



Effect of graphite sizes and carbon nanotubes content on flowability of bulk-molding compound and formability of the composite bipolar plate for fuel cell

Min-Chien Hsiao^a, Shu-Hang Liao^a, Ming-Yu Yen^a, Ay Su^b, I-Ting Wu^c, Min-Hsuan Hsiao^a, Shuo-Jen Lee^b, Chih-Chun Teng^a, Chen-Chi M. Ma^{a,*}

^a Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30013, Taiwan, ROC

^b Fuel Cell Center, Yuan Ze University, Tao-Yuan 32003, Taiwan, ROC

^c EN-LIANG ENTERPRISE Co., Ltd, Hsin-Chu 30352, Taiwan, ROC

ARTICLE INFO

Article history:

Received 11 February 2010

Received in revised form 22 March 2010

Accepted 23 March 2010

Available online 27 March 2010

Keywords:

Fuel cell

Composite bipolar plate

Polymer composite

Carbon nanotube

Flowability

ABSTRACT

This study investigates the flowability of the bulk-molding compound (BMC) on composite bipolar plates containing graphite content from 70 to 80 wt% with different graphite sizes. A small quantity (from 0.25 to 2 wt%) of multi-walled carbon nanotubes (MWCNT) is also added. Findings show that the flowability of BMC material decreases with decreasing graphite size and with increasing graphite content. The BMC material containing large size graphite (177–125 μm) entirely exhibits a relatively higher flowability within the analysis graphite contents, in the range of 73.3–11.3 cm, compared to the small size (74–45 μm), in which flowability is in the range of 40.3–6.67 cm. Further adding MWCNT causes decreased flowability of the BMC material especially when the percolated networking structure is formed through the resin. Therefore, with flowability below 10 cm, the formability of a large area (300 mm \times 300 mm \times 3 mm) or thin (100 mm \times 100 mm \times 0.5 mm) composite bipolar plate shows a large area of surface porosity or visible defects. Results indicate that the flowability of the thermoset-based BMC material is an important design parameter to fabricate cost-effective, large, or thin composite bipolar plates.

Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.

1. Introduction

The proton exchange electrolyte membrane fuel cell (PEMFC) exhibits the most promising alternative source of energy for a variety of portable electronic devices, stationary and vehicle applications [1–3] due to its attractive features such as high power density, relatively low operation temperature, convenient fuel supply, long life time, etc. [4,5]. To generate useful currents and voltages, individual single fuel cells are connected in series to assemble cell stacks. Thus, as one of the significant components of a PEMFC stack, bipolar plates account for about 80% of total weight [6] and for as much as 60% of stack cost for graphite plates with machined flow channels [7]. Hence, widespread commercialization and popularization of PEMFC, cost and weight reduction of bipolar plates, are major issues. Composite bipolar plates are the promising alternative materials due to their low cost, easy direct molding flow channels on the plate during processing, good corrosion resistance

and low weight [8–11]. Therefore, researches have extensively developed graphite-based composite bipolar plates [1,3,8–11]. Cost models estimate that, with composites, the cost of bipolar plates would be only 15–29% of the stack cost [12]. High graphite loading (>60 wt%) is needed to provide the required electrical conductivity [1,3,8–11,13]. However, high filler loading may cause a substantial reduction in strength and ductility of the composite bipolar plate. Therefore, researches have selected different reinforcements including carbon fiber (CF) [14,15], carbon black (CB) [16–18], and carbon nanotube (CNT) [1,3,11,19,20], to prepare reinforced composite bipolar plates to meet the optimum design for composite bipolar plates. Among these reinforcements, CNTs exhibit the suitable nano-materials to fabricate high performance nanocomposite bipolar plates [1,3,8–11] due to their extraordinary intrinsic properties [21] and relatively low quantity of loading for the same reinforcing effect [13].

Hot-compression molding is the most common mass production technology of composite bipolar plates with thermoset resin as a polymer matrix [1,8–11], resulting in cost-effective composite bipolar plates. However, to obtain enough electrical conductivity, fabricating an integrated large area or thin plates associated with high stack power densities [2,22,23] is predictably difficult due to

* Corresponding author. Tel.: +886 3571 3058; fax: +886 3571 5408.

E-mail addresses: ccma@che.nthu.edu.tw, d9532814@oz.nthu.edu.tw, g9732517@oz.nthu.edu.tw (C.-C.M. Ma).

Table 1
Formulation of BMC process.

Components	Composition	
	Resin composition	BMC composition (wt%)
Vinyl ester (wt%)	75	30–20
Low profile agent (wt%)	8	
Styrene monomer (wt%)	17	
TBPB (phr ^a)	1.8	
Zinc Stearate (phr ^a)	3.5	
Magnesium Oxide (phr ^a)	1.8	
MWCNTs (wt%)	0–2	
Graphite Powder (wt%)		70–80
Total		100

^a phr: parts per hundred parts of resin, based on the amount of vinyl ester, low profile agent and styrene monomer.

the high viscosity of materials. In addition, to satisfy the formability of a large area or thin composite bipolar plate, it would be difficult to maintain the electrical conductivity of plates. Some literatures have recently compared the effect of graphite size [8,15] and filler [14] on composite bipolar plate properties. However, the relationship between the flowability of bulk-molding compound (BMC) materials and the formability of a produced large area or thin composite bipolar plates has not been reported yet.

To achieve cost/performance and weight reduction of proton exchange membrane fuel cells (PEMFCs) in the stack, fabricating large size or thin composite bipolar plates is a key technology. This study investigates the flowability effect of vinyl ester-based/graphite BMC material with different graphite contents, graphite particle sizes and the MWCNT contents on the formability of the composite bipolar plate.

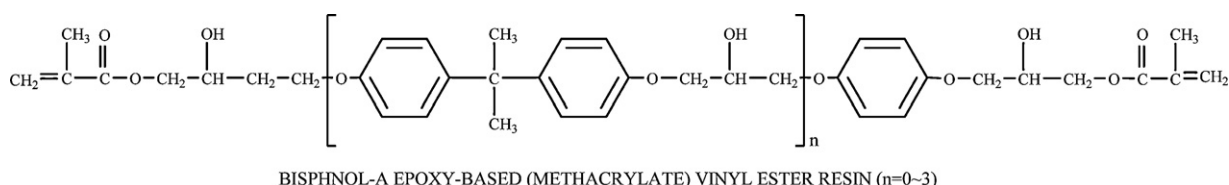
2. Experimental

2.1. Materials

Graphite powder was obtained from the Great Carbon Co. Ltd., Taiwan. The density of the graphite powder was 1.88 g cm^{-3} and the particle size was less than $1000 \mu\text{m}$. Various sizes of graphite particle (177–125, 125–105, 105–74, and 74–45 μm) were also prepared by the screen mesh method. The bisphenol-A epoxy-based vinyl ester (VE), was provided by the Swancor Co., Taiwan. Scheme 1 shows the chemical structure of the bisphenol-A vinyl ester. MWCNTs (trade name: C_{tube} 100) with a purity of 95% and a surface area of $150\text{--}250 \text{ m}^2 \text{ g}^{-1}$ were obtained from the CNT Co., Ltd., Korea. The diameters of MWCNTs are 10–50 nm and the lengths are 1–25 μm .

2.2. Preparation of bulk-molding compound (BMC) material with various graphite sizes and different MWCNTs

The BMC material was prepared by mixing the vinyl ester (VE) mixtures, low profile agent (Polystyrene/Styrene monomer (PS/SM) series), styrene monomer, thickening agent (MgO), release agent (Zinc Stearate, ZnSt), initiator (t-butyl peroxybenzoate, TBPB) and with various graphite sizes, respectively, in a kneader for 30 min. After thickening for 36 h, the BMC was compression molded for 5 min at 150°C .



Scheme 1. Chemical structure of bisphenol-A vinyl ester.

MWCNT with various weight percentages of 0.25, 0.5, 1, and 2 of were added into VE and mixture, and BMC material was prepared by the same way as mentioned above. The BMC formulation is summarized in Table 1.

2.3. Characterization of the flowability

The flowability was determined by means of injection molding of the constant weight of BMC material injected into a spiral channel mold with scale (the spiral channel contains a slightly sunken lines for every one cm), and the channel radius is 1.6 mm. The injection gun is installed attaching to the top of hot-compression molding mechanism. This measurement was preceded as following: (1) the applied mold pressure was kept at 2100 psi, and 150°C , which is the same as the hot pressing temperature of composite bipolar plate; (2) BMC material (35 g) was injected into the mold by the pressure of 1400 psi for 30 s; (3) the injected material was kept at 150°C for 2 min. Fig. 1 shows the schematic of the flowability measurement setup, and the actually forming shape is shown in the inserted photograph.

3. Results and discussion

3.1. The effect of graphite size on the flowability of BMC material

During the processing of thermoset-based composite bipolar plates, the BMC material undergoes A, B, and C stages, respectively, depending on the degree of cross-linking. The A-stage is the initial stage of chemical cross-linking with continuous flow of the resin by an initial decreasing viscosity; the B-stage is the intermediate stage with a progressive increase viscosity; and the C-stage is the final stage of curing with removing the resin by forming a high cross-linking 3D structure. Based on this concept, the initial viscosity decreasing stage (A-stage) mainly determines the flowability of BMC material in the mold. Fig. 2 plots the flowability of BMC material as a function of different graphite contents and various sizes of graphite. For four sizes of a graphite particle system, the

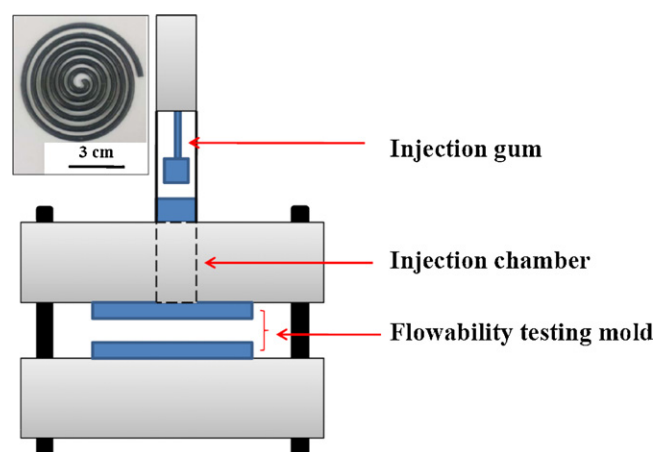


Fig. 1. The flowability measurement setup.

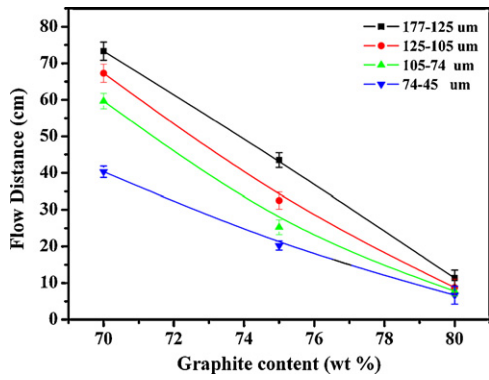


Fig. 2. The flowability of BMC material with different graphite particle sizes and various graphite content.

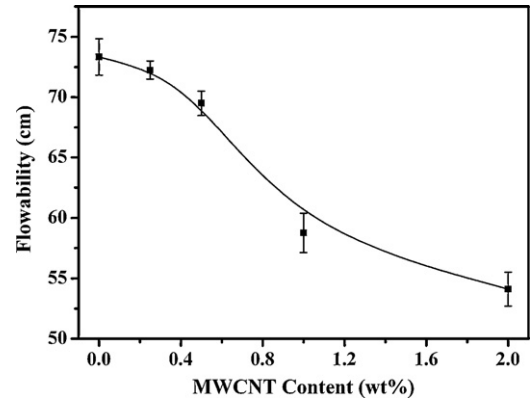


Fig. 4. The flowability of BMC material with 70 wt% of 177–125 μm of graphite particle as a function of MWCNT content.

flowability trend is almost linear and decreases continuously with increasing graphite content. The flowability increases in the order of 74–45 μm < 105–74 μm < 125–105 μm < 177–125 μm.

As previously mentioned, the viscosity of BMC material at the initial stage decreases on account of decreasing resin viscosity. As shown in Fig. 3(a), at low graphite content (the light parts), the BMC materials contain higher resin content, and thus each graphite particle can be well wetted by the resin (the dark parts), leading increased distance between the graphite particles compared to the high graphite content of BMC materials (Fig. 3(b)). Consequently, resin viscosity reduces at the A-stage, and serves as a “lubricant” to decrease friction among graphite particles, consequently affecting the flow distance. However as graphite content increases, the flowability of BMC material is hindered by the resin surrounding graphite particle reduction, as shown in Fig. 3(b).

The following explains the effect of graphite particle size on flowability. As shown in Fig. 3(a) and (c), when graphite particle size is large with 70 wt% graphite content, the BMC material contains a low amount of graphite particle per volume, thus the resin drives the graphite particle to flow more easily. However, with increasing graphite content up to 80 wt%, the volume of particle–particle holes of graphite particles dramatically decreases, as shown in Fig. 3(b) and (d). As a result, the resin distribution discontinues due to more compact contact with each graphite particle, especially for the case of small graphite particle size (74–45 μm). The smaller the graphite particle size, the more compact graphite particle accumulation is. Therefore, the resin surrounding graphite particles cannot penetrate easily; hence, the BMC material becomes too sticky to flow smoothly.

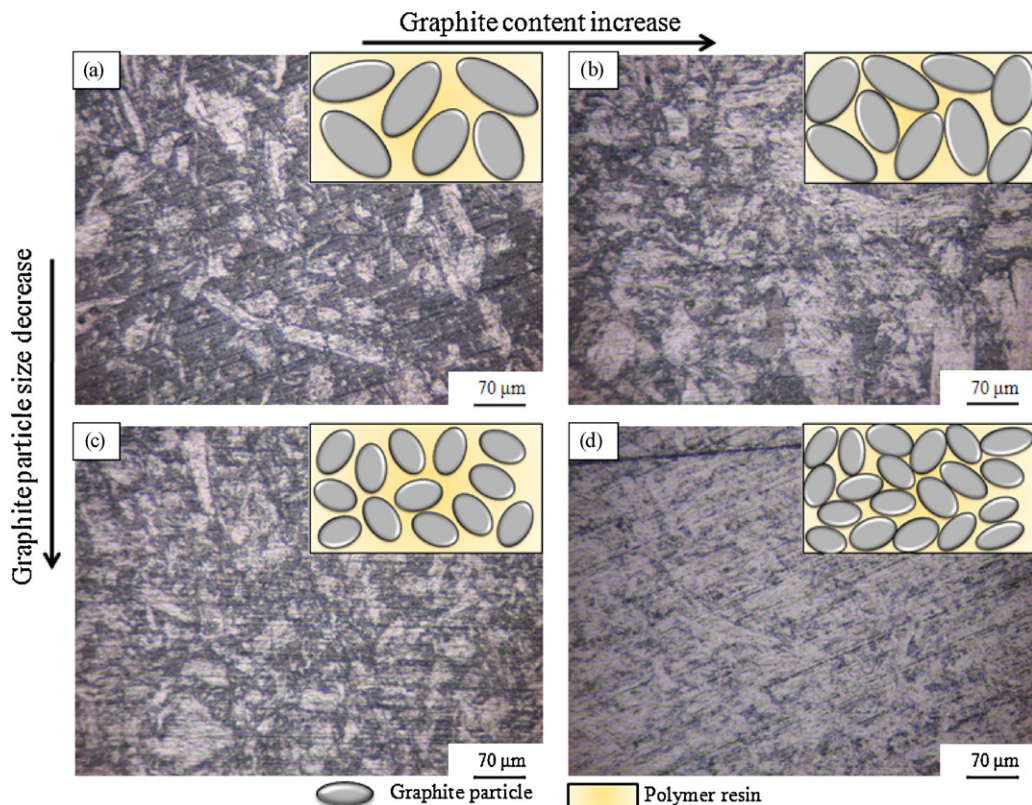


Fig. 3. Optical microphotographs of composite bipolar plate with different graphite sizes/contents (a) 70 wt% of 177–125 μm, (b) 80 wt% of 177–125 μm, (c) 70 wt% of 74–45 μm and (d) 80 wt% of 74–45 μm.

Table 2
The integrity of composite bipolar plates in a variety of dimension sizes.

Graphite size (μm)	Graphite content (wt%)	Composite bipolar plates of different size (mm \times mm \times mm)				
		300 \times 300 \times 3	200 \times 200 \times 3	100 \times 100 \times 3	100 \times 100 \times 1.5	100 \times 100 \times 0.5
177–125	70	○	○	○	○	○
	75	○	○	○	○	○
	80	×	△	○	○	△
125–105	70	○	○	○	○	○
	75	△	○	○	○	○
	80	×	△	○	○	△
105–74	70	△	○	○	○	○
	75	×	△	○	○	○
	80	×	△	○	○	△
74–44	70	×	○	○	○	○
	75	×	△	○	○	△
	80	×	△	○	△	×

○: No imperfections can be observed.

△: Slight imperfections can be observed.

×: Large imperfection area, or the failure of formation.

3.2. The effect of MWCNT on the flowability of BMC material

High performance composite bipolar plates should possess high electrical conductivity, excellent mechanical properties, thermal stability, etc. Owing to the compromise among electrical con-

ductivity, with high loading of graphite fillers, and mechanical strength, with low loading of graphite fillers, reinforcement must be added. Recently, CNT seems a promising nano-reinforcement [1,3,11,19] compared to zero-dimension carbon black (CB) and micrometer-scale carbon fiber (CF), due to its intrinsic high aspect

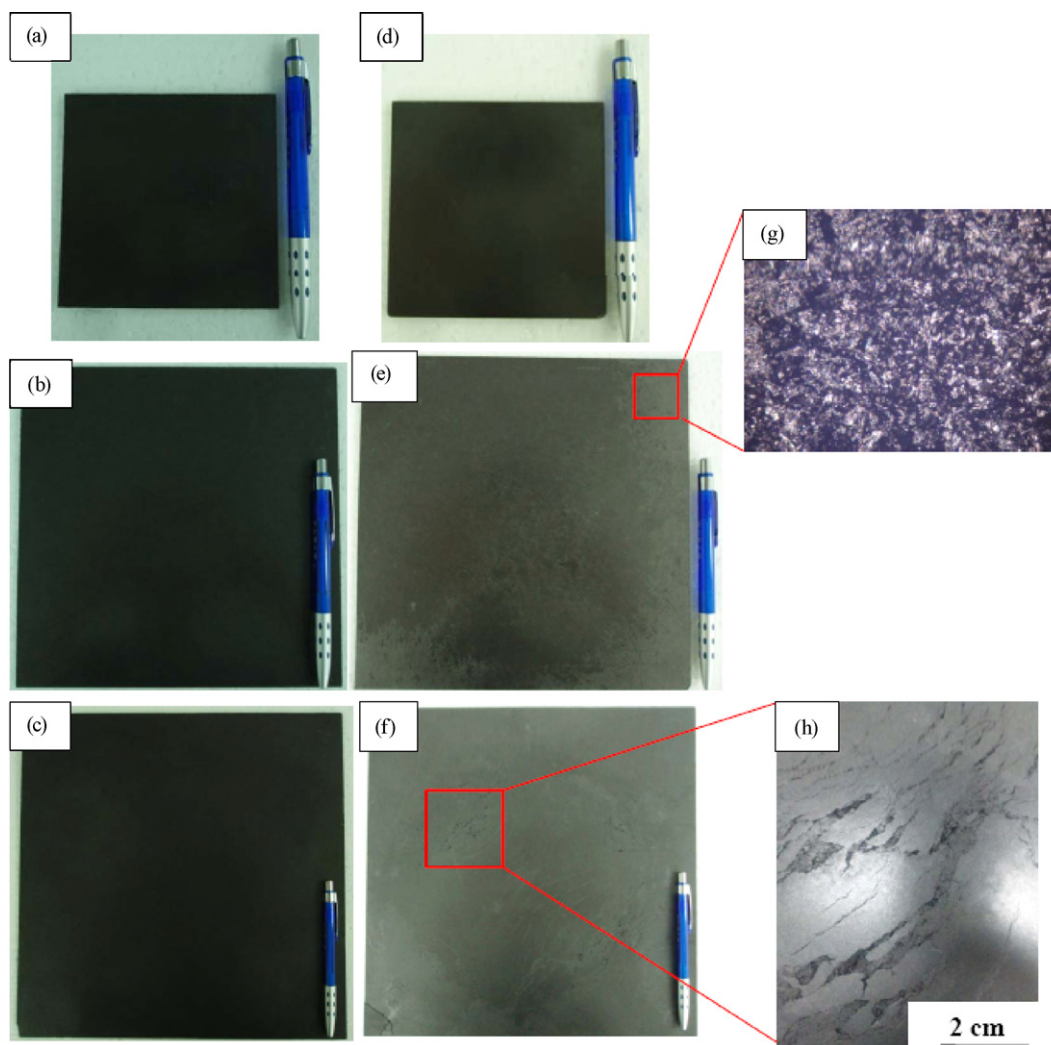


Fig. 5. Composite bipolar plates with different dimension sizes from left to right are 300 mm \times 300 mm \times 3 mm, 200 mm \times 200 mm \times 3 mm, and 100 mm \times 100 mm \times 3 mm. (a)–(c) are 70 wt% of 177–125 μm , (d)–(f) are 80 wt% of 74–45 μm , (g) optical microscopic image of porous area of (e), and (h) image of unfilled area of (f).

ratio, high flexibility, low mass density, and other unusual properties.

Before the BMC process, the resin has been first incorporated with CNT by high shear mixing to break CNT aggregations to gain a more homogeneous dispersion in polymer resin. However, several researches [24–26] have found that the rheological properties of CNT-based nanocomposite are affected by CNT dispersion throughout the resin. Adding CNT increases resin viscosity with increasing CNT content. Fig. 4 illustrates the flowability of BMC material with 70 wt% of 177–125 μm graphite particle as a function of MWCNT content. The figure shows that flowability of BMC material decreases from 77.0 to 54.1 cm with increasing MWCNT content. Below 0.5 wt% MWCNT content the decrease of BMC flowability material is not as significant as that of high MWCNT content. This implies that a percolation threshold may occur when the loading of MWCNTs is higher than 0.5 wt%. In our previous studies [1,10], electrical conductivity and flexural strength of the MWCNT/vinyl ester nanocomposite bipolar plate significantly increased in the range of 0.25–1 wt% content of MWCNT, due to the formation of interconnected continuous percolated MWCNT–MWCNT networking structures within the polymer resin [24,27]. The addition of MWCNT above percolation value was necessary to provide considerable property enhancement of nanocomposite bipolar plates on account of MWCNT–MWCNT interactions beginning to dominate. However, the result indicates that flowability of BMC materials is also affected by the formation of a 3D network structure, which exhibits a relatively large decrease in flowability due to the increase of resin viscosity. When the loading of MWCNTs increases up to 2 wt%, the distance between MWCNTs become so small that the strong π – π interactions cause MWCNTs to hold together easily. Thus, the flowability of BMC material slightly decreases due to the entanglement between CNTs as agglomerates, but the decreased flowability level of BMC material compared to that of the percolation threshold effect is not significant.

3.3. The effect of flowability on the formability of composite bipolar plate

Available composite bipolar plates are only possible when the mold is filled with BMC materials. The unfilled mold will compromise the produced composite bipolar plates and then cause the bipolar plate function to fail, such as weak mechanical properties,

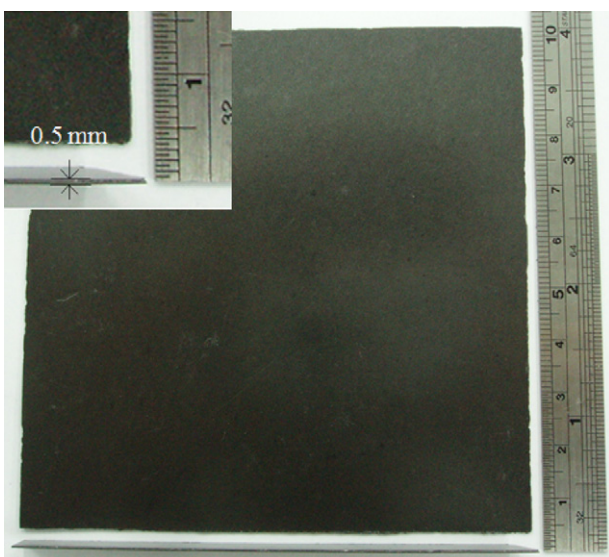


Fig. 6. Thin composite bipolar plate with the dimension of 100 mm \times 100 mm \times 0.5 mm (70 wt% of 177–125 μm).

gas leakage, and non-desired durability. Therefore, it is important to understand the effect of flowability on the formability of fabricated composite bipolar plates.

Table 2 evaluates the formability of composite bipolar plates with various dimensions sizes. The effect of flowability of BMC material on formability can be divided into two parts. One is the plate area with the same thickness, analyzed by fabricating different plate dimensions, including 100 mm \times 100 mm, 200 mm \times 200 mm, and 300 mm \times 300 mm.

The other one is plate thickness with the same plate area (100 mm \times 100 mm), analyzed by fabricating different plate thicknesses (z-direction), including 3 mm, 1.5 mm, and 0.5 mm. Findings show that composite bipolar plates (70 wt%/177–125 μm graphite particle) can be fabricated successively without any defects for the all dimensional size (as shown in Fig. 5(a)–(c)), due to its high flowability of BMC material. However, for the case of composite bipolar plates with low flowability (80 wt%/74–45 μm graphite particle), as shown in Fig. 5(d)–(f), the defects of the fabricated composite bipolar plate will occur with decreased flowability of BMC materials. First, the defects only occur near the edge of the bipolar plate, with lower flowability, when larger surface porosity is formed, as shown in Fig. 5(g). Finally, the plate cannot form or obvious crevices are observable if flowability of BMC material further decreases, as shown in Fig. 5(h). It is contributed that the BMC material is too viscous to flow; hence, the mold cannot be filled up with the material, causing composite bipolar plate formation to fail.

This research investigated the high flowability needed to ensure formability of a large area (300 mm \times 300 mm) or thin (0.5 mm, as shown in Fig. 6) composite bipolar plates by measuring flowability of the BMC material, to estimate the processability needed for yielding a final product.

4. Conclusions

The present researches have used various graphite particle sizes, graphite contents, and MWCNTs contents to analyze the effect of flowability on BMC material. Results indicate that the flowability of BMC material is affected by graphite particle content and size. Low flowability with increasing graphite content (but the same particle size) could be related to increased friction between individual graphite particles, owing to reduced resin content per volume. With decreasing graphite particle size, accumulation density increases and causes the number of graphite–graphite holes to drop dramatically, thus the resin cannot penetrate between graphite particles to form a continuous flow channel. The flowability of BMC material also decreases with adding MWCNTs, especially as the loading achieves the percolation threshold and forms a MWCNT–MWCNT network. Conclusively, higher flowability of the BMC material obtains larger or thinner composite bipolar plates. Therefore, understanding the flowability and formability response of BMC material is of the utmost importance for optimum processing of parameters for composite bipolar plates. From processing and massive manufacture points of view, high flowability of BMC material shows great potential for successively fabricating large area/thin composite bipolar plates which can be controlled by selecting certain graphite particle sizes.

Acknowledgement

The authors are grateful to the Fuel Cell Center, Yuan Ze University, Taiwan, for financial support.

References

- [1] S.H. Liao, C.H. Hung, C.C.M. Ma, C.Y. Yen, Y.F. Lin, C.C. Weng, J. Power Sources 176 (2008) 175.

- [2] B.D. Cunningham, J. Huang, D.G. Baird, J. Power Sources 165 (2007) 764.
- [3] S.H. Liao, C.Y. Yen, C.C. Weng, Y.F. Lin, C.C.M. Ma, C.H. Yang, M.C. Tsai, M.Y. Yen, M.C. Hsiao, S.J. Lee, X.F. Xie, Y.F. Hsiao, J. Power Sources 185 (2008) 1225.
- [4] S.G. Chalk, J.F. Miller, F.W. Wagner, J. Power Sources 86 (2000) 40.
- [5] S.J. Lee, S. Mukerjee, Electrochim. Acta 43 (1998) 3693.
- [6] H. Tsuchiya, O. Kobayashi, Int. J. Hydrogen Energy 29 (2004) 985.
- [7] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Appl. Electrochem. 30 (2000) 101.
- [8] H.C. Kuan, C.C.M. Ma, K.H. Chen, S.M. Chen, J. Power Sources 134 (2004) 7.
- [9] J. Huang, D.G. Baird, J.E. McGrath, J. Power Sources 150 (2005) 110.
- [10] S.H. Liao, C.Y. Yen, C.H. Hung, C.C. Weng, M.C. Tsai, Y.F. Lin, C.C.M. Ma, C. Pan, A. Su, J. Mater. Chem. 18 (2008) 3993.
- [11] C.Y. Yen, S.H. Liao, Y.F. Lin, C.H. Hung, Y.Y. Lin, C.C.M. Ma, J. Power Sources 162 (2006) 309.
- [12] B.O.R. Kirchain, R. Roth, J. Power Sources 109 (2002) 71.
- [13] J.H. Lee, Y.K. Jang, C.E. Hong, N.H. Kim, P. Li, H.K. Lee, J. Power Sources 193 (2009) 523.
- [14] P.H. Maheshwari, R.B. Mathur, T.L. Dhami, J. Power Sources 173 (2007) 394.
- [15] 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, J. Power Sources 184 (2008) 90.
- [16] L. Du, S.C. Jana, J. Power Sources 172 (2007) 734.
- [17] S.R. Dhakate, S. Sharma, M. Borah, R.B. Mathur, T.L. Dhami, Energy Fuels 22 (2008) 3329.
- [18] R. Dweiri, J. Sahari, J. Power Sources 171 (2007) 424.
- [19] S.H. Liao, C.C. Weng, C.Y. Yen, M.C. Hsiao, C.C.M. Ma, M.C. Tsai, A. Su, M.Y. Yen, Y.F. Lin, P.L. Liu, J. Power Sources 195 (2010) 263.
- [20] Q. Yin, K.N. Sun, A.J. Li, L. Shao, S.M. iLiu, C. Sun, J. Power Sources 175 (2008) 861.
- [21] S. Iijima, Nature 345 (1991) 56.
- [22] M. Wu, S.L. Leon, J. Power Sources 136 (2004) 37.
- [23] L.D. Andrew, J. Power Sources 156 (2006) 128.
- [24] Y.T. Sung, C.K. Kum, H.S. Lee, N.S. Byon, H.G. Yoon, W.N. Kim, Polymer 46 (2005) 5656.
- [25] M. Abdel-Goad, P. Po'tschke, J. Non-Newton Fluid Mech. 128 (2005) 2.
- [26] F. Du, R.C. Scogna, W. Zhou, S. Brand, J.E. Fischer, K.I. Winey, Macromolecules 37 (2004) 9048.
- [27] D. Stauffer, A. Aharony, Introduction to Percolation Theory, Taylor & Francis, London, 1991.