

Preparation and properties of high performance nanocomposite bipolar plate for fuel cell

Chuan-Yu Yen, Shu-Hang Liao, Yu-Feng Lin,
Chih-Hung Hung, Yao-Yu Lin, Chen-Chi M. Ma*

Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu 30043, Taiwan, ROC

Received 1 May 2006; received in revised form 26 June 2006; accepted 26 June 2006

Available online 1 August 2006

Abstract

This study aims at developing lightweight and high performance composite bipolar plates for use in polymer electrolyte membrane fuel cells (PEMFCs). The thin polymer composite bipolar plates (the thickness <1.5 mm) containing of vinyl ester resin, graphite powder, organoclay have been fabricated by bulk molding compound (BMC) process. Organoclay was prepared by ionic exchange of montmorillonite (MMT) with three different molecular weight (M_w) of poly(oxypropylene)-backboned diamine intercalating agents. Results indicate that the basal spacing and content of MMT varied with M_w of POP-diamines are critical in determining the resultant mechanical properties for bipolar plates. Flexural strength of MMT composite plates was increased from 30.21 to 45.66 MPa by adding 2 phr of MMT. The flexural strength of the plate was also ca. 38% higher than the pristine graphite plate as the basal spacing of MMT was increased from 1.71 to 5.43 nm. Meanwhile, the unnotched impact strength of the composite plates was increased from 58.11 to 80.21 J m⁻¹. The unnotched impact strength of the plate was ca. 30% higher than that of the original graphite plates as the basal spacing of MMT was increased from 1.71 to 5.43 nm. The limiting oxygen index (LOI) and the UL-94 test revealed that the bipolar plate possesses excellent flame retardant with LOI >50 and UL-94-V0. The thermal decomposition temperature of each MMT composite plate is also higher than 250 °C. In addition, the bulk electrical conductivity of the bipolar plate with different MMT contents and basal spacing of MMT is higher than 100 S cm⁻¹. The corrosion current is less than 10⁻⁷ A cm⁻². Results confirm that the addition of MMT leads to a significant improvement on the performance of the composite bipolar plate.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fuel cell; Bipolar plate; Nanocomposite; Organoclay; Bulk molding compound (BMC); Properties

1. Introduction

Recently, polymer electrolyte membrane fuel cells (PEMFC) exhibit the most promising power sources for various portable electronic devices and transportation applications. They offer the advantages of compactness, lightweight, high power density and low temperature operation. The potential commercial applications include cellular phones, PDAs, laptop computers, military back power packs, etc. [1–4]. With the bipolar plate accounting for the bulk of the stack, it is desirable to fabricate bipolar plates which are as thin and lightweight as possible. Bipolar plates electrically connect successive cells in a fuel-cell stack, and also provide the gas flow field. Hence, bipolar plates must have high

electrical conductivity, sufficient mechanical properties, excellent corrosion resistance, light-weight, etc. The most commonly used bipolar plate is made from graphite. Owing to its brittleness and the difficulty in machining, the graphite bipolar plate has to be made in several millimeters thick, which causes a fuel-cell stack to be heavy and voluminous [5]. In place of graphite bipolar plates and in order to lower the weight of stack, graphite-based composite bipolar plate is made from the combination of graphite, or carbon powder filler, reinforcements and polymer resin utilizing conventional polymer processing methods. They offer the advantages of lower cost, lightweight, high electronic conductivity and greater thermal properties. However, in regard to the fabrication of the slim type PEM fuel cells, the following issues associated with high graphite carbon loadings in thinner polymer composite bipolar plates are the substantial reduction in the strength and ductility of polymer composites. To maintain the high electrical conductivity and good mechanical properties,

* Corresponding author. Tel.: +886 3571 3058; fax: +886 3571 5408.
E-mail address: cma@che.nthu.edu.tw (C.-C.M. Ma).

further work on polymer composite bipolar plates has become an important research subject [3–8].

Research on the polymer–clay nanocomposites has received significant attention for the large-scale improvement in the mechanical and physical properties. Some of the other properties such as heat distortion temperature (HDT), gas permeability; impact strength, thermal stability, flame retardant and corrosion resistance also have been observed at low filler weight fraction [9–13]. Polymer/organically modified layered silicates nanocomposites technology has already proven to be a good method to improve these properties [9,11,14]. In general, it is believed that the large interfacial area and the nanoscopic dimension of the clay enhance the clay–polymer interactions owing to the changes of morphology and performance [9–10].

In this study, the slim type composite bipolar plate (thickness <1.5 mm) for use in polymer electrolyte membrane fuel cells (PEMFCs) has been prepared by BMC process. The organoclays prepared by POP-diamines intercalation were used to enhance the physical properties of thin polymer composite bipolar plates. The effect of the clay content and the basal spacing of organoclays on the electrical, physical, mechanical, thermal properties and *I–V* curves of the polymer composite bipolar plate were investigated.

2. Experimental section

2.1. Materials

Na⁺–MMT, a Na⁺ type of smectite clay (trade name: PK802) with a cation exchange capacity of 1.14 mequiv. g⁻¹, was supplied by the Pai Kong Nanotechnology Co., Taiwan. Poly(oxyalkylene)amines were purchased from the Huntsman Chemical Co., Philadelphia, PA, USA, include poly(oxypropylene) (POP)-backboned diamines with the molecular weight, *M_w*, 230, 400 and 2000 g mol⁻¹ used as the intercalants and denoted as POP230, POP400 and POP2000, respec-

tively. Phenolic-novolac, epoxy-based vinyl ester resin was used (as shown in Table 1), which was provided by the Swancor Co., Taiwan. Graphite powder was obtained from the Great Carbon Co. Ltd., Taiwan. The density of the graphite powder is 1.88 g cm⁻³ and the particle size is less than 1000 μm.

2.2. Preparation of MMT/POP-diamines organoclay

Organoclay was prepared by cation exchange between Na⁺ in clay galleries and poly(oxypropylene) (POP)-backboned diamines cations in aqueous solution [14]. A total of 10 g of Na⁺–MMT was dispersed homogeneously in 1 L of deionized water at 80 °C. The slurry was added to amine salts prepared from poly(propylene glycol)-bis(2-aminopropyl ether) with a molecular weight of 2000 g mol⁻¹ (POP2000, 22.8 g, 11.4 mmol) and the equivalents of hydrochloric acid in water. After being stirred at 80 °C for 5 h, the precipitate was collected at ambient temperature, washed thoroughly with deionic water/ethanol several times and dried under vacuum.

2.3. Preparation of BMC materials [15]

The bulk molding compound (BMC) was preparing by mixing vinyl ester, low profile agent (PS/SM series) styrene monomer, thickening agent (MgO), release agent (ZnSt), graphite and clays in a kneader for 30 min. The BMC formulation is summarized in Table 1. The BMC was thickened for 48 h before the hot-pressing process. The processing temperature was 165 °C and the processing time was 15 min.

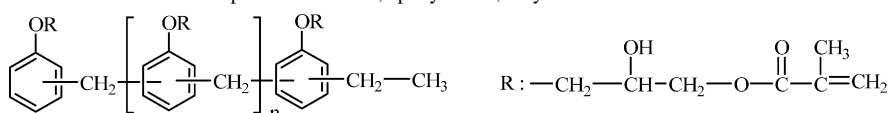
2.4. Characterization and Instruments

The *d*-spacing of MMT/POP-diamines organoclays was scanned at a rate of 4° min⁻¹ by using Shimadzu XD-5 X-ray diffraction (XRD; 45 kV, 30 mA) with copper target and Ni filter. The basal spacing (*n* = 1) was calculated according to

Table 1
Formulation of BMC process

Component	Composition	
	Resin composition	BMC composition
Vinyl ester ^a (wt.%)	75	25
Low profile agent (wt.%)	8	
Styrene monomer (wt.%)	17	
TBPP ^b (phr)	1.8	
Zinc stearate (phr)	3.5	
Magnesium oxide (phr)	1.8	
Montmorillonite (phr)	1–4	
Graphite powder (wt.%)		75
Total (wt.%)		100

^a Chemical structure of phenolic-novolac, epoxy-based, vinyl ester is as follows:



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

Bragg's law, $n\lambda = 2d \sin \theta$, through the observed peaks of $n = 2, 3, \dots$, etc. Thermogravimetric analysis (TGA) was conducted utilizing a DuPont-TGA951 by heating samples from ambient temperature to 800 °C with a heating rate of 10 °C min⁻¹ in N₂. The porosity of each composite bipolar plate was determined according to the ASTM C20 test procedure. The flexural strength tests were performed based on the procedure of ASTM D-790 by an Instron Model 4468, universal tester and the specimen dimensions were 60.0 mm × 13.0 mm × 3.0 mm ($L \times W \times T$). The unnotched izod impact tests were performed on a Tinius Olsen 92T Impact Tester based on ASTM D-256. The sample dimensions were 64.0 mm × 12.7 mm × 3.3 mm. The coefficient of thermal expansion (CTE) was determined at a temperature range from 30 to 145 °C in both the X and Y direction according to ASTM D-696 [16]. The bulk electrical conductivity of the composite bipolar plate was examined with a four-point probe detector (C4S-54/5S, Cascade Microtech, USA). The limiting oxygen index (LOI) of the composite plate was measured by the ASTM D-2836 oxygen index method with a specimen bar of 7.0–15.0 cm × 6.5 ± 0.5 mm × 3.0 ± 0.5 mm. The UL-94 vertical test was performed according to the procedure of ASTM D-3801.

A single stack PEMFC was developed at our laboratory. The catalyst ink for the electrodes was prepared by mixing the catalyst powders (20 wt.% Pt/C, E-TEK), Nafion solution, and *iso*-propyl alcohol. Then the prepared catalyst ink was sprayed on to the wet-proofed carbon paper with a platinum loading of 0.4 mg cm⁻² for the anode and cathode, respectively. The membrane-electrode assembly (MEA) was fabricated by placing the electrodes at both sides of pre-treated Nafion 115 membrane, followed by hot pressing at 140 °C and 200 kg cm⁻² for 90 s. The active electrode area was 4 cm². A single fuel cell was constructed from the prepared MEA, Teflon gasket, and the prepared composite bipolar plate on both sides of the MEA. The thickness of the bipolar plates was 1.5 mm. The operating pressure of the single fuel cell was 1 atm. The performance of the single fuel cell was evaluated by measuring the I - V characteristics using an electronic load (Agilent, N3301A).

3. Results and discussion

3.1. Analysis of MMT/POP-diamines organoclay

Various spatially enlarged organoclays were prepared by using POP-backed quaternary ammonium salts of various molecular weights M_w . 230, 400 and 2000 as the intercalating agents for Na⁺-MMT [14]. The wide d -spacing of modified silicates were measured as 13.9, 17.8 and 54.8 Å, respectively, and were correlated to the molecular weight of the intercalating agents (Table 2). Results implicated these POP-diamines intercalate into the MMT interlayer spacing have a similar orientation. The XRD of MMT/POP2000 exhibited a series of Bragg peaks in the Fig. 1 from $n = 1$ to 5, indicating a more ordered gallery structure was formed comparing the pristine montmorillonite. Meanwhile, the organoclay became highly organophilic as POP-diamines molecular weight was increased [17,18]. Since, MMT/POP2000 organoclay was much easier to disperse

Table 2

Basal spacing and solvophilicity of Na⁺-MMT intercalated by POP-diamines

Intercalating agent	d -Spacing (Å) ^a	Weight fraction (w/w, %) ^b	Solvophilicity ^c		
			Toluene	Ethanol	Water
None	12.1	0/100	–	–	+
POP230	13.9	19/81	–	+	–
POP400	17.8	27/73	–	+	–
POP2000	54.8	60/40	+	+	–

^a Basal spacing was determined by X-ray diffraction.

^b Weight fraction: organic composition/clay (measured by TGA).

^c +: dispersible; –: aggregated.

in the nonpolar solvent than the POP230 and POP400 derived MMT (Table 1). Result showed that the modified MMT was dispersed much better in organic monomers and polymer matrix with the increase of the molecular weight of POP-diamine. Three types of organoclays have been compared regarding the relative effectiveness of enhancing the physical properties of the composite bipolar plates by correlating the results to the content and dispersion of MMT in the BMC materials.

3.2. Mechanical properties of the composite bipolar plates

The bipolar plates should have adequate mechanical properties to be used in the fuel-cell stacks. For example, the target values in literatures 4, 6 indicate the requirement (flexural strength >49 MPa, impact strength >40.5 J m⁻¹) [4,6]. However, the polymer composites doped with high graphite powder loadings are difficult to reach high conductivity and sufficient mechanical properties at the same time. As a result, the mechanical properties (such as flexural strengths) of composite bipolar plates available so far are still significantly lower than the target values, as shown in Table 3.

Three types of modified organoclays have been used to enhance the mechanical properties of the composite bipolar plates. Thin polymer composite bipolar plates (the thick-

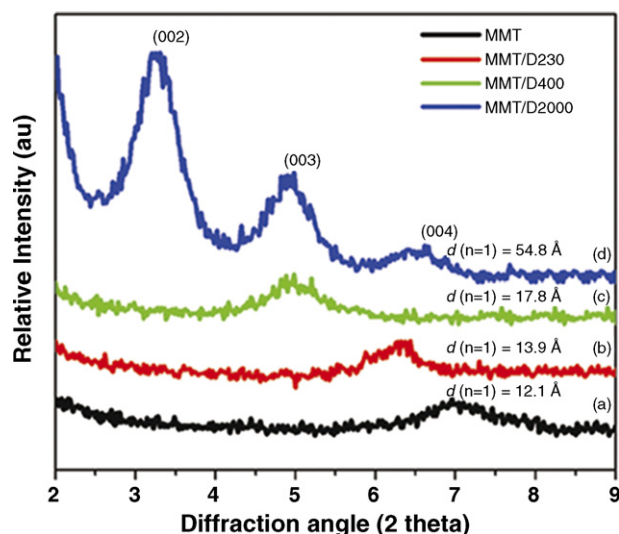


Fig. 1. XRD patterns of: (a) original MMT, (b) MMT/POP230, (c) MMT/POP400 and (d) MMT/POP2000.

Table 3
Properties of polymer composite bipolar plates containing conductivity particles

Trade names ^a	Polymer	Graphite (wt.%)	In-plane conductivity ($S m^{-1}$)	Flexural strength (MPa) ^b
LANL	Vinyl ester	68	60	29.6
Premix	Vinyl ester	68	85	28.2
BMC	Vinyl ester	69	30	37.9
Commercial			105	20.7
BMC 940	Vinyl ester		100	40.0
Plug Power	Vinyl ester	68	55	40.0
This study ^c	Vinyl ester	75	260	50.1

^a The trade names of composite bipolar plates commercially available today.

^b Based on the procedure of ASTM D-790.

^c The polymer bipolar plate with 4 phr MMT/POP2000 was prepared by this study.

ness <1.5 mm) of organoclay-added BMC materials have been prepared. The flexural strengths of these composite plates were improved significantly by adding different clays, as shown in Fig. 2. The flexural strength of the composite plates was increased with increasing content of different types modified clays from 31.51 MPa (0 phr) to 39.68–50.11 MPa (4 phr), respectively. Fig. 2 exhibits that the improvement of flexural strength was greater by adding organoclay than by adding pristine clay. Furthermore, significant differences in the properties among the modified organoclays of three types M_w , the intercalated MMT/POP230, MMT/POP400 and MMT/POP2000 can be observed. The improvement of 45.52 MPa (MMT/POP2000) versus 39.11 MPa (MMT/POP400) and 36.15 MPa (MMT/POP230) for 2 phr clay loading were compared, the reinforcement effect of organoclay was increasing with the increase of modified MMT basal spacing. The improvement on the flexural strength is attributed to the increasing of the organophilic degree of MMT, and the difference of interaction between platelets and the BMC materials [19].

The improvement of unnotched impact strength of clay-composite bipolar plates exhibits similar trend to the flexural property of clay-composite plates, as shown in Fig. 3. The unnotched izod impact strength of the composite plates

was increased with increasing clays content of different modified types from 58.21 $J m^{-1}$ (0 phr) to 66.22–87.1 MPa (4 phr), respectively. Fig. 3 indicates that the enhancing effect of organoclays was greater than that of pristine clay. The increase of unnotched impact strength also increased with the intercalated MMT basal spacing.

Results reveal that all intercalated MMT/POP-diamines are effectively improving the flexural and impact strengths. The improvement level of mechanical properties for composite bipolar plates adding organoclays was increased in the order of MMT/POP2000 > MMT/POP400 > MMT/POP230 > MMT. Result indicates addition of organoclays, especially, MMT/POP2000, could achieve certainly the requirements of industry for composite bipolar plates.

3.3. Electrical conductivity of the composite bipolar plate

The bulk electrical conductivity is one of the most important properties of bipolar plates. If the material is tough enough, a thinner plate and higher stack compaction pressure can be used to reduce the bipolar plate resistance and interfacial resistance within the stack, and, thus, improve the performance of the fuel cells. The thinner composite bipolar plates (<1.5 mm) with clays prepared by BMC procedure in this study all have high conduc-

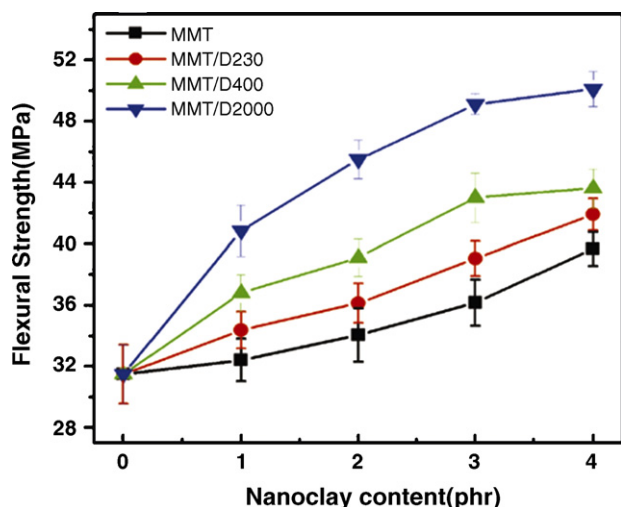


Fig. 2. The flexural strengths of composite bipolar plates with different modified organoclays.

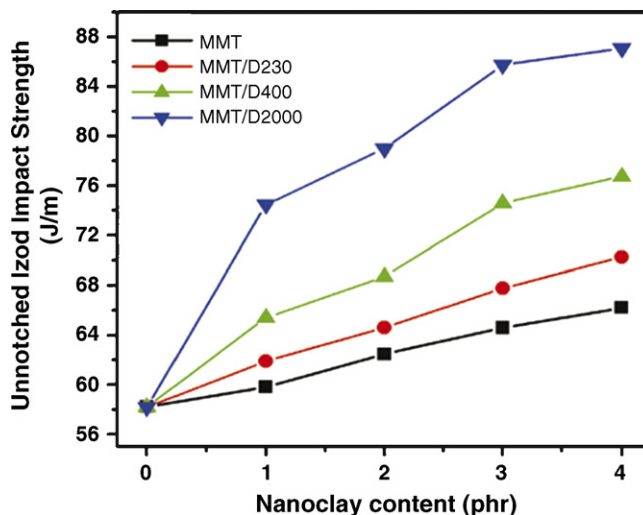


Fig. 3. The unnotched izod impact strengths of composite bipolar plates with different modified organoclays.

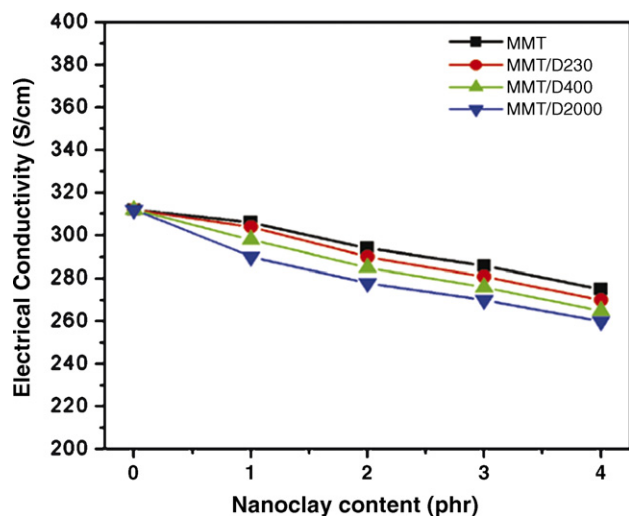


Fig. 4. The electrical conductivity of composite bipolar plates with different modified organoclays.

tivity ($>200 \text{ S cm}^{-1}$), as shown in Fig. 4, result in all these values exceeding the requirements of DOE and industry ($>100 \text{ S cm}^{-1}$) for composite bipolar plates [20].

Fig. 4 shows that the reduced tendency of bulk electrical conductivity properties was more obvious by adding organoclays than pristine clay, and the bulk electrical conductivity of the composite plates was decreased from 312 S cm^{-1} (0 phr) to $290\text{--}260 \text{ S cm}^{-1}$ (4 phr) with the increasing of modified organoclay content. The reason was proposed that in the composite system the clay layers interrupt the effective doping process and induce the weak interchain and intrachain interactions, resulting in decreasing the bulk electrical conductivity of composite plates [21]. Moreover, the decreasing of the bulk electrical conductivity from 304 to 298 and 290 S cm^{-1} for 1 phr organoclays loading were compared, the bulk electrical conductivity was slightly decreased with the increasing of organoclays basal spacing. This result may be attributed to the dispersion of organoclays in composite plates. For example, MMT/POP2000 organoclay was much easier to disperse in polymer matrix than the POP230 and POP400 derived MMT, therefore, it may have a greater impediment to extend the movement path of the electron, consequently, reduce the bulk electrical conductivity of the composite bipolar plates [22].

3.4. Anticorrosive protection properties of composite bipolar plates

Anticorrosive performance of clay-composite bipolar plates can be examined from the corrosion current, as shown in Fig. 5. The composite plates containing clays show a lower corrosion current value than that of pristine plates. The value of corrosion current was found to decrease gradually with the increasing of clay loading. Meanwhile, there were also differences among three kinds of MMT/POP-diamines studied. Result exhibits that the sample with higher basal spacing organoclay shows greater anticorrosive performance than the pristine composite plate. These properties of enhanced anticorrosion effect for clay-

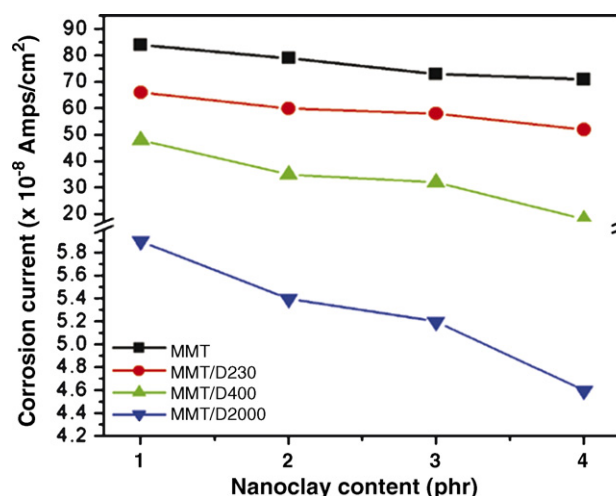


Fig. 5. The corrosion current of composite bipolar plates with different modified organoclays.

composite bipolar plates compared to that of original one might have arisen from dispersing silicate nanolayers of clay in vinyl ester matrix to increase the tortuosity of the diffusion pathway of oxygen [23]. However, owing to the corrosion current of the bipolar plates was less than $10^{-7} \text{ A cm}^{-1}$, the result clearly demonstrates that the composite bipolar plates were corrosion-resistant under this condition.

3.5. Porosity analysis of composite bipolar plates

Our previous study [1] showed that the porosity of the composite bipolar plate reaches a minimum at 75 wt.% graphite powder content, and increases with the decreasing of graphite size. The characteristic behavior may be due to the phase separation of styrene with BMC materials [24]. It is proposed that the high free energy resulted from the great surface area of small size graphite causing the aggregation of graphite particles; therefore, graphite powder may not be completely wetted by vinyl ester resin, consequently, the insufficient vinyl ester resin may induce holes in the composite bipolar plates. This contention also implied that the well dispersible filler in polymer matrix may be effective for the decreasing of the porosity in composite bipolar plates. Fig. 6 illustrates the effect of clays on the porosity of composite plates. The tendency of porosity in the composite materials was more significant reduced by adding organoclays than pristine clay, and decreased from 1.8% (0 phr) to 0.2–1.4% (4 phr) with the increasing of the modified organoclay content. In the composite system, the clay layers interrupt the phase separation resulting from styrene diffusion. Furthermore, the decreasing of 0.5, 1.4 and 1.6% for 1 phr organoclays loading were compared as shown in Fig. 6, the porosity of composite materials was decreased with the increasing of organoclays basal spacing. Result may be attributed to the organophilic degree and the dispersion of organoclays in composite plates. The lower porosity caused by adding MMT/POP2000 might be related to the higher organophilic property of the organoclay which can act as a compatibilizer. Meanwhile, since MMT/POP2000 organoclay was much easier to disperse in polymer matrix than those

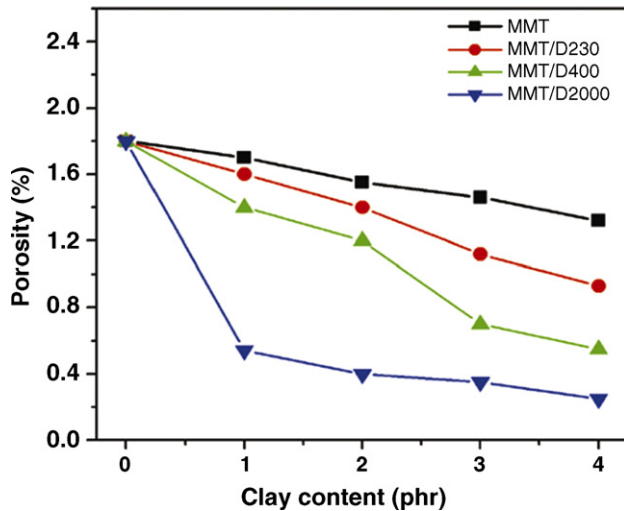


Fig. 6. The porosity of composite bipolar plates with different modified organoclays.

of POP230 and POP400 derived MMT, it has a greater impediment to extend the movement path of the styrene molecules, and, thus, restrain the phase separation in the composite materials.

3.6. The thermal expansion behavior of composite bipolar plates

The thermal expansion of composite bipolar plates was measured by thermal mechanical analysis (TMA). The coefficient of thermal expansion (CTE) in units of $\mu\text{m}/\text{m}^\circ\text{C}$ was determined under stress and deformation as a function of temperature was found to be significantly increased with clays content in the range of 1–4 phr loading, as shown in Fig. 7. The CTE of composite plates was increased from $16.7 \mu\text{m}/\text{m}^\circ\text{C}$ (pristine) to 31.4 – $41.2 \mu\text{m}/\text{m}^\circ\text{C}$ depending on the amount of MMT added (1–4 phr). It might be attributed to the decrease of composite porosity formed by the addition of clays. However, there were differences among organoclays. It was found the CTEs of com-

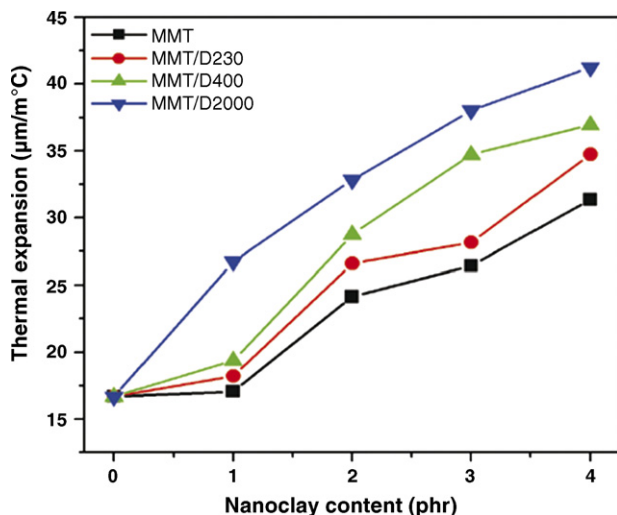


Fig. 7. The coefficient of thermal expansion of composite bipolar plates with different modified organoclays.

Table 4

The UL-94V-0 and LOI test results of composite bipolar plate with 75 wt.% graphite and with various nanoclay contents

Organoclays ^a (phr)	Flaming drops	Cotton ignited	UL-94V-0 standard	LOI
1	N/A ^b	N/A ^b	94V-0	>50
2	N/A	N/A	94V-0	>50
3	N/A	N/A	94V-0	>50
4	N/A	N/A	94V-0	>50

^a The organoclays were prepared by intercalating telechelic POP-diamines.

^b N/A: not available.

posite plates are 26.62 , 28.75 and $32.82 \mu\text{m}/\text{m}^\circ\text{C}$ with 2 phr MMT/POP230, MMT/POP400 and MMT/POP2000, respectively. Explain that decrease in the free volume of the composite plates was a result of the increase in the intercalating agent content in modified MMT [25]. Furthermore, the CTE of the bipolar plates prepared in this study was significantly lower; this result indicates that the thermal stability of composite bipolar plates was still high enough for fuel-cell application.

3.7. Flame retardance

The flame resistance of the composite bipolar plates containing organoclay was significantly increased with clays content in the range of 1–4 phr loading, as shown in Table 4. The measured flame retardance for composite bipolar plates with different types of clay content all meet UL-94V-0 and LOI >50 specifications. Thus, it can be seen all composite bipolar plates prepared in this study possess good flame retardance.

3.8. Single cell performance test

The I - V and I - P performances of a composite bipolar plate and a graphite bipolar plate for single cell are given in Fig. 8. Photograph of the single cell using the composite bipolar plate is presented in Fig. 9. The I - V performance of composite bipolar plate is very similar to that of the graphite bipolar plate, and so is the I - P performance. The data indicate that the opti-

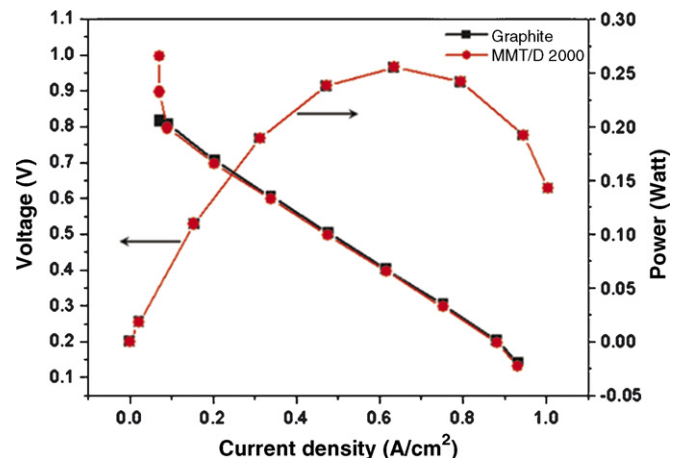


Fig. 8. The I - V and I - P performance of the composite bipolar plates with MMT/POP2000 (2 phr) and the graphite composite bipolar plate.

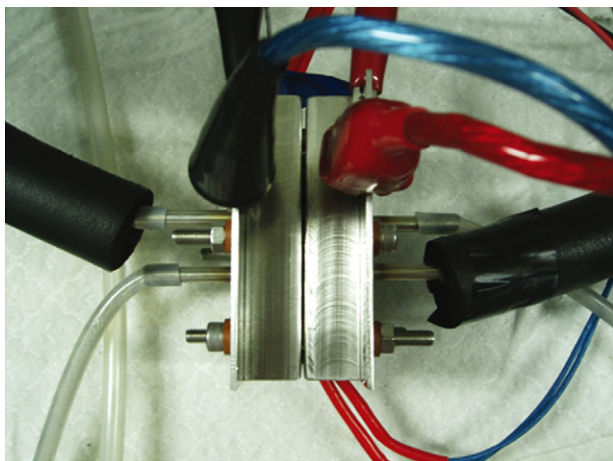


Fig. 9. The photograph of single cell using the composite bipolar plate.

imum composition (MMT/POP2000, 2 phr) of the composite bipolar plate provides a suitable reinforcement of the composite plates.

4. Conclusions

A novel composite bipolar plate composed of vinyl ester resin, graphite and organoclays has been successfully prepared by the BMC process. The dispersion and the organic content of clays in BMC materials are correlated to the composite properties. All intercalated MMT/POP-diamines, especially MMT/POP2000, were effective in improving flexural strength, impact strength, anticorrosive protection and porosity properties. Composite bipolar plates containing different types organoclays contents meet UL-94V-0 specification and the LOI are higher than 50. However, after adding of organoclays (1–4 phr), the thermal expansion coefficients of the composite bipolar plate were increased from pristine $16.7 \mu\text{m}/\text{m}^\circ\text{C}$ to $31.4\text{--}41.2 \mu\text{m}/\text{m}^\circ\text{C}$, and the electrical conductivity of composite bipolar plate decreases slightly from 312 to $290\text{--}260 \text{ S cm}^{-1}$. Both CTE and high electrical conductivity of the bipolar plates were in line with the DOE targets. Both $I\text{--}V$ and $I\text{--}P$ test show that composite bipolar plates with optimum composition possess equivalent performance to a graphite bipolar plate.

Acknowledgements

The authors are grateful to the Ministry of Economics Affairs for financial support. Assistance with cell testing by Enliang Enterprise Co., Ltd., Taiwan is also great appreciated.

References

- [1] H.C. Kuan, C.M. Ma, K.H. Chen, S.M. Chen, *J. Power Sources* 134 (2004) 7–17.
- [2] B.K. Kho, I.H. Oh, S.A. Hong, H.Y. Ha, *Electrochim. Acta* 50 (2004) 781–785.
- [3] M.H. Oh, Y.S. Yoon, S.G. Park, *Electrochim. Acta* 50 (2004) 777–780.
- [4] E.A. Cho, U.S. Jeon, H.Y. Ha, S.A. Hong, I.H. Oh, *J. Power Sources* 125 (2004) 178–182.
- [5] M. Wu, L.L. Shaw, *Int. J. Hydrogen Energy* 30 (2005) 373–380.
- [6] J. Huang, D.G. Baird, J.E. McGrath, *J. Power Sources* 150 (2005) 110–119.
- [7] A. Hermann, T. Chaudhuri, P. Spagnol, *Int. J. Hydrogen Energy* 30 (2005) 1297–1302.
- [8] M. Wu, L. Shaw, *J. Power Sources* 136 (2004) 37–44.
- [9] M.A. Osman, V. Mittal, M. Morbidelli, U.W. Suter, *Macromolecules* 37 (2004) 7250–7257.
- [10] B.K. Kuila, A.K. Nandi, *Macromolecules* 37 (2004) 8577–8584.
- [11] S.S. Ray, K. Yamada, M. Okamoto, A. Ogami, K. Ueda, *Chem. Mater.* 15 (2003) 1456–1465.
- [12] J.M. Yeh, S.J. Liou, C.Y. Lai, P.C. Wu, *Chem. Mater.* 13 (2001) 1131–1136.
- [13] M.A. Osman, V. Mittal, M. Morbidelli, U.W. Suter, *Macromolecules* 36 (2003) 9851–9858.
- [14] D.J. Chaiko, A.A. Leyva, *Chem. Mater.* 17 (2005) 13–19.
- [15] J.J. Lin, I.J. Cheng, R. Wang, R.J. Lee, *Macromolecules* 34 (2001) 8832–8834.
- [16] B.B. Fitts, V.R. Landi, S.K. Roy, US Patent 6,811,917 (2004).
- [17] A. Marmur, *J. Am. Chem. Soc.* 122 (2000) 2120–2121.
- [18] H. Ishida, S. Campbell, J. Blackwell, *Chem. Mater.* 12 (2000) 1260–1267.
- [19] X. Fu, S. Qutubuddin, *Polymer* 42 (2001) 807–813.
- [20] K. Robberg, V. Trapp, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), *Handbook of Fuel Cells—Fundamentals, Technology and Applications, Fuel Cell Technology and Applications*, vol. 3, Wiley and Sons, New York, 2003, pp. 308–314.
- [21] B.H. Kim, J.H. Jung, S.H. Hong, J. Joo, A.J. Epstein, K. Mizoguchi, J.W. Kim, H.J. Choi, *Macromolecules* 35 (2002) 1419–1423.
- [22] J.J. Hwang, H.J. Liu, *Macromolecules* 35 (2002) 7314–7319.
- [23] J.M. Yeh, S.J. Liou, C.Y. Lin, C.Y. Cheng, Y.W. Chang, K.R. Lee, *Chem. Mater.* 14 (2002) 154–161.
- [24] Z. Zhang, S. Zhu, *Polymer* 41 (2000) 3861–3870.
- [25] D. Kilburn, G. Dlubek, J. Pionteck, D. Bamford, M.A. Alam, *Polymer* 46 (2005) 859–868.