

Modification of C/C Composite Bipolar Plate by Addition of Electro-Conductive Carbon Black

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(Received November 23, 2001; accepted December 23, 2001)

Abstract

Modification of C/C composite bipolar plate for improving electrical conductivity was carried out by addition of electro-conductive carbon black (EC-CB). Carbon black was carefully mixed to methanol-containing phenolic resin, impregnated into 2D-carbon fabrics, hot pressed and then carbonized to obtain composite plate. Inclusion of electro-conductive carbon black enhanced the electrical conductivity of the C/C composites by increasing the conduction path. Addition of 10 vol% carbon black increased the electrical conductivity from 5.5/ Ω cm to 32/ Ω cm and reduced the crack formation by filling effect, resulting in the increase of flexural properties of composite plate. However, at carbon black content over 10 vol%, flexural properties decreased by delaminating role of excess carbon black at the interface in C/C composites.

Keywords : Carbon/carbon composite, Impregnation, Electrical and mechanical property

1. Introduction

Fuel cells constitute at present one of the most promising sources of energy for the future [1]. In the existing polymer fuel batteries, one of the structural elements requiring improvement is the so-called bipolar plate, which is the connecting device between the single cell units, conventionally made of graphite [2]. The bipolar plate is a multi-functional component within a solid polymer fuel cell (SPFC) prismatic stack [3]. Its primary function is to supply reactant gases to the gas diffusion electrodes *via* a flow field in the surface. It must also provide series of electrical connection between the individual cells, and effectively remove product water. To satisfy these requirements, the base materials for bipolar plates require certain properties. The majority of SPFC stack producers utilize bipolar plates based on graphite, carbon composites or metals. Each of these materials has characteristics that are beneficial for fuel cell applications, but are limited by others. An ideal bipolar plate would incorporate the merits of these materials, such that it would be high in electrical conductivity and corrosion protection, of low density but with high mechanical strength, impermeable to reactant gases, chemically inert, and allow for ease of manufacture [4].

Carbon fiber reinforced carbon (C/C) composites are receiving interest and are considered as the most important candidate for bipolar plate, because of the high ratio of strength-to-density and the excellent corrosion resistance as well as the high electrical conductivity [5]. Its electrical con-

ductivity, however, is inherently insufficient to apply it to a bipolar plate. In this study, thus, to enhance the electrical conductivity of C/C composite bipolar plate, modification of the plate was carried out via addition of electro-conductive carbon black which also can play a role to prevent the crack-growth of the composite [6].

2. Experimental

PAN-based 2/2 twill-weave carbon fabric (Toray Co. Ltd., $\rho = 1.76$ g/cm³) and resol type phenol-formaldehyde resin (KRD-HM2, Kolon Chemical Co., phenol resin (60 wt%) dissolved in methanol (40 wt%)) were used for preparation of C/C composite bipolar plate. Electro-conductive carbon black (EC-CB, HIBLACK 41, Korea Carbon Black Co., average particle diameter = 19 nm, apparent density = 0.17 g/cm³, specific surface area = 153 m²/g) was used for enhancing the electrical conductivity of C/C composite bipolar plate.

Fig. 1 shows the schematic diagram of bipolar plate manufacturing process. Carbon black (EC-CB) was mixed to phenol resin with methanol to control the EC-CB content and the matrix fluidity. Carbon fabrics were impregnated with EC-CB containing phenol resin to prepare prepreps. Ten prepreps were laminated in a hot press mold (250 × 250 × 5 mm) followed by pressing the prepreps at 120°C, 500psia for 1 h. Prepreps were pressed again at 160°C, 1000 psia for 2 h and at 180°C for 2 h to get a green body [7]. Excess of

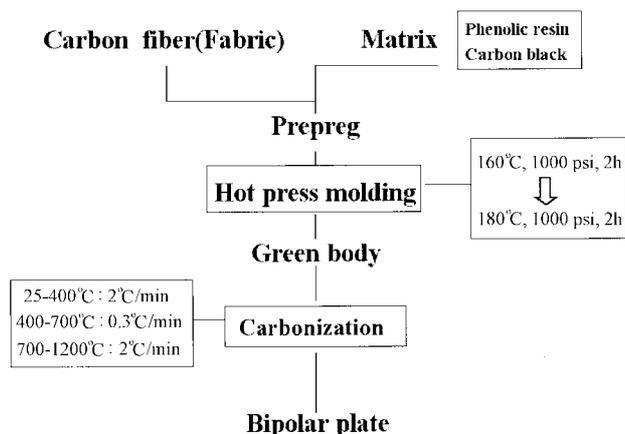


Fig. 1. Fabrication process of the C/C composite bipolar plate.

matrix was flowed out from the green body in this molding process. Green bodies were carbonized in nitrogen atmosphere as following steps; i) heating up to 400°C with 2°C/min. under 1000 psia pressure, ii) reducing the heating rate to 0.3°C/min. from 400°C to 700°C in order to reduce possible thermal shock, iii) holding at 700°C for 2 h to remove volatile materials and pressing again with 1000 psia, iv) heating up to 1200°C with 2°C/min. and holding at that temperature for 6 h to get the C/C bipolar plate.

Thermogravimetric analysis (TGA) of phenol resin (KRD-HM2) in nitrogen was performed to investigate the thermal decomposition of resin with Perkin-Elmer TGA-7. Carbon yield is defined by the weight ratio of the carbonized plate to the green body, and can be calculated by weighing the green body and carbonized plate. Carbon yield per unit volume is defined as the bulk density ratio before and after carbonization. The open porosity was calculated by measuring the weight and density of the C/C plate. Flexural strength and modulus were determined by three point bending test (ASTM D 790M), while interlaminar shear strength (ILSS) was tested by short beam shear method (ASTM D 2344). The electrical conductivity of C/C plate was determined using a four point probe technique introduced by Chandrasekhar [8]. Measurements were carried out with a DC current source (Yokogawa model 2553 CV Standard) and a voltmeter (Fluke 45 Multimeter). The conductivity is given by:

$$\sigma = [I/E] \times [S / (t w)]$$

where I , E , S , t and w are the applied current, measured voltage, probe spacing, sample thickness and sample width, respectively. Morphology of fracture surface of C/C plate was observed by SEM (JEOL, JSM-840A).

3. Results and Discussion

In Fig. 2, TGA curve of phenol resin (KRD-HM2) shows

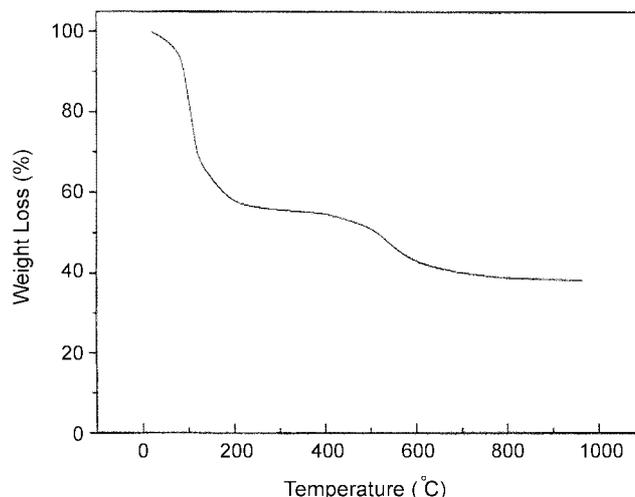


Fig. 2. TGA thermogram of the phenol resin in nitrogen atmosphere.

two step weight loss. One is showing the evaporation of methanol between 80 and 180°C, the other step shows the conversion of phenol resin to carbon between 350 and 600°C by producing CO_2 and CO . This means the phenol resin in green body decomposed into gases around 350°C. Kuwamura and Jenkins [9] reported a significant weight loss took place between 300 and 400°C, and critical temperature for the conversion of phenol-hexamine resin into carbon was 350°C. Fitzer *et al.* [10] reported that surface oxide of carbon fiber decomposed to evolve CO_2 between 300 and 600°C and CO , which started at 600°C.

Fig. 3 shows carbon yields and carbon yields per unit volume with respect to EC-CB content in the carbonized plates. Up to 10 vol% of EC-CB content, it is natural that the carbon yields of carbon plate increase with the addition of

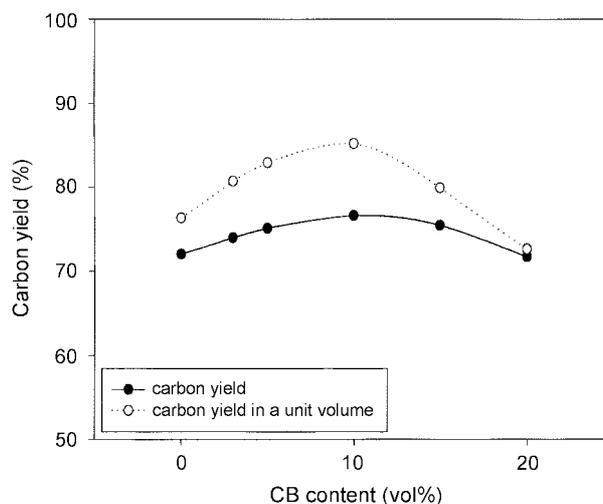


Fig. 3. Carbon yield and carbon yield per unit volume of C/C plate with respect to EC-CB content.

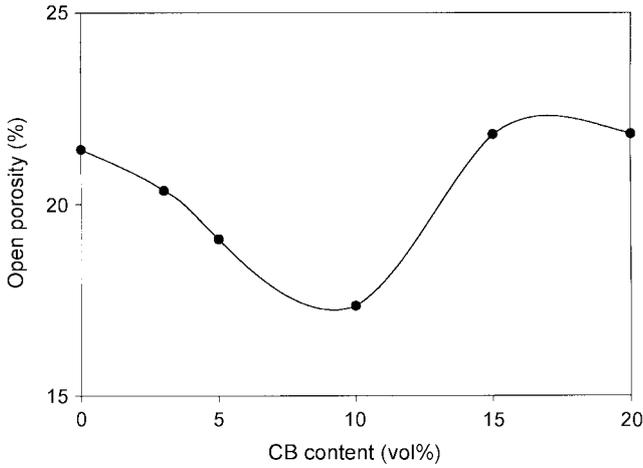


Fig. 4. Open porosity of C/C plates with respect to EC-CB content.

thermo-stable carbon. The carbon yield per unit volume was larger than yield because of higher density. On the contrary, over 10 vol% of EC-CB content, both yields were reduced by the increased volume of C/C plate due to the delamination effect by excess EC-CB on the interface.

Fig. 4 shows the open porosity of the C/C composite related to the porous structure of the C/C plate. By addition of 10 vol% of EC-CB, the open porosity of C/C plate reaches the lowest value of 17.90%, while the bulk density shows the highest value of 1.42 g/cm³ at that point. Thus, we regarded the addition of 10 vol% of EC-CB as the optimum condition for the C/C composite due to the good filling effect.

Electrical conductivities of green body and carbon plate with respect to EC-CB content were shown in Fig. 5. Green body shows poor electrical conductivity in spite of EC-CB addition. Electrical conductivity of green body increased by

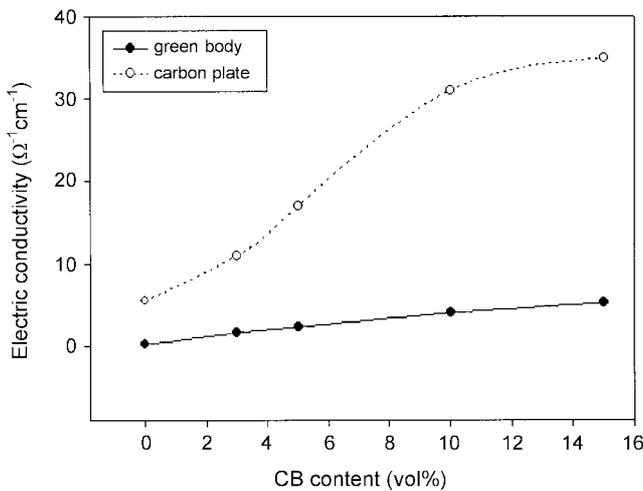


Fig. 5. Electrical conductivities of C/C plates with respect to EC-CB content.

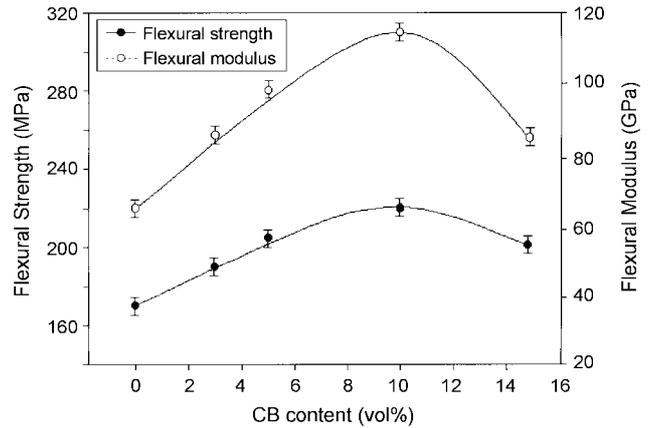


Fig. 6. Flexural strength and modulus of C/C plate with respect to EC-CB content.

carbonization. The electrical conductivity of carbon plate without EC-CB was around 5.5/Ωcm, while that of C/C plate increased with the increase of EC-CB content, and reached up to 35.7/Ωcm at the highest (15 wt%) EC-CB content. Enhancement of electrical conductivity is resulted from the increase of conduction path in the C/C plate by the inclusion of EC-CB [11-14].

Flexural strength and modulus of carbon plate with different EC-CB content were shown in Fig. 6. Flexural strength and modulus of plate without EC-CB were about 170 MPa and 67 GPa, respectively. These increased with the increase of EC-CB content and showed the maximum values of 220 Mpa and 117 GPa at 10 vol% EC-CB content. This is originated from the decrease of porosity in C/C plate. However, flexural strength and modulus decreased with EC-CB content over 10 vol% due to the delaminating role of excess EC-CB at interface between fibers and matrix.

Fig. 7 shows the interlaminar shear strength (ILSS) of C/C plate with different EC-CB content. The ILSS has a maxi-

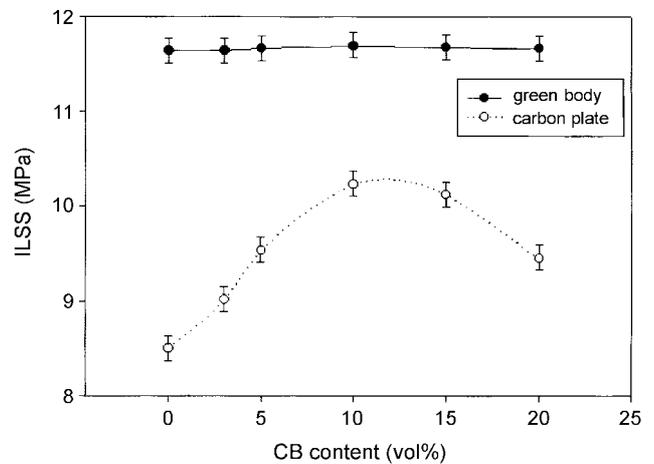


Fig. 7. Interlaminar shear strength (ILSS) of C/C plate with respect to EC- CB content.

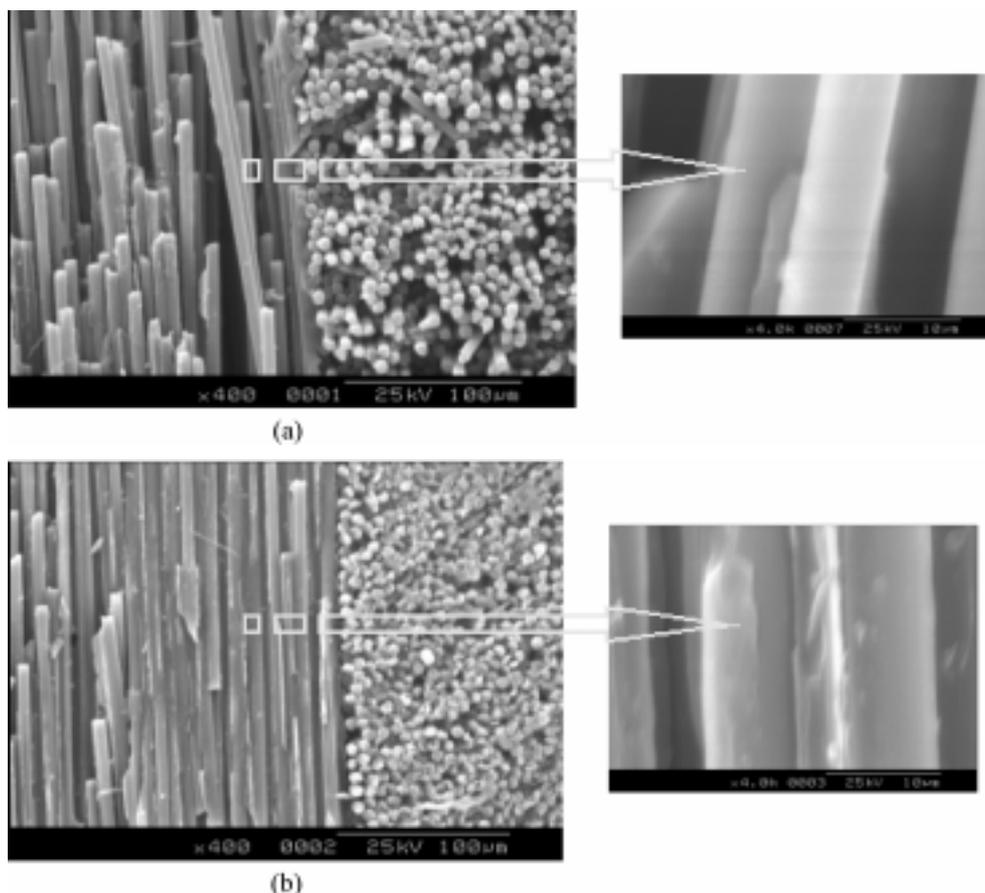


Fig. 8. SEM microphotographs of the cross-sectional view of C/C plate without EC-CB(a) and with 10 vol% EC-CB(b).

imum value at 10 vol% of EC-CB content similar to the flexural properties. Therefore, we considered that the mechanical properties of C/C plate depend upon the EC-CB content and the reinforcing filler effect of EC-CB in the C/C plate is optimal at 10 vol%. On the other hand, excess content of EC-CB over 10 vol% causes poor interfacial adhesion and high porosity (as shown in Fig. 4) and, thus, induces low ILSS value of C/C plate. The ILSS of green body was higher than C/C plate because of good adhesion force of matrix.

Fig. 8 shows the cross-sectional view of C/C plate without EC-CB(a) and with EC-CB(b). There were lots of cracks and pores and relatively smooth fiber surface in C/C plate(a). While, as shown in Fig. 6(b), the smaller amount of pores and some traces of CB on the carbon fiber appeared with almost crack-free feature. This explains the high flexural properties and high density of the EC-CB containing C/C plate up to 10 vol%.

4. Conclusions

Modification of C/C bipolar plate for improving the electric conductivity was carried out by addition of electro-con-

ductive CB. Inclusion of EC-CB enhanced the electrical conductivity of the C/C composites largely by increasing the conduction path and also improved its flexural properties to some extent. In EC-CB containing C/C composite, crack formation was reduced by the filling effect of CB. At 10 vol% of EC-CB content, C/C composite showed the maximum flexural properties as well as the high electrical conductivity ($32/\Omega\text{cm}$). However, at EC-CB content over 10 vol%, flexural properties were reduced by the delaminating role of excess EC-CB at interface in C/C composite. As a consequence, we can obtain a C/C composite plate with the improved conductivity and flexural properties by addition of proper content (10 vol%) of EC-CB compared to the conventional C/C composites.

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