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A graphite-coated carbon fiber epoxy composite bipolar plate for polymer electrolyte membrane fuel cell

Ha Na Yu[a], Jun Woo Lim[a], Jung Do Suh[b], Dai Gil Lee[a,*]

[a] School of Mechanical Aerospace & Systems Engineering, Korea Advanced Institute of Science and Technology, ME3221, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea
[b] Fuel Cell Vehicle Team1, Eco-Technology Center, Research & Development Division, Hyundai-KIA Motors, 104 Mabuk-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-912, Republic of Korea

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ABSTRACT

A PEMFC (polymer electrolyte membrane fuel cell or proton exchange membrane fuel cell) stack is composed of GDLs (gas diffusion layers), MEAs (membrane electrode assemblies), and bipolar plates. One of the important functions of bipolar plates is to collect and conduct the current from cell to cell, which requires low electrical bulk and interfacial resistances. For a carbon fiber epoxy composite bipolar plate, the interfacial resistance is usually much larger than the bulk resistance due to the resin-rich layer on the composite surface.

In this study, a thin graphite layer is coated on the carbon/epoxy composite bipolar plate to decrease the interfacial contact resistance between the bipolar plate and the GDL. The total electrical resistance in the through-thickness direction of the bipolar plate is measured with respect to the thickness of the graphite coating layer, and the ratio of the bulk resistance to the interfacial contact resistance is estimated using the measured data. From the experiment, it is found that the graphite coating on the carbon/epoxy composite bipolar plate has 10% and 4% of the total electrical and interfacial contact resistances of the conventional carbon/epoxy composite bipolar plate, respectively, when the graphite coating thickness is 50 μm.

1. Introduction

A unit cell of the PEMFC (polymer electrolyte membrane fuel cell or proton exchange membrane fuel cell) stack is composed of MEAs (membrane electrode assemblies), GDLs (gas diffusion layers), and bipolar plates, as shown in Fig. 1. The bipolar plates have several functions in a fuel cell stack. They connect cells electrically in series, separate the gases in adjacent cells, provide structural support for the stack, conduct heat from active cells to the coolant, and typically house the flow field channels [1]. Therefore, a significant amount of research has been conducted regarding the development of the bipolar plate using various materials such as graphite, metal, and composite [2–6]. Graphite was first used for PEMFC bipolar plates, however, it was not a suitable material for the mass production which is necessary for the full-scale commercialization of fuel cells for passenger vehicles because of its sophisticated machinery manufacturing process. Even though, metallic bipolar plates are currently used due to their ease of mass manufacturing, the metallic bipolar plates require an expensive protective coating layer because the bipolar plates are exposed to a corrosive acidic environment inside of a fuel cell (pH2 to pH3 at 60–80 °C) [1]. Continuous-carbon-fiber-reinforced composite bipolar plates are an attractive option for PEM fuel cell material because they offer the advantage of low cost, high corrosion resistivity, low heat capacity for cold start, lower weight, and greater ease of manufacture than traditional graphite. In addition, their mechanical properties exceed the DOE (Department of Energy) target [7]. The low electrical conductivity of the composite material in the through-thickness direction, however, continues to be a problem due to the resin-rich layer on the surface of the composite bipolar plate.

The electrical properties of the bipolar plate material are important for the efficiency of the fuel cell stack. Low electrical resistance of the bipolar plates for the PEMFC will lead to less electrical loss and higher energy conversion efficiency. The resistance of the bipolar plate of the PEMFC consists of the bulk material resistance and the interfacial contact resistance. The bulk resistance is not a significant source of voltage loss in fuel cells, even for relatively high-resistivity plates. Although the electrical conductivity of the composite is several orders of magnitude lower than the conductivity of the metallic plates, the bulk resistive losses are on the order of several millivolts. A significantly higher resistance results from the interfacial contacts, such as between the bipolar plate and a GDL [8].

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* Corresponding author. Tel.: +82 42 350 3221; fax: +82 42 350 4481.
E-mail address: dglee@kaist.ac.kr (D.G. Lee).

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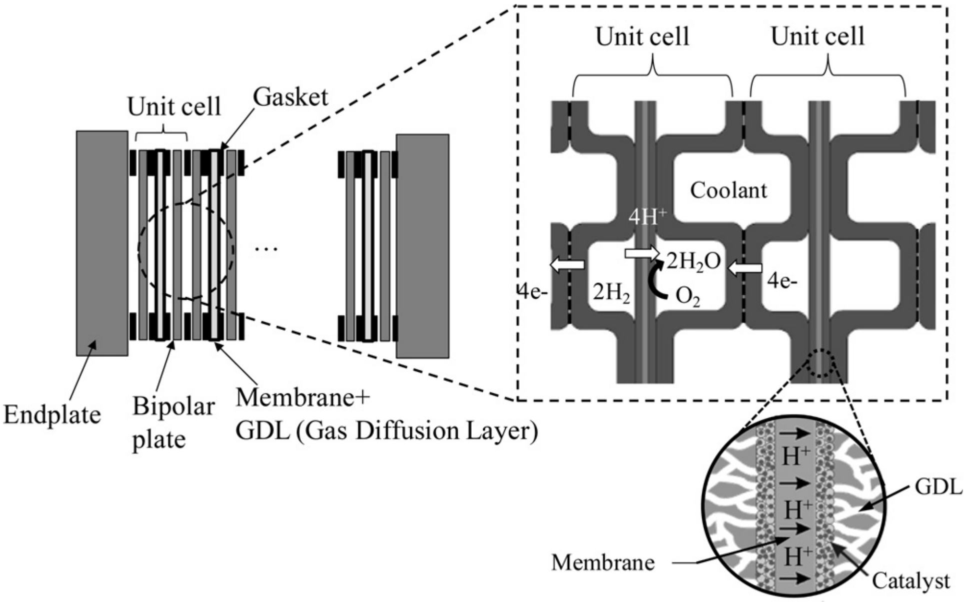

Fig. 1. Schematic drawing of a unit cell of a PEMFC stack.

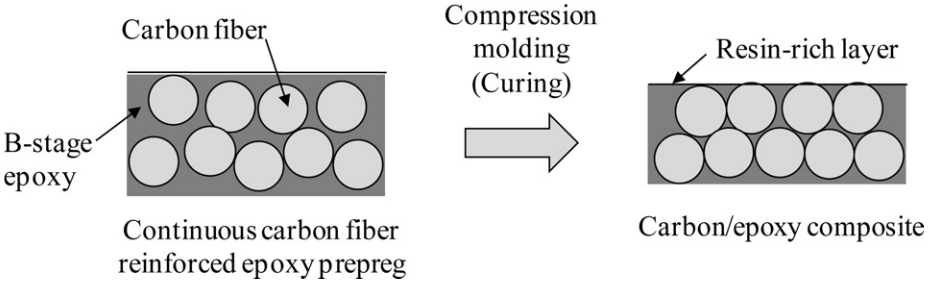

Fig. 2. Schematic drawings of the surface conditions of the composite plate without treatment.

Therefore, this study focused on using the surface treatment method to reduce the interfacial contact resistance between the composite and the GDL. The graphite coating method for the composite bipolar plate was developed because graphite foil has a very low contact resistance due to its conformability [1]. Additionally, a method to calculate the ratio of the bulk resistance to the interfacial contact resistance was developed.

2. Experimental

2.1. Graphite coating on the carbon fiber epoxy composite

A resin-rich layer is generally produced on the surface of the carbon/epoxy composite during the curing process, such as in the compression molding process shown in Fig. 2, which increases the interfacial contact resistance. The interfacial contact resistance is also affected by the surface characteristics of GDL, which provides a pathway for reactant gases from the flow field channels to the catalyst layer, allowing them access to the entire active area with an electrical connection from the catalyst layer to the bipolar plate [1]. As shown in Fig. 3(a) and (b), the GDL usually consists of a randomly oriented carbon fiber mat with a binder such as PTFE (polytetrafluoroethylene). The randomly oriented carbon fiber side is the contact surface with the bipolar plate. A coating on the surface of the bipolar plate with a soft conductive material is more effective to reduce the interfacial contact resistance than other surface treatment methods because the carbon fiber in the GDL could contact a large surface area of the bipolar plate. Other methods to make the carbon fibers of the GDL and the exposed carbon fibers on the surface of the composite bipolar plate directly contact each other include sanding, etching, or plasma treatment, as shown in Fig. 4. The carbon fiber in the GDL penetrated into the soft conductive layer, which increased the contact area between the bipolar plate and the GDL. Consequently, the contact electrical resistance decreased drastically compared to those with other surface treatments [9–11].

Therefore, a thin graphite layer as a soft conductive material was coated on the surface of the composite bipolar plate to decrease the

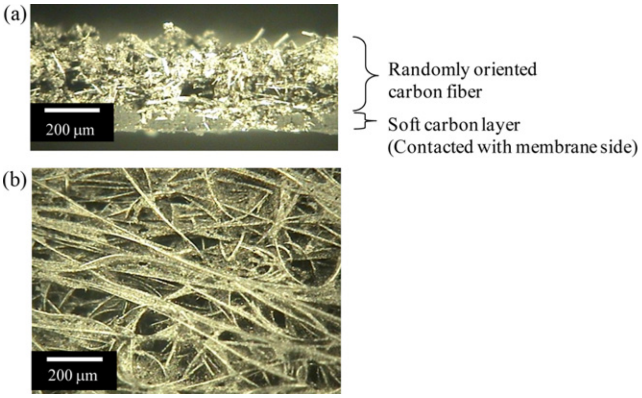

Fig. 3. Optical microscope images: (a) cross-section of the GDL; (b) surface of the GDL contacted with the bipolar plate.

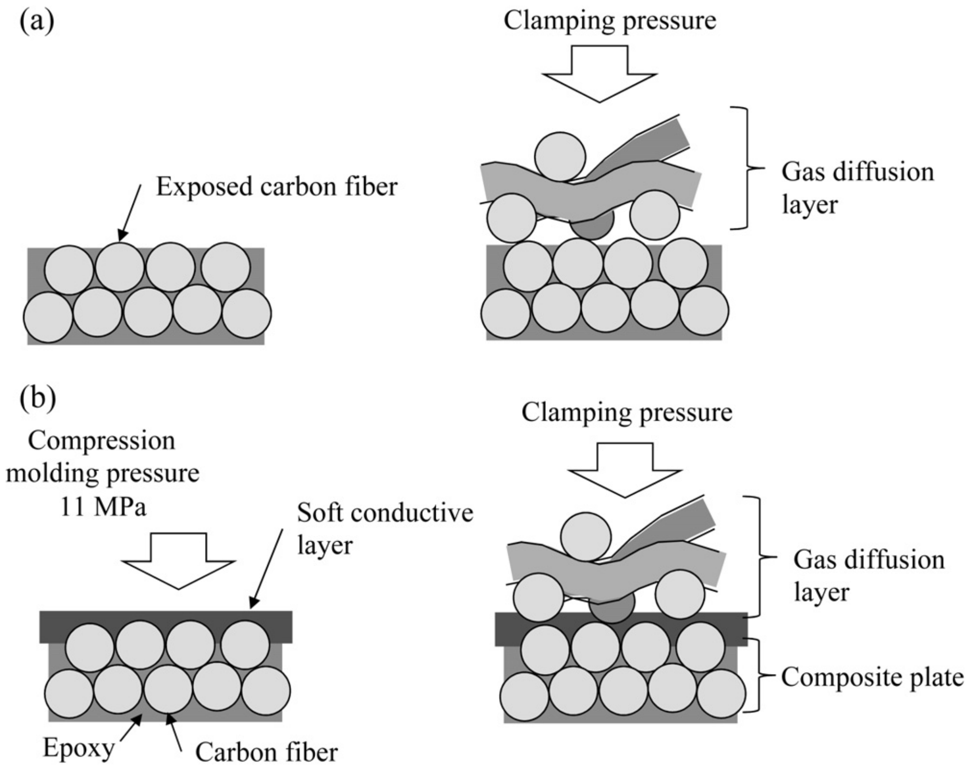

Fig. 4. Schematic drawings of interfacial contact conditions between the GDL and the composite specimens: (a) removing the resin rich layer with mechanical abrading; (b) graphite coating.

contact resistance and to increase the conformability between the bipolar plate and the GDL. The other advantages of the graphite coating method are that it does not require any surface treatment after de-molding the composite plate from a mold as well as it is not susceptible to corrosion in the acid environment of the PEMFC stack.

The graphite coating method follows the procedure shown in Fig. 5. Thin layer of expanded graphite with a outside backup film was placed on the stack of carbon fiber epoxy composite prepregs. The prepreg is the short terminology for pre-impregnated fiber reinforced plastics. In other words, it is composed of the reinforcements and partially cured epoxy resin (B-stage) [12]. After laminating the stacked prepregs between two hot rollers at 80 °C under 1 MPa, the graphite foils stuck to the prepregs because the viscosity of the B-stage epoxy resin decreases at 80 °C. And then, the backup film was peeled, which resulted in thin graphite layer coating the surface of the prepregs. The thickness of the graphite coating layer on the composite was controlled over the range of 2–50 µm by adjusting the amount of graphite of backup film.

2.2. Fabrication of the flat carbon/epoxy composite plate

The properties of the carbon fiber epoxy prepreg and the graphite foil are listed Table 1. The reinforcement type of the carbon/epoxy prepreg which is used in this study is continuous unidirectional carbon fiber sheet. A ply thickness of carbon/epoxy prepreg before curing is 20 µm and the stacking sequence of the composites is $[0_2/\pm 30]_s$. The stacking sequence can be easily described for composites composed of layers of the same material with equal ply thickness by simply listing the ply orientations θ ($-90 < \theta \leq 90$) from the bottom of the laminate to the top using brackets when the ply is an anisotropic material with principal axes in the direction of the fibers (longitudinal), normal to the fibers in the plane of the lamina (in-plane transverse), and normal to the plane of the lamina. Thus, the notation $[0_2/\pm 30]_s$ indicates an eight-layer laminate. A subscript 'number' is utilized to denote the number of repeating plies and a subscript 's' denotes that the stacking sequence is repeated symmetrically [12].

Table 1
Properties of the prepregs (USN 020) and graphite foil (BD-100).

Prepreg (USN 020, SK Chemical, Korea)	Fiber properties	Modulus (GPa)	230
		Strength (GPa)	3.5
	Ply thickness (µm)		20
Graphite foil (BD-100, Samjung CNG, Korea)	Density (kg m^{-3})		1.0
	Thickness (µm)		100

The graphite coated composite prepregs were cured with the compression molding process under a pressure of 11 MPa at 160 °C, as shown in Fig. 6(a). The degree of curing was monitored using a dielectrometry method, and the temperature of the composite was measured using thermocouples [13–15]. From the dielectrometry measurement, it was found that the composite prepreg was fully cured within 40 min, as shown in Fig. 6(b). The thickness of the carbon/epoxy composite plate was 0.15 mm because a ply thickness after curing was about 18.5 µm.

The morphologies of the thin composite plates were observed with a SEM (scanning electron microscope) (Sirion, FEI, Netherlands) when the graphite coating layers were 2 µm and 50 µm. The total resistance of the composite plate in the through-thickness direction was measured with a specimen size of 100 mm × 100 mm by the experimental setup as shown in Fig. 7. The total resistance depends on several resistances in series, such as the resistance of the two copper electrodes (R_{Cu}), the two GDLs (R_{GDL}), the bulk resistance of the specimen (R_b), and more significantly, the contact resistances between the GDL and the specimen, such as the carbon/epoxy composite bipolar plate ($R_{GDL/b}$). The areal density and thickness of the GDL (SGL, Germany) used are

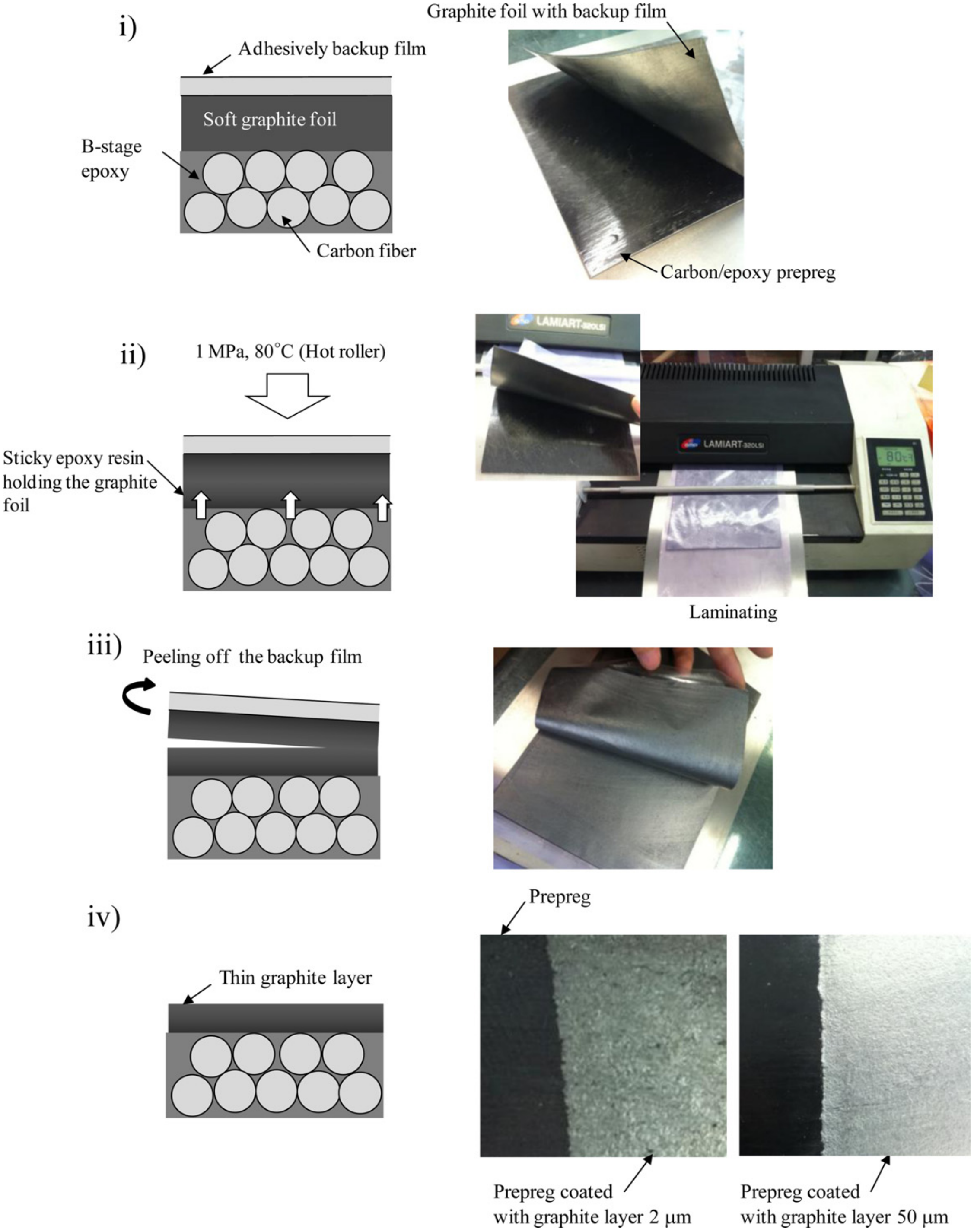

Fig. 5. Photos and schematic drawing of graphite coating process on the composite prepreg.

$0.143\ \mathrm{kg\,m^{-2}}$ and 335 μm, respectively. The electrical resistances in the through-thickness direction were measured under the three bipolar plate compaction pressures of 0.5 MPa, 1.0 MPa and 1.5 MPa [16]. Also, the total resistances of the graphite plate (0.4 mm) and the composite plate without treatment were measured to compare them to those of the graphite-coated composite plate.

2.3. *Fabrication of the prototype composite bipolar plate*

The prototype composite bipolar plate was manufactured with the same channel dimensions as the conventional shell type bipolar plate. The stacking sequence of the composite bipolar plate was $[0_3/\pm 30]_s$. After coating both surfaces of the stacked prepregs with the graphite layers, the prepregs were placed in the channel-shaped mold and cured under the same curing condition in Section 2.2. The measured thickness of the composite bipolar plate after manufacture was 0.19 mm, including the two graphite layers of 2 μm thickness. When the thickness of coated graphite layer was 50 μm, the thickness of the composite bipolar plate was approximately 0.3 mm. The total resistance of the composite plate with the same channel shape as the bipolar plate was measured in the through-thickness direction with respect to the thickness of the coated graphite layer and the clamping pressure. The specimen dimension was 100 mm × 100 mm.

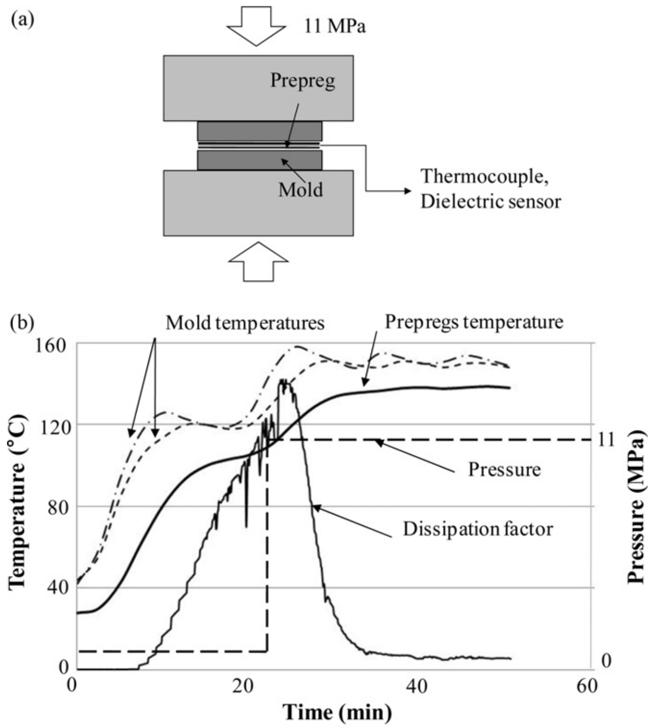

Fig. 6. Compression molding method for the carbon/epoxy composite bipolar plate: (a) schematic drawing; (b) curing cycle for the prepreg.

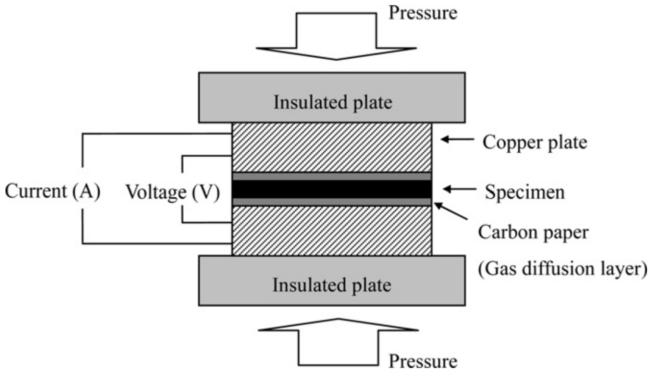

Fig. 7. Schematic drawing of the experimental setup to measure the total resistance in the through-thickness direction of the carbon/epoxy composite plate.

3. Result and discussion

3.1. Electrical resistances of the flat carbon/epoxy composite plate

The cross-sections of the composite plate surface are showed in Fig. 8 when the thicknesses of the graphite layer are 2 μm and 50 μm. As the thickness of the graphite layer increases, the total resistance in the through-thickness direction of the thin composite bipolar plate decreases, as shown in Fig. 9. When the thicknesses of the graphite coating layer are 2 μm and 50 μm, the carbon/epoxy composite bipolar plates have only 14% and 10% of the total electrical resistance of the composite bipolar plate without surface treatment, respectively, under compaction pressure of 1 MPa. Moreover, the total resistance of the composite is similar to that of a neat graphite plate when the thickness of the graphite layer is 50 μm. Therefore, it could be concluded that the thin graphite layer reduced the interfacial contact resistance between the composite and the GDL significantly.

The ratio of the bulk resistance to the interfacial contact resistance is estimated to investigate quantitatively the effect of the graphite coating on the resistance of a composite plate in the through-thickness direction.

As in Fig. 7, the total resistance of a unit cell in the through-thickness direction can be written as follows:

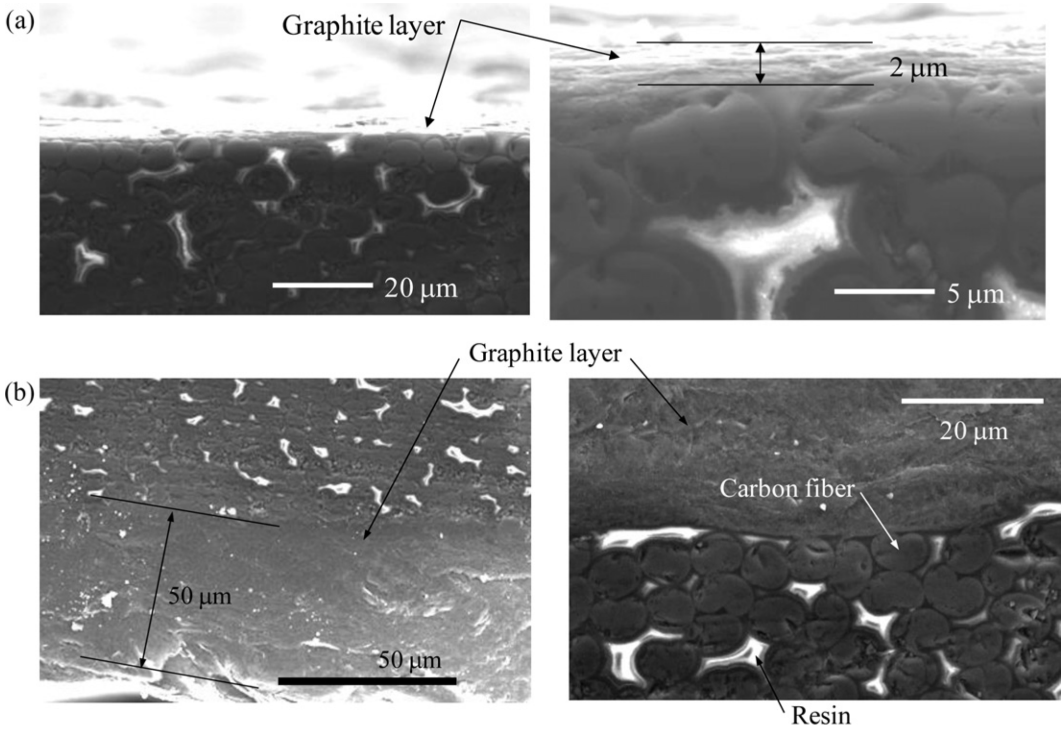

Fig. 8. SEM images: (a) composite plate coated with a 2-μm-thick graphite layer; (b) composite plate coated with a 50-μm-thick graphite layer.

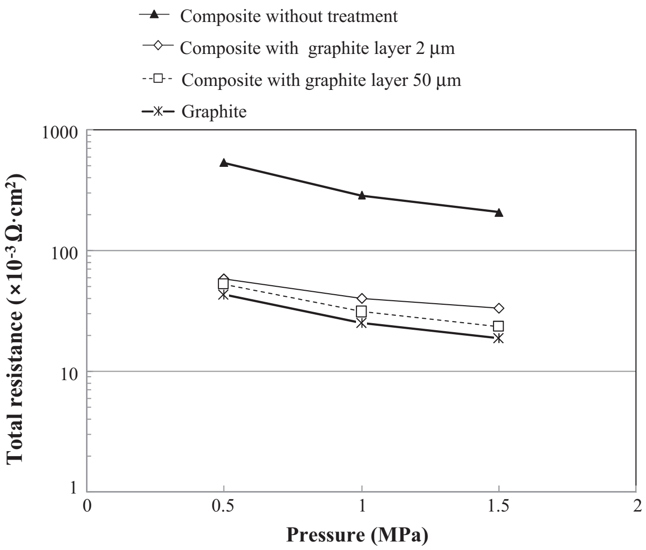

Fig. 9. Total resistances of the specimens in the through-thickness direction with respect to surface treatments.

$$
\begin{aligned}
R_{\mathrm{total}} &= 2R_{\mathrm{GDL/Cu}} + 2R_{\mathrm{GDL}} + 2R_{\mathrm{GDL/b}} + R_{\mathrm{b}} \\
R_{\mathrm{sys}} &= 2R_{\mathrm{GDL/Cu}} + 2R_{\mathrm{GDL}} \\
\text{ASR (Area Specific Resistance)} &= R_{\mathrm{total}} - R_{\mathrm{sys}} = 2_{\mathrm{RGDL/b}} + R_{\mathrm{b}}
\end{aligned}
\tag{1}
$$

The ASR (Area Specific Resistance) can be determined by subtracting the system resistance ($2R_{\mathrm{GDL/Cu}} + 2R_{\mathrm{GDL}}$) from the total resistance; therefore, the ASR includes the bulk resistance of the specimen and the two interfacial contact resistances between the specimen and the GDL [1,17].

In the case of an isotropic material, such as metal, the bulk resistivity could be measured by the four-probe measurement method [18]. Then the interfacial contact resistance with respect to the compacting pressure can be calculated easily by subtracting the bulk resistance from the total resistance because the bulk resistance of the plate is independent of the clamping force. On the other hand, it is not easy to measure the bulk resistivity of anisotropic materials, including composites, because their electrical conductivities are different in each direction. It is especially difficult to measure the bulk resistivity of composites in the through-thickness direction because the specimens must be sufficiently thick. Additionally, it is difficult to calculate the resistance when considering the effect of various staking angles of composite prepregs, such as 30° and 45°, for sufficient strength in the perpendicular direction from the channel when the bipolar plate is clamped with a high pressure to decrease the contact resistance. Therefore, the bulk and the interfacial contact resistances of the carbon composite plate with complex stacking sequences are calculated indirectly using the graphite coating method, as shown in Fig. 10. First, the bulk resistance of the composite specimen with the stacking sequence of $[0]_{20}$ is measured in the transverse direction (2-direction) of the carbon fiber, as shown in Fig. 11. This measurement assumes that the in-plane (2-diretion) bulk and through-thickness (3-direction) bulk resistivities are the same when the unidirectional carbon fibers are line-contacted to each other. After measuring the total resistance of a dummy composite plate of $[0]_8$ with the coated graphite layer, the interfacial contact resistance of the dummy composite plate of $[0]_8$ with the coated graphite layer can be calculated from Eq. (2) as follows:

$$2R_{\mathrm{GDL/b(dummy)}} = R_{\mathrm{dummy}} - R_{\mathrm{b(dummy)}} \tag{2}$$

where R_{dummy}: ASR of the dummy composite plate (composite of $[0]_8$ with the coated graphite layer); $R_{\mathrm{b(dummy)}}$: bulk resistance of the dummy composite plate (composite of $[0]_8$ with the coated graphite layer); $R_{\mathrm{GDL/b(dummy)}}$: interfacial contact resistance between the GDL and the dummy composite with the coated graphite layer.

It is assumed that the interfacial contact resistances of the dummy composite plate of $[0]_8$ and the composite plate of $[0_2/\pm 30]_s$, which is the stacking sequence for the bipolar plate, are the same because both of the specimens are coated with the same graphite layer.

$$R_{\mathrm{dummy}} - R_{\mathrm{b(dummy)}} = 2R_{\mathrm{GDL/b(dummy)}} = 2R_{\mathrm{GDL/b}} \tag{3}$$

Using this method, the bulk and interfacial contact resistances of composite plates of various stacking sequences in the through-thickness direction are calculated as shown in Fig. 12. Although the electrical resistivity of the carbon composite in the through-thickness direction is approximately 164 mΩ cm, which is very high compared to metals, the voltage loss would be approximately

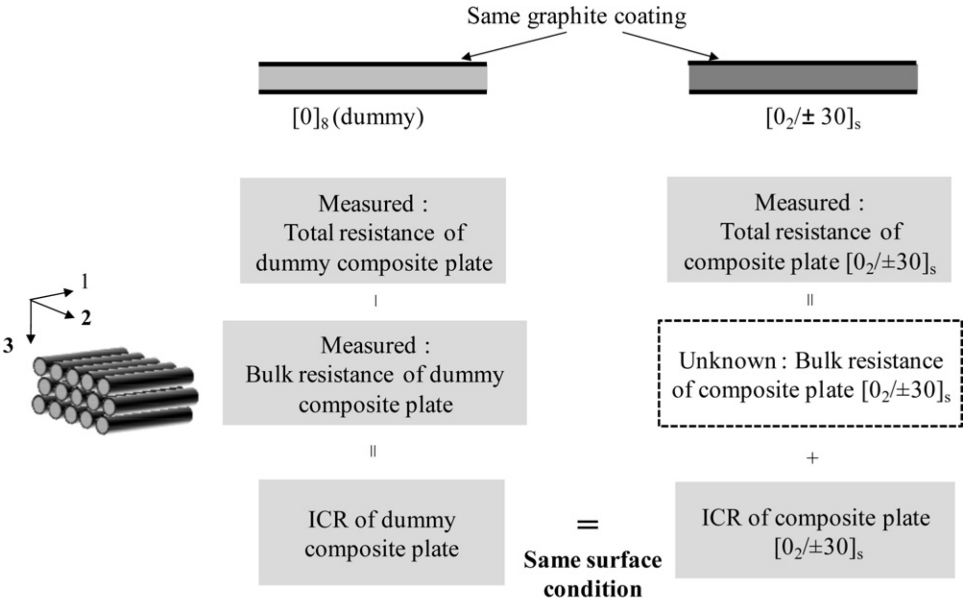

Fig. 10. Two composite specimens with same surface condition using the graphite coating method (ICR: interfacial contact resistance).

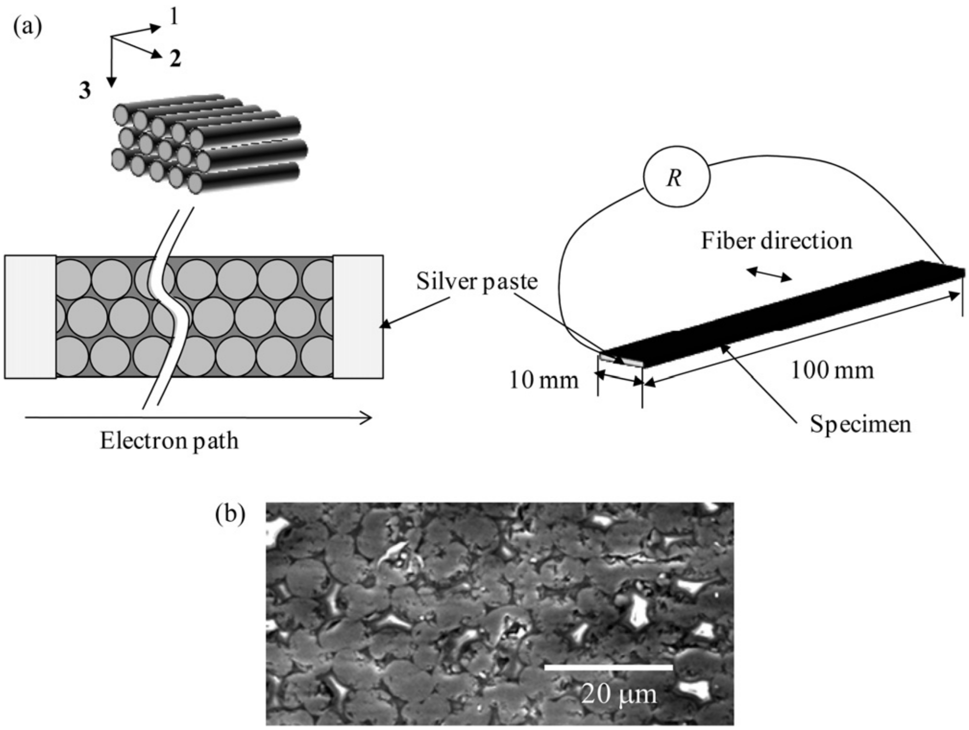

Fig. 11. (a) Schematic drawing to measure the electrical conductivity of the composite specimen ($[0]_n$) in the through-thickness direction; (b) SEM image of the cross section of the composite specimen ($[0]_n$).

2–3 mV at the current density of 1.2 A cm^{-2} because the composite plate is only 0.1–0.2 mm thick. This means that a significant amount of resistance originates from the interfacial contact between the composite plate and the GDL rather than from the bulk resistance. From the experiments, it was found that the composite plate with the coated graphite layer had only 4% of the interfacial contact resistance of the composite plate without treatment.

3.2. Electrical resistances of the prototype carbon/epoxy composite bipolar plate

Images of the cross section and surface condition of the composite bipolar plate coated with the 2-μm-thick graphite layer are showed in Fig. 13. As shown in Fig. 14, the total resistance of the

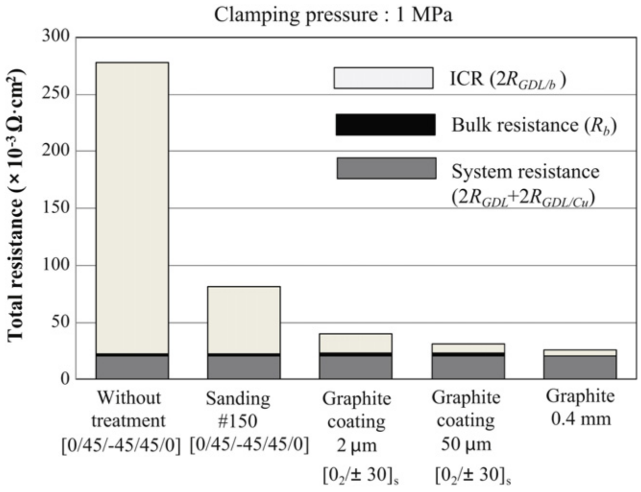

Fig. 12. Total resistances including the system resistance, bulk resistance and interfacial contact resistance with respect to the surface conditions of the composite plate (ICR: interfacial contact resistance).

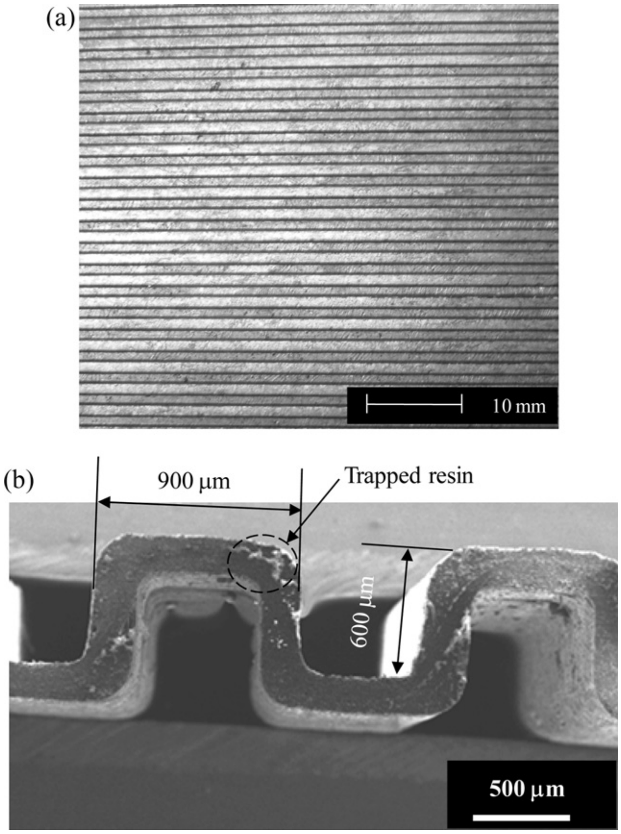

Fig. 13. (a) Surface condition; (b) cross-section of the real size composite bipolar plate coated with the graphite layer of 2 μm.

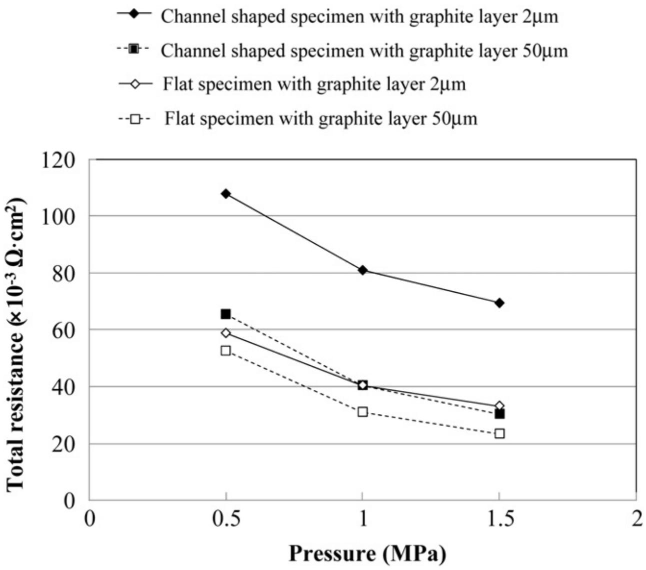

Fig. 14. Total resistances of the flat specimens and the channel-shaped specimens in the through-thickness direction with respect to surface treatments.

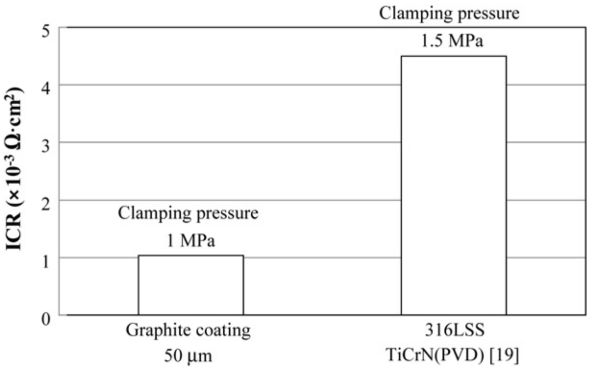

Fig. 15. Comparison of the interfacial contact resistances of the composite plate with a graphite layer of 50 μm and the metallic bipolar plate (ICR: interfacial contact resistance).

channel-shaped composite bipolar plate is higher than that of the flat composite specimen because the clamping pressure, which is defined as the applied load divided by the chemical activation area, is different from the actual pressure applied to the contact area between the composite bipolar plate and the GDL. Another cause for the increased resistance might be the increased bulk resistivity of composite materials due to the insufficient contact of carbon fibers and the resin trapped at the corner part of the channel. In terms of the interfacial contact resistance, however, it is found that the composite bipolar plate with a graphite layer of 50 μm is more efficient than the metallic bipolar plate as shown in Fig. 15 [19] because the interfacial contact resistance is dependent on the kinds of bipolar plate materials used and their hardness.

4. Conclusion

A thin graphite layer of 2, 50 μm is coated on a carbon fiber epoxy composite to decrease the interfacial contact resistance between the GDL and carbon/epoxy composite plate. Stacked prepregs with graphite foils on both sides are hot-rolled at 80 °C under 1 MPa, follow by curing in the mold at 160 °C under 11 MPa.

From the measurement of the total resistances in the through-thickness direction of the carbon/epoxy composite, it is found that the carbon/epoxy composite bipolar plates coated with graphite layers of 2 μm and 50 μm have 14% and 10% of the total electrical resistance of the composite bipolar plate without surface treatment, respectively, under compaction pressure of 1 MPa. It is also determined that the graphite coating on the surfaces of the carbon/epoxy composite yields an interfacial contact resistance similar to that of the single graphite plate. Additionally, using this method, the bulk resistivity of the composite with complex stacking sequences in the through-thickness direction can be estimated, and it is found that the carbon/epoxy composite plate coated with graphite layers of 50 μm has only 4% of the interfacial contact resistance of the conventional carbon/epoxy composite plate.

The prototype composite bipolar plate is manufactured using this graphite coating method, and it is determined that the interfacial contact resistance of the composite bipolar plate coated with a 50-μm graphite layer is smaller than that of the metallic bipolar plate because the interfacial contact resistance is dependent on the kinds of bipolar plate materials used and their hardness. Therefore, it can be concluded that the composite bipolar plate coated with a thin graphite layer would be a suitable alternative to metal bipolar plates.

Acknowledgments

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