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Electromagnetic-carbon surface treatment of composite bipolar plate for high-efficiency polymer electrolyte membrane fuel cells

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ABSTRACT

Polymer electrolyte membrane (PEM) or proton-exchange membrane fuel cell systems are environmentally friendly power sources for many applications. Bipolar plates are essential components of a PEM fuel cell. Recently, composite bipolar plates have received considerable interest due to their superior performance. The most important properties of bipolar plates are electrical resistance and contact resistance, which are largely dependent on the surface morphology of the bipolar plate, because low electrical resistance improves the efficiency of PEM fuel cells. In this study, a selective surface preparation technology is developed using an electromagnetic field and carbon black (electromagnetic-carbon surface treatment). The carbon black is heated by an electromagnetic field on the surface of the bipolar plate with a high rate of temperature rise. The non-electrically conducting surface resin is removed, without damaging the carbon fibre to give a low electrical resistance. It is found that the surface-treated composite bipolar plate has a lower electrical resistance than those of conventional composite bipolar plates, and that the electromagnetic-carbon surface treatment can be applied for production of the composite bipolar plates in a fast and efficient process.

1. Introduction

Polymer electrolyte membrane (PEM) or proton-exchange membrane fuel cell systems are a very promising power source for residential and mobile applications due to their wide operating range, low operating temperature, high efficiency, high power density and long lifetimes [1–3]. In spite of these many advantages, however, commercialization has been delayed due to the high manufacturing cost of bipolar plates. Since the plates make up more than 60% of the stack cost, an efficient manufacturing process needs to be developed [3].

A PEM fuel cell stack is composed of a bipolar plate with flow channels, end plates, a membrane-electrode assembly (MEA) and a gas-diffusion layer (GDL) as shown schematically in Fig. 1 [4,5]. The bipolar plates provide electrical connection between the cells and have many channels for the provision of coolants and reactants to the PEM fuel cell. The functional requirements of the bipolar plate are high mechanical stiffness and strength, low electrical resistance, low density, low thickness, high gas tightness, and chemical stability. For the material of the bipolar plate, graphite is widely used due to its high electrical conductivity. Unfortunately, however, graphite bipolar plates have high void contents and brittle properties, which decrease the gas tightness and increase the production cost and time. Although, stainless steel has been tried as a bipolar material, it has corrosion problems and high contact resistance, so that expensive coating processes are required. A composite bipolar plate composed of carbon fibres and a polymeric matrix has been developed by compression moulding of continuous or chopped carbon fibres [4,5]. Nevertheless, the low electrical conductivity of the composite bipolar plate is a remaining concern to be addressed for its commercialization and mass production. The non-electric conducting polymeric resin on the surface of the composite bipolar plate should be reduced to increase the electrical conductivity. Different surface treatment techniques have been applied to remove the surface resin. Although mechanical surface treatment techniques using sandpaper and sand blasting are efficient and inexpensive, carbon fibre can be damaged by the abrading process, which could degrade the mechanical properties. Chemical surface treatment using acid to remove selectively the surface resin without damage to carbon fibre could possibly be applied, although a long process time is required, and thereby could increase costs. Flame treatment can induce the degradation of the composite material, and its energy efficiency is very low. Therefore, for the surface treatment of composite bipolar plates, a new technique that is fast and has low cost and high energy efficiency has to be developed.

In this study, a method to increase the electrical conductivity of composite bipolar plates composed of continuous carbon fibre

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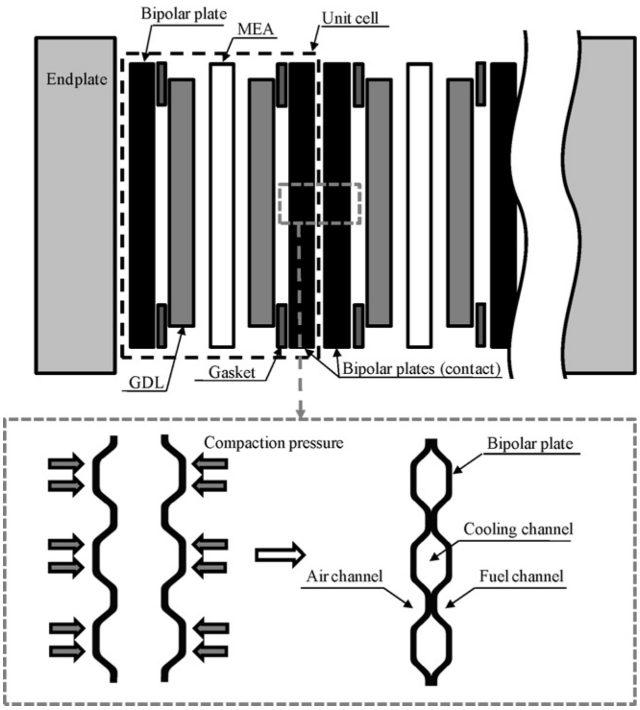


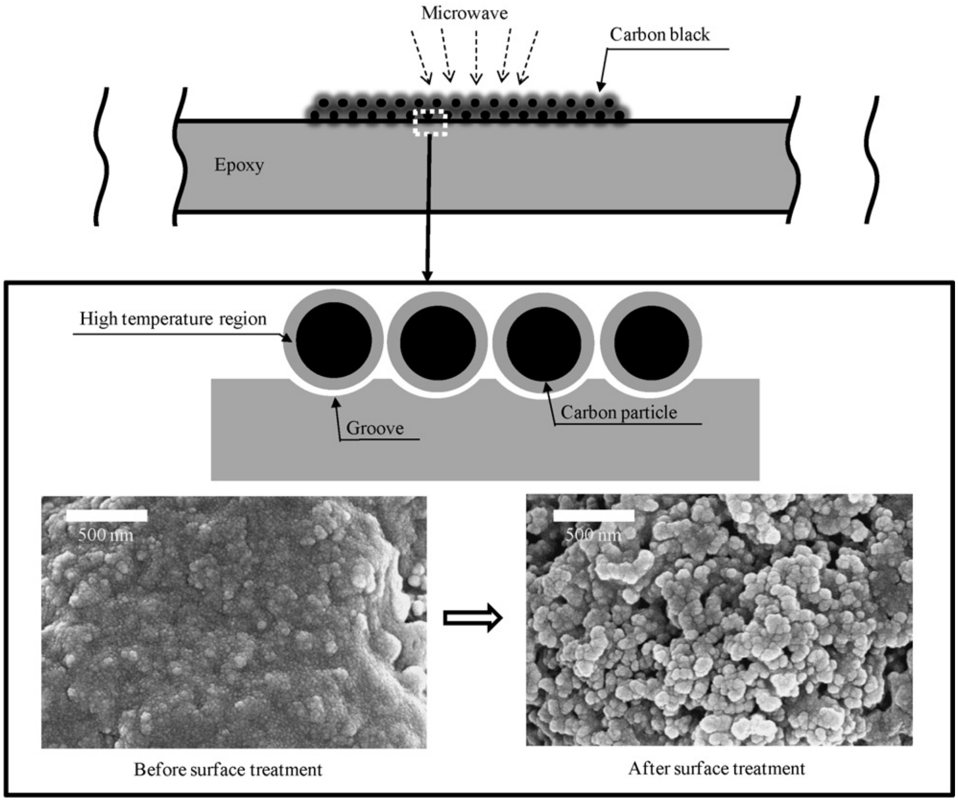
Fig. 1. Schematic drawing of PEM fuel cell.

and an epoxy matrix is investigated to increase the electrical conductivity. For high electrical conductivity of the bipolar plate, the bulk resistance and contact resistance between the bipolar plate and other components have to be reduced; the two parameters are largely dependent on the surface morphology of the bipolar plate. In this study, the non-electrically conducting surface resin is removed by selective surface treatment using an electromagnetic field (microwave) and carbon black.

Activated carbon with a large surface area can be easily heated with an electromagnetic field. Under an electromagnetic field, space charge polarization in a material takes place and thereby makes entire macroscopic regions of the material become either positively or negatively synchronized with the field. This mechanism is often called the Maxwell–Wagner effect [6,7]. The polarization synchronizes its orientation with the field at a low frequency, but as the frequency of the wave increases, there is a phase lag between the polarization and the applied field. This leads to the absorption of energy and Joule heating of the carbon particles [6,7]. In the case of spherical particles such as carbon black distributed throughout a material with non-electrically conducting air entrapped, the heating rate can be estimated by the loss factor ε'' as follows [8],

$$\varepsilon'' = \frac{9v\varepsilon' f_{\max}}{1.5 \times 10^{10}\kappa} \frac{w\tau}{1 + w^2\tau^2} \tag{1}$$

where: v is the volume fraction of conducting material present in the mixture; $f_{\max}$ is the frequency at the maximum loss; ε' is the real part of the dielectric constant of the non-electrically conducting material; κ is the electrical conductivity; w in rad s^{-1} is the frequency; τ is the relaxation time constant. From Eq. (1), the heating rate can be increased at a high frequency in a limited range. One gram of carbon black can be heated to over 300 °C in 3 s using microwaves of 1 kW at 2.45 GHz, as determined from experiments. Although metal powders are electrically conducting materials, they cannot be used under electromagnetic fields due to their high reflectivity [9] and explosiveness. Therefore, in this study, high electrically conducting carbon black (EC-300J, PHC, Korea) is chosen due to its low cost, high melting temperature (3500 °C), and stability in a microwave environment. Carbon black consists of small particles of nanometer size. Each carbon particle



Before surface treatment

After surface treatment

Fig. 2. Electromagnetic-carbon surface treatment of epoxy.

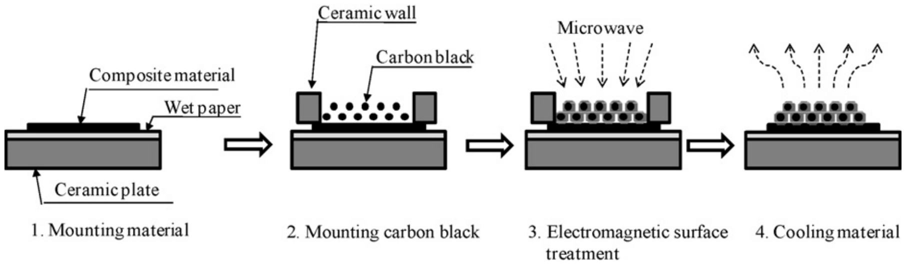


Fig. 3. Schematic drawing of electromagnetic-carbon surface treatment process.

can be heated with an electromagnetic field. Therefore, a high-temperature region is generated around the carbon particles, which generates small grooves on the surface of the material, as shown in Fig. 2. The groove size can be controlled according to the size of the carbon particles and the local heating region. Although the temperature of the carbon black is very high, degradation of the matrix can be avoided due to the low heat capacity of carbon particles and the local heating region around each carbon particle. In this study, carbon black is placed on a composite bipolar plate and heated at a rapid rate by an electromagnetic field for surface treatment. The surface resin is removed after a few seconds without damage to the carbon fibres. The cross-section of the composite bipolar plate is observed using SEM (scanning electron microscopy). The electrical resistance of the composite bipolar plate is measured to investigate the change in electrical conductivity.

2. Experimental

2.1. Effect of electromagnetic-carbon surface treatment

A carbon black layer of 5 mm in height with a bulk density of 200 kg m^{-3} was placed on the surface of cured epoxy (YD-114F, Kukdo chemical, Korea) and heated for 7 s with an electromagnetic field generated by microwave device [10]. The frequency and power of the microwave was 2.45 GHz and 1 kW, respectively. The surface was observed by means of SEM, as shown in Fig. 2. Many grooves of 50 nm width were generated by the electromagnetic-carbon surface treatment. Part of the resin was burned and removed due to the high temperature of the treatment process, and part of the remaining resin was converted into carbon by carbonization. The temperature of the surface was raised above 300 °C in 7 s. The small grooves generated may increase the surface area of the composite due to the low surface resin content. Therefore, electromagnetic-carbon surface treatment can be widely used to generate high electrical conductivity in carbon composites and high bonding strength in composite structures. In this study, electromagnetic-carbon surface treatment is applied to increase the electrical conductivity of a composite bipolar plate.

2.2. Electromagnetic-carbon surface treatment for composite bipolar plate

The electromagnetic-carbon surface treatment process for the composite bipolar plate is shown schematically in Fig. 3. First, the composite bipolar plate was placed on a ceramic plate with wet paper. The ceramic plate was used as a supporting jig for the electromagnetic-carbon surface treatment process. Since the material near the carbon black was heated during the electromagnetic-carbon surface treatment process, the supporting jig was made of a high melting temperature material. The wet paper was used to prevent degradation of the composite material at high temperature. Second, the carbon black was placed on the composite material with a small compressive pressure of 200 kg m^{-3} to make the carbon particles and composite surface contact each other and to control the bulk density of the carbon black. The bulk volume of carbon black can increase at high temperature because the entrapped air between the carbon particles can expand due to heating. Therefore, the carbon black was compressed to expel the entrapped air for stable heating of the carbon black. A ceramic wall was used to maintain the high temperature during the electromagnetic-carbon surface treatment process because the ceramic material has a low thermal conductivity of 0.05 W m^{-1} K^{-1}. Third, the carbon black was heated with microwave irradiation at a frequency of 2.45 GHz and a power of 1.0 kW. The rate of temperature increase was varied in a range of 30–100 °C s^{-1}, and was controlled by the total mass of the carbon black. The surface resin of the composite material could be burned and removed at extremely high temperature, while the carbon fibre was not damaged due to its high melting temperature. Some resin was converted into carbon by carbonization, which increased the electrical conductivity. Although the gap between the carbon fibres of the composite was small, nanosized carbon particles can penetrate into the gap and contact the surface resin. The resin on the lower surface was not damaged due to the thermal protection of the wet paper. Finally, the ceramic wall was removed from the composite surface. The surface of the composite was cooled at a rapid rate of over 20 °C s^{-1} due to the high thermal conductivity of carbon black, which is higher than 100 W m^{-1} K^{-1}. The cooling process was found to prevent degrada-

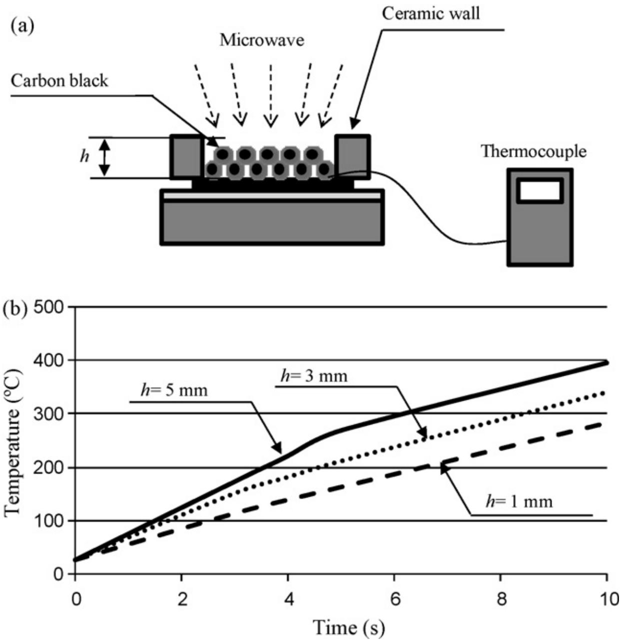


Fig. 4. Experimental method to measure rate of temperature increase: (a) experimental set-up; (b) experimental results.

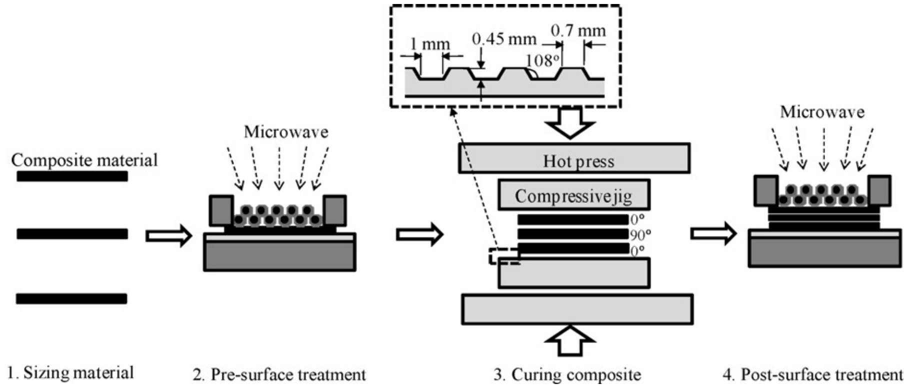


Fig. 5. Schematic drawing of fabricating process.

tion of the composite materials, and this could be used to decrease the manufacturing cost of PEM fuel cells.

The experimental set-up to measure the rate of temperature increase of carbon black on the composite surface is shown in Fig. 4(a). The bulk density of carbon black was 200 kg m^{-3} and the thickness of carbon black layer *h* was varied to control the total mass of carbon black. The carbon black was placed on carbon fibre epoxy prepreg, which was the material of the composite bipolar plate in this study. The temperature at several points was measured using thermocouples. Fig. 4(b) shows the rate of temperature increase on the surface of the composite with respect to time. The rise in temperature is higher than 40 °C s^{-1} when the thickness of the carbon black layer is 5 mm. By contrast, the increase in temperature at the bottom and middle surfaces of the composite layer is lower than 20 °C s^{-1}. Therefore, the thickness of the carbon black layer is found to be 5 mm and the treatment time is set at 5 s for surface treatment without degradation of the composite bipolar plate. The maximum temperature of the composite surface is 280 °C, while the temperature of the middle surface of the composite is lower than 120 °C. The total time for the surface treatment process is 10 s.

2.3. Fabrication of specimens

The process for fabricating the composite bipolar plate by means of electromagnetic-carbon surface treatment is shown in schematically in Fig. 5. Carbon fibre epoxy prepreg (USN 150, SK chemical, Korea) was used with a stacking sequence of [0/90/0] to avoid warping after curing and for retaining the low thickness of the bipolar plate. Before laminating the prepregs, both surfaces of the prepreg plies were treated with the electromagnetic-carbon surface treatment to remove the surface resin. After surface treatment, laminated specimens were placed on a compressive jig with grooves because the bipolar plate requires grooves to channel the

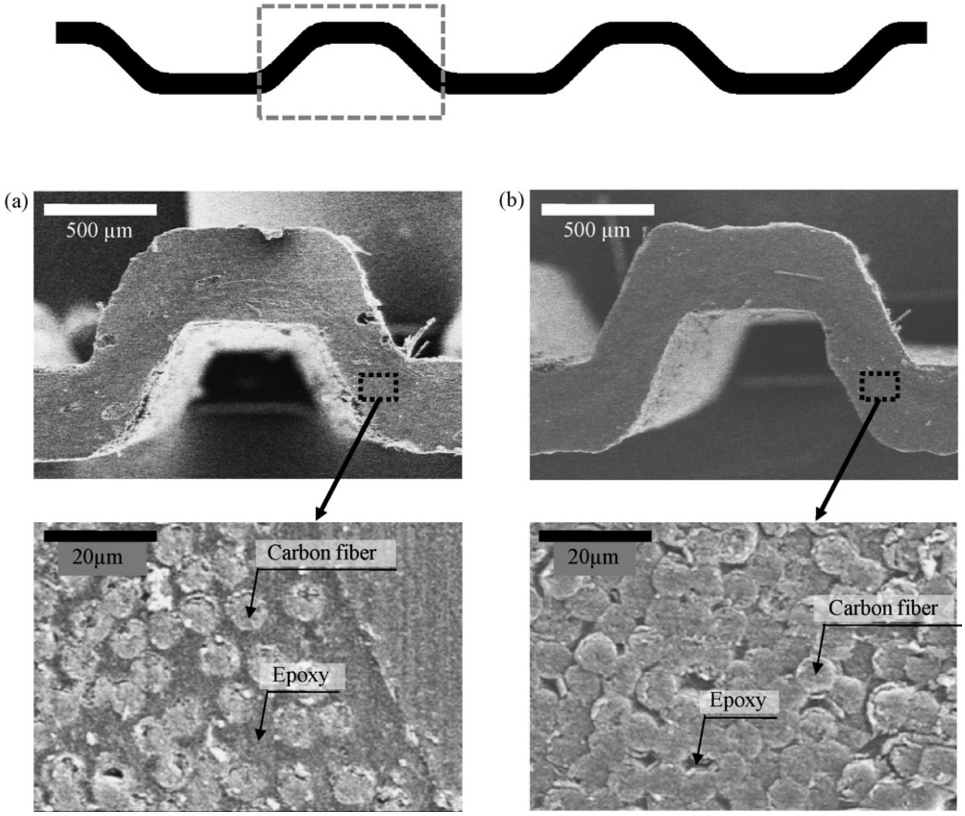


Fig. 6. SEM images of fabricated bipolar plate: (a) without surface pre-treatment; (b) with surface pre-treatment.

coolants and reactants. The specimens were cured in a hot press with a temperature profile of 80 °C for 1 h and then 125 °C for 1 h. The curing pressure was 20 MPa and a mould release was used for an easy de-moulding process. After curing, both surfaces were again subjected to electromagnetic-carbon surface treatment to remove contaminants such as the mould release and moisture. Also, neat specimens without surface treatment were fabricated using the same curing conditions. Fig. 6 shows SEM images of the specimens. The treated specimens have a high fibre volume fraction, while the neat specimens have resin-rich areas, which lower the electrical conductivity. Without the resin-rich areas, carbon fibres can contact carbon fibres of the neighbouring bipolar plate. The large contact area of the carbon fibres can increase the electrical conductivity. The contact area of the carbon fibres increases between the plies of the composite bipolar plate when the electromagnetic-carbon surface treatment process is applied to the bipolar plate. Defects that could lower the mechanical properties and gas tightness are not observed.

3. Results and discussion

The total resistance of the composite bipolar plate was measured to investigate the electrical conductivity. The total resistance is an important property of a PEM fuel cell system because the energy loss is largely dependent on the total resistance. The experimental method to measure the total resistance is shown in Fig. 7 [5,11]. Specimens of 40 mm × 40 mm size are placed between the gas-diffusion layers. Two copper plates are used to connect a power supply and the measurement devices. After compression, the current and voltage are measured with a INSTRON 5566 material test system. The temperature of the specimens is maintained at 25 ± 1 °C.

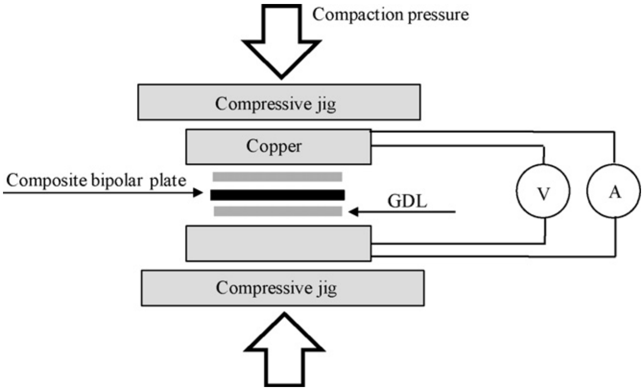


Fig. 7. Experimental method to measure the total resistance.

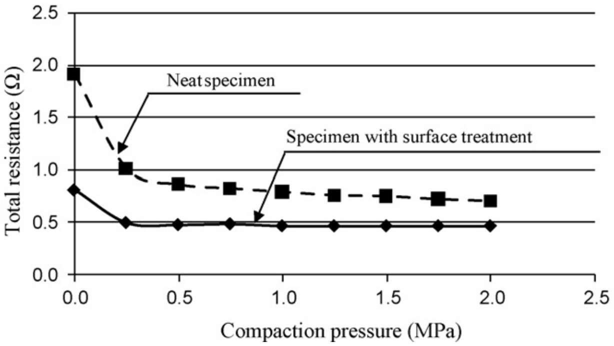


Fig. 8. Total resistance with respect to compaction pressure.

The total resistance of the composite bipolar plate with respect to compaction pressure is shown in Fig. 8. It is found that the total resistance of the surface-treated bipolar plate is 0.45 Ω at 1 MPa, which is 42% lower than that of the neat composite bipolar plate. As shown in Fig. 6, many carbon fibres could contact directly with each other due to removal of the surface resin. Therefore, the fibres could contact directly during the laminating process, as shown in Fig. 9(a). Without surface pre-treatment, the surface resin could be squeezed out between the carbon fibres by compressing the prepreg, as shown in Fig. 9(b). Since the flow of resin in fibre bundles can be assumed to be a flow in a porous medium, it has generally been analyzed based on Darcy's law [12]. Compaction in the cure process simultaneously occurs in the whole composite thickness, and the thickness of the composite is a function of the applied pressure [12]. Therefore, the curing pressure is used to induce resin flow and compact the fibres by deformation, which increases the con-

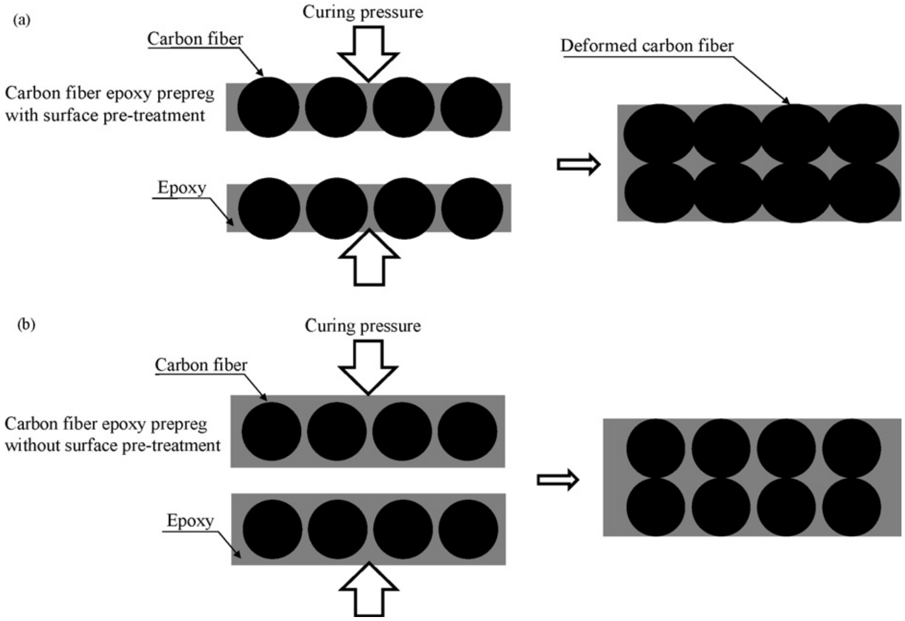


Fig. 9. Fibre deformations with different initial volume fractions: (a) with surface pre-treatment; (b) without surface pre-treatment.

tact area of the carbon fibres, as shown in Fig. 9. The magnitude of stress σ required for fibre deformation can be estimated as follows [12]

$$\sigma = \frac{3\pi E}{\beta^4}\frac{\sqrt{V_f/V_0}-1}{(\sqrt{V_a/V_f}-1)^4} \tag{2}$$

where: V_a is the maximum available fibre volume fraction, V_0 is the initial fibre volume fraction, E is the longitudinal Young's modulus of a fibre and β is the material constant depending on the fibre bundle shape. From Eq. (2), the curing pressure can be solely used to deform the carbon fibres instead of the resin flow when the initial fibre volume fraction is high. From the experiments, it is found that the initial fibre volume fraction of the composite treated with the surface pre-treatment process is increased from 56 to 69%. Additionally, the large fibre deformation can increase the contact area between the carbon fibres, which lowers the electrical resistance of the composite bipolar plate for high efficiency in a PEM fuel cell.

4. Conclusions

An electromagnetic-carbon surface treatment using carbon black with microwave irradiation is developed to increase the electrical conductivity of a composite bipolar plate for fast processing with low cost and high energy efficiency. For the fast and efficient surface treatment process, the Maxwell–Wagner effect is considered by placing carbon black on the surface of the composite material and heating with microwave irradiation at a rate of temperature increase above 40 °C s^{-1}. During the process, the non-electrically conducting surface resin is burned and removed without damage to the carbon fibre. Degradation of the carbon fibre is not observed due to the low heat capacity of carbon black and the local heating region around each carbon particle. The surface and cross-section of the treated composite have been observed by means of SEM. A significant increase in contact area between the carbon fibres is observed, which lowers the electrical resistance of the composite bipolar plate.

The total time for surface treatment is about 10 s. The total resistance of the surface-treated specimen is 42% lower than that of the composite bipolar plate without surface treatment. From experiments, it is found that the developed electromagnetic-carbon surface treatment technique can be used for high-performance composite bipolar plates with low treatment costs. Therefore, a PEM fuel cell of high efficiency can be achieved by the developed surface treatment technique.

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References

[1] A.J. Appleby, Fuel Cells; Trends in Research and Application, Hemisphere Publishing Corp., Washington, DC, 1987.
[2] D. Linden, Handbook of Batteries and Fuel Cells, McGraw-HillNY, New York, 1984.
[3] E.A. Cho, U.S. Jeon, H.Y. Ha, S.A. Hong, I.H. Oh, Journal of Power Sources 125 (2004) 178–182.
[4] Theodore M. Besmann, James W. Klett, John J. Henry Jr., Edgar Lara-Curzio, Journal of the Electrochemical Society 147 (2000) 4083–4086.
[5] I.U. Hwang, H.N. Yu, S.S. Kim, D.G. Lee, J.D. Suh, S.H. Lee, B.K. Ahn, S.H. Kim, T.W. Lim, Journal of Power Sources 184 (2008) 90–94.
[6] P.J.M. Carrott, J.M.V. Nabais, M.M.L. Ribeiro Carrott, J.A. Menendez, Microporous and Mesoporous Materials 47 (2001) 243–252.
[7] Andrzej Zlotorzynski, Critical Reviews in Analytical Chemistry 25 (1995) 43–76.
[8] A.C. Metaxas, R.J. Meredith, Industrial Microwave Heating, Institution of Engineering and Technology, London, 1983.
[9] B.G. Kim, D.G. Lee, Measurement Science and Technology 20 (2009) 065204.
[10] TSE V. Chow Ting Chan, Howard C. Reader, Understanding Microwave Heating Cavities, Artech House, London, 2000.
[11] M.H. Oh, Y.S. Yoon, S.G. Park, Electrochimica Acta 50 (2004) 777–780.
[12] D.G. Lee, N.P. Suh, Axiomatic Design and Fabrication of Composite Structures, Oxford University Press, London, 2006.