energy density was obtained.

RESULTS AND DISCUSSION

Preparation of Bamboo Fibers. Figure 1 shows the OM images (magnification $\times 250$) of both the pristine bamboo strips

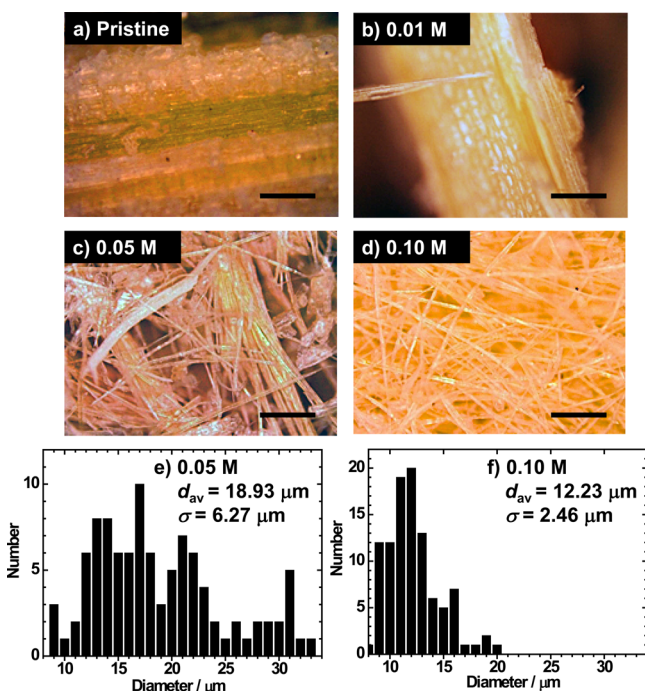


Figure 1. Optical microscopic (OM) images and diameter profiles. OM images of (a) the pristine bamboo strips and after delignification in (b) 0.01 M, (c) 0.05 M, and (d) 0.10 M solutions of NaOH for 3 h. Each bar represents 250 μm in length. The diameter profiles for the fibrous products are also shown for (e) 0.05 M and (f) 0.10 M.

and treated strips with NaOH solution (0.01, 0.05, 0.10 M) for 3 h. When 0.01 M NaOH solution was used, large fiber bundles remained even after 3 h, as shown in Figure 1b), indicating that full defibrillation does not take place under this condition. As the NaOH concentration was increased to 0.05 M, a number of single bamboo fibers (monofilaments) could be observed within the remaining fiber bundles, as indicated in Figure 1c). Because the number and size of the fiber bundles were clearly lower than those treated with the 0.01 M NaOH solution, it could be considered that in order to produce single bamboo fibers by delignification and subsequent defibrillation, the appropriate concentration of NaOH solution must be used. Indeed, even when the concentration of the NaOH solution was increased to 0.10 M, small fiber bundles remained after 2 h, and single bamboo fibers were only successfully obtained after 3 h, as shown in Figure 1d).

The diameter profiles of the products after 3 h of delignification using 0.05 and 0.10 M solutions of NaOH are also summarized in Figure 1e and f, along with the average diameters (d_{av}) and standard deviations (σ). In the case of the 0.05 M NaOH solution, d_{av} was found to be 22.06 μm after 1 h but had decreased to 18.93 μm after 3 h (Figure 1e). The standard deviation, σ , also decreased from 8.21 to 6.27 μm over this time. The large value of σ obtained in the case of the 0.05 M NaOH solution is mainly caused by residual fiber bundles having diameters greater than 25 μm . A decrease in d_{av} and σ values with increased treatment time were also observed for the 0.10 M NaOH solution. As shown by comparison of Figure 1e and f, an increase in the NaOH concentration clearly

corresponds with a decrease in d_{av} and σ , with the lowest d_{av} and σ values achieved being about 12.2 and 2.6 μm , respectively. In addition, no fiber bundles were observed in this case. On the basis of these results, we could obtain the bamboo single fibers (monofilaments) with average diameters of approximately 12 μm under the condition previously described. These monofilaments will be referred to as “bamboo fibers”.

The pH values of NaOH solutions decreased during treatment of the bamboo strips (Figure S3, Supporting Information). For example, the pH of the 0.01 M NaOH solution had dramatically reduced from 12 to 6 after 1 h and had dropped to 5 after 3 h. In this case, large fiber bundles remained, and no bamboo fibers were obtained, as shown in Figure 1b). As previously discussed, the pH of the NaOH solution (i.e., concentration of OH^- species) is an essential factor in the production of bamboo fibers via delignification. Interestingly, when the concentration of the NaOH solution was increased to 0.05 M, the pH remained above 9 after 3 h, even though the fiber bundles had not yet been broken down. On the other hand, the pH of the solution remained at approximately 12 when the 0.10 M NaOH solution was used, and as mentioned previously, the d_{av} and σ values of the products significantly decreased. From these results, we could determine that the pH of the NaOH solution should be maintained at approximately 12 in order to consistently produce bamboo fibers via the delignification process outlined above.

Gierer summarized the methods and reaction mechanisms for the delignification process, which is the first stage in the preparation of the bamboo fibers.¹⁴ In his report, lignin was decomposed by reaction with OH^- to give proton abstraction and nucleophilic addition.¹⁴ Indeed, the pH, which reflects the concentration of OH^- , strongly relates to obtain the bamboo fibers as previously discussed. We then further investigated the qualitative relation between pH and delignification. In addition, the effect of pH on the hemicellulose content was also investigated.

The hemicellulose and lignin contents in the pristine bamboo strips were measured as 29.8 and 18.1 wt %, respectively. After delignification in 0.10 M NaOH solution for 3 h, the lignin content had decreased to 10.4 wt %, whereas the hemicellulose content showed no significant change (approximately 3 wt %), suggesting that lignin was mainly decomposed and extracted from the bamboo strips as described by Gierer.¹⁴ The lignin extraction rate and pH change are dependent on the concentration of NaOH (Figure 2a). Moreover, a good linear relationship was observed between pH change and lignin extraction rate, where a good linear relationship with a coefficient of determination of 0.981 was observed (Figure 2b). In the case of the 0.01 M NaOH solution, a large drop in pH along with a small lignin extraction rate was observed, and bamboo fibers were not produced at this NaOH concentration as previously described. In contrast, for the 0.10 M NaOH solution, only a small change in pH was observed in combination with a large extraction rate, with the bamboo fibers being obtained successfully in this case. Therefore, it could be concluded that delignification of the bamboo strips catalyzed by NaOH is essential for the production of bamboo fibers, according to the methods employed in this study. At this point, it was discovered that a significant quantity (approximately 10 wt %) of lignin remained in the resulting bamboo fibers. However, lignin is a polyaromatic compound, and it can

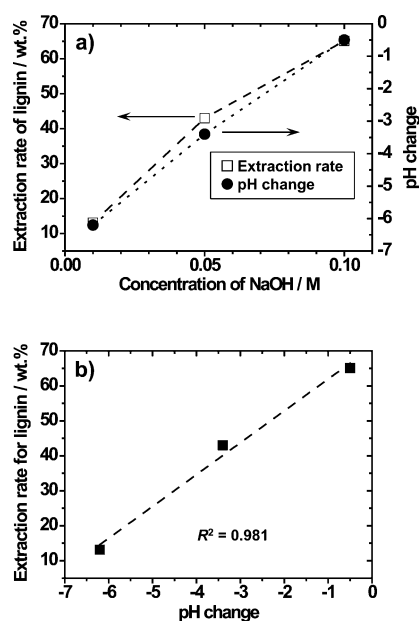


Figure 2. Effect of pH and NaOH concentration on lignin extraction. (a) Dependencies of the extraction rate of lignin and pH change on the concentration of NaOH. (b) Relationship between pH change and lignin extraction rate, where a good linear relationship in the coefficient of determination is observed.

also be subjected to carbonization along with cellulose and hemicellulose. Thus, the use of lignin-containing bamboo fibers is not a concern in this study.

In order to determine the metals present in bamboo fibers, ICP measurements were carried out for the bamboo fibers produced after 3 h of delignification. It was observed that metals such as Na, Mg, Al, Si, K, Ca, Fe, and Zn were detected, and the net content was 0.02 wt %. Thus, it could be concluded that the bamboo fibers prepared according to the above method were composed of cellulose, hemicellulose, and lignin in the region of approximately 70, 20, and 10 wt %, respectively, and these fibers were subjected to further carbonization before use as the GDL of PEMFC as outlined below.

Carbonization of BFS and Characterization of CBFS.

Following the carbonization procedure, it was observed that the color of the BFS changed from pale brown to black, indicating that the BFS successfully undergo carbonization to form CBFS (Figure S4, Supporting Information).

Typical FE-SEM images of the carbonized bamboo fibers in various CBFS and in commercially available carbon fiber in CP are shown in Figure 3. The morphology of the carbonized bamboo fibers remained “fibrous” irrespective of the carbonization temperature; however, the surface morphology did indeed vary according to the temperature. After carbonization at 1000 °C, the surface of the fibers was relatively rough. However, an increase in the carbonization temperature yielded smoother fibers, with the fibers having a smooth surface after carbonization at 3000 °C. It is hypothesized that this variation in surface morphology with temperature may relate to the crystalline development with carbonization, as discussed in more detail later.

The average diameter of the fibers decreased further through carbonization, with a decrease from approximately 12.2 to 7 μm being observed (Figure S5, Supporting Information). Both the average diameter and rate of weight loss (approximately 80 wt %) were irrespective of the temperature in this case, suggesting

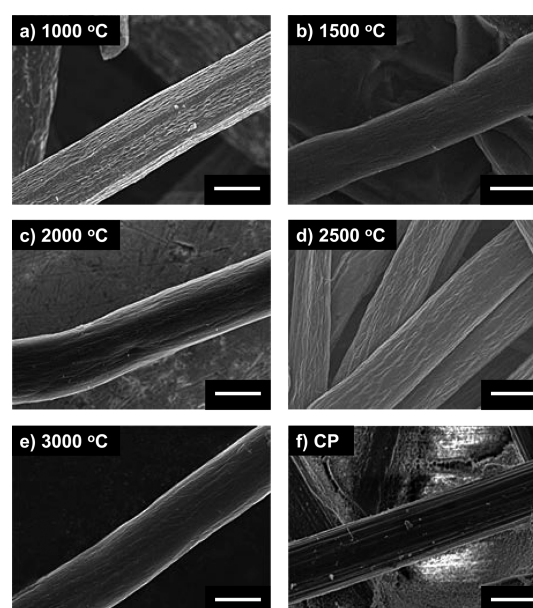


Figure 3. FE-SEM images of CBFS taken after heating BFS at (a) 1000 °C, (b) 1500 °C, (c) 2000 °C, (d) 2500 °C, and (e) 3000 °C. (f) FE-SEM image of GDL commercially available CP. Each bar represents 1 μm in length.

that pyrolysis mainly occurred before carbonization in bamboo fibers at temperatures up to 1000 °C. Shafizadeh and Shimada et al. investigated the pyrolysis reaction mechanism of bamboo and cellulose as a potential source of carbonaceous materials.^{15,16} In particular, Shimada et al. investigated the mechanism using mass spectrometry by analysis of the gaseous products released during both pyrolysis and carbonization reactions.¹⁶ They detected both CO_2 and CO as major products, with the release of CO_2 being observed between 300 and 400 °C, proposing that bond breaking and aromatization of cellulose were responsible for this phenomenon. We also investigated the volatile products released during the carbonization process at temperatures up to 1000 °C using an EI (electron impact) mass spectrometer coupled with thermogravimetric analysis. At temperatures up to 500 °C under a flow of He gas, the release of H_2O ($m/z = 18$), CO (28), O_2 (32), and CO_2 (44) was detected (Figure S6, Supporting Information), along with 2-furanone, 3-methylcyclopentanone, and 2, 6-dimethoxyphenol, which were considered to be decomposition products released from the bamboo fibers. Therefore, BFS was initially decomposed with release of such products, and following polycondensation and aromatization take place to give the resultant CBFS as described for carbonization process of organic polymers.¹⁷

Figure 4a and b show the XRD patterns and Raman spectra of CBFS prepared at a range of carbonization temperatures. In XRD patterns, complex peaks and weak broad peaks were observed between 20° and 30° and at around 43°, respectively. The net intensity and the peak fraction of the signal at 26° increased with higher carbonization temperatures. This peak fraction can be assigned to diffraction from basal planes (hexagonal carbon layers) of the graphitic carbon structure. Poor resolution of this signal at 1000 °C was likely because the carbon layers were not fully developed and were still relatively disordered. The peak that appeared at around 43° corresponded to the 10 diffraction of the turbostratic carbon structure, which was also observed in the carbonization of

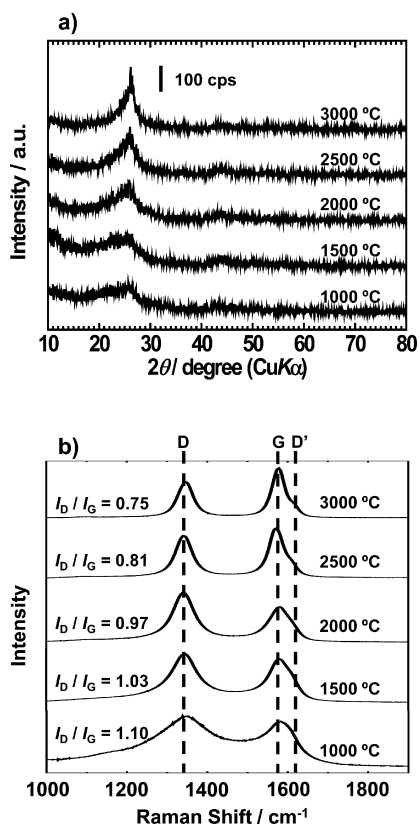


Figure 4. XRD patterns and Raman Spectra of CBFS. (a) XRD patterns and (b) Raman Spectra of the CBFS prepared at various carbonization temperatures.

hardwood acetic acid lignins.¹⁸ After carbonization at 3000 °C, both signals were also visible, with the peak at 26° being more pronounced than at lower temperatures. On then basis of these results, it appeared that a fully graphitic structure was not achieved, and therefore, this series of CBFS can be classified as “hard carbon.”

The Raman spectrum of the CBFS produced at 1000 °C contains broad D and G bands at 1360 and 1580 cm^{-1} , respectively. The latter (G) band is particularly broad and may indeed be a divided D' band at 1620 cm^{-1} , which was clearly observed at temperatures above 2500 °C. Indeed, both the G and the D bands became sharper and better resolved with an increase in temperature. In terms of characterization, the G band can be assigned to the development of a graphitic carbon structure in the carbonaceous materials, whereas both the D and D' bands are expected to be due to structural disorders, such as edge or defect sites on the hexagonal carbon layers. This is supported by the fact that the Raman spectrum of highly oriented pyrolytic graphite, a typical graphite material, does not show D or D' bands, and only a sharp G band is observed. On the other hand, it is well known that typical nongraphitizable carbon species show three mode bands, thus bearing similarities with CBFS. The intensity ratio of the D to G bands (I_D/I_G), as shown in Figure 4, can be used as a parameter for the structural characterization of carbonaceous materials. It was observed that the I_D/I_G of CBFS decreased with increasing carbonization temperature, thus demonstrating that the numbers of edge and defect sites were reduced due to the development of a greater number of ordered carbon layers with an increase in carbonization temperature. This phenomenon is likely to be

related to the surface morphology changes, as shown in Figure 3.

In order to employ CBFS for use as a GDL in PEMFC, several essential physicochemical properties are required, namely, high hydrophobicity, high electrical conductivity, high gas permeability, and stability. Thus, investigations of both hydrophobicity and electrical conductivity were carried out before the use of the CBFS in the operation test of PEMFC.

For measurement of the hydrophobicity of CBFS, the contact angle (θ) was utilized. The contact angle could not be measured at carbonization temperatures below 1500 °C, as the water droplets were immediately absorbed by the CBFS. Because of lower electrical conductivity as well as hydrophobicity, we considered that CBFSs produced at temperatures below 1500 °C are unsuitable for use as a GDL in the present study. The contact angle was therefore measured at carbonization temperatures of 2000, 2500, and 3000 °C. The contact angle recorded at these temperatures exceeded 130°, which is slightly higher than the 123° recorded in the hydrophobic treatment of CP and Teflon (TGP-H-120), thus confirming that the hydrophobicity of such CBFS is suitable for incorporation into a GDL.

The in-plane and through-plane electrical conductivities (κ) of CBFS are shown in Figure 5. It was observed that the

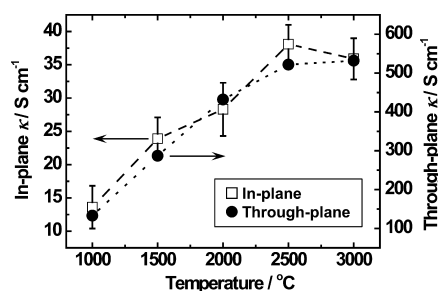


Figure 5. Electrical conductivities (κ) of CBFS. (a) In-plane and (b) through-plane conductivities. An error bar is shown for the in-plane electric conductivity.

electrical conductivities gradually increased with an increase in temperature, up to 2500 °C, and then slightly from 2500 to 3000 °C. Shimada et al. reported the relationship between the specific electric resistance and carbonization temperature for bamboo strips, where the resistance decreased at carbonization temperatures up to 1000 °C and where no appreciable change was observed up to 3000 °C.¹⁶ They concluded from this result that the crystalline structure, composed of hexagonal carbon layers, was not fully developed, even when the carbonization process was carried out at 3000 °C. In this study, it was observed that the electrical conductivity increased with an increase in carbonization temperature up to 3000 °C, which is likely to be related to further ordering of the carbon layer taking place, as suggested by the XRD and Raman results. Consequently, both the in-plane and through-plane electrical conductivities were measured and were found to be approximately 35 and 550 S cm^{-1} , respectively, after treatment at 3000 °C. The electrical conductivities measured for CP were approximately 150 and 1500 S cm^{-1} , respectively, and are significantly larger than those of CBFS. Therefore, further improvement in the electrical conductivity is one point to be improved before CBFS can be implemented as a competitor for the commercially available CP (e.g., TGP-H-120) as a GDL.

Single PEMFC Operation Tests Results. Figure 6 shows the polarization and power density curves for the single

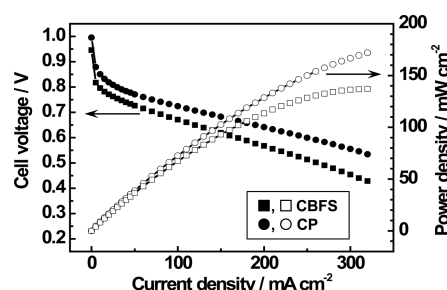


Figure 6. Results for PEMFC operation tests employed CBFS (squares) and CP (circles) as GDL for the cathode. A commercially available CP (TGP-H-120) was employed as the GDL for the anode in both cases. Solid and blank symbols show cell voltage and power density, respectively.

PEMFC operation tests. The power density per unit surface area of the electrodes can be easily calculated by multiplication of the cell voltage by the discharge current density. For the operation test, CBFS obtained via carbonization at 3000 °C was employed because of its higher electrical conductivity and higher hydrophobicity. The open-circuit voltage (OCV) obtained for the cell based on CBFS was approximately 0.95 V and the maximum power density was 140 mW cm⁻¹ at 0.45 V, demonstrating that the PEMFC could indeed be operated using CBFS as the GDL. On the other hand, the OCV obtained for the cell based on CP was slightly higher (50 mV) than that based on CBFS, and the maximum power density recorded was 170 mW cm⁻¹ at 0.55 V. These OCV values were slightly lower than the theoretical OCV calculated for PEMFC under these conditions (1.18 V). The difference between the theoretically calculated OCV and that obtained using CP and CBFS is likely due to the gas crossover and mixed potential.¹⁹ On the other hand, the lower power density recorded for CBFS compared to CP may be owing to the ohmic losses in the electrolyte and electrodes.¹⁹ From these results, it therefore appears that the CBFS prepared by defibration via delignification, molding, and subsequent carbonization may be a suitable candidate material for the GDL of PEMFC in the future.

Currently, GDLs are mainly prepared using carbon fiber, which is produced from fossil fuel sources such as coal and petroleum; therefore, it raises sustainability concerns. Meanwhile, bamboo is a plant-based source, with high annual yield and rapid reproducibility as described above, leading to high sustainability compared to coal or petroleum. The present operation test result shows that PEMFC could be operated using CBFS prepared through defibration, molding, and carbonization of bamboo fibers, as GDL. Further studies are now underway for performance under different operating conditions, assessment of the durability, and improvement of the electrical conductivity of CBFS. The results will be reported in due course.

CONCLUSION

A gas diffusion layer (GDL) for proton exchange membrane fuel cells (PEMFC) was prepared from bamboo fibers via delignification, defibration, molding, and carbonization. Bamboo fibers with an average diameter of 12.2 μm obtained from delignification were molded into bamboo fiber sheets (BFS) and were subjected to carbonization to give carbonized bamboo

fiber sheets (CBFS). The PEMFC operation test was demonstrated using CBFS, with a maximum power output comparable to that of commercially available CPs. As current the GDL is based on carbon fiber obtained from fossil fuel resources, the implementation of a plant-based method for GDL production is environmentally beneficial as well as having material sustainability for future societies.

ASSOCIATED CONTENT

Supporting Information

A schematic illustration of the apparatus for the electric conductivity measurements, PEMFC, pH change of NaOH solutions during delignification of the bamboo strips, appearance of BFS and CBFS, fiber diameters and weight loss rates of bamboo fibers after carbonization, and TG curves and mass spectra of bamboo fibers during carbonization up to 1000 °C under He atmosphere. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00115.

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Notes

The authors declare no competing financial interest.

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