

Short communication

Effects of resin content and preparing conditions on the properties of polyphenylene sulfide resin/graphite composite for bipolar plate

Li-gang Xia^a, Ai-ju Li^{a,*}, Wei-qiang Wang^b, Qiang Yin^a, Heng Lin^c, Yi-bo Zhao^c

^a Key Laboratory for Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University,

Shandong Key Laboratory of Engineering Ceramics, Shandong University, Jinan 250061, PR China

^b School of Mechanical Engineering, Shandong University, Jinan 250061, PR China

^c School of Material Science and Engineering, Shandong University, Jinan 250061, PR China

Received 27 November 2007; accepted 29 November 2007

Available online 5 December 2007

Abstract

In the paper, a kind of polyphenylene sulfide (PPS) resin/graphite (G) composite for bipolar plate was prepared by using the PPS resin as adhesive and simple hot pressing. The influences of the resin content, the molding temperature and holding time on the conductivity and the bending strength of the PPS/G composite bipolar plate were investigated firstly and then the optimum content and the preparing conditions of the composite were obtained. The experimental results show that the electrical conductivity decreases and the bending strength reveals a serrated variation with increase in PPS resin content; when the holding time is certain, the conductivity decreases and the bending strength increases with the molding temperature increasing. The experimental results further show that the effect of the holding time on the properties of the composite is different at different molding temperatures. The PPS/G composite with 20% PPS resin content has electrical conductivity of 118.9 S cm^{-1} and bending strength of 52.4 MPa when it molded at 380°C for 30 min, and has electrical conductivity of 105 S cm^{-1} , bending strength of 55.7 MPa when it molded at 390°C for 30 min. The properties of the composites can meet the requirements of United States Department of Energy (DOE). © 2007 Elsevier B.V. All rights reserved.

Keywords: Fuel cell; Bipolar plate; Graphite; Polyphenylene sulfide

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is one of the most promising power sources for stationary and transportation applications in the future due to its high efficiency, high-power density, relatively low-operating temperature, convenient fuel supply and long-life time [1]. Bipolar plates are important components in PEMFC, which account for approximately 80% of the fuel cell volume, 70% of the fuel cell weight and as much as 60% of the entire stack cost [2]. The cost of the bipolar plate has become a major barrier to its commercialization.

Recently, polymer-carbon composite bipolar plates have been investigated since their lower cost and less weight compared with available materials such as graphite or metallic bipolar plates. Thermoplastic and thermo-set polymer can be

selected and compression molding or injection molding can be used to fabricate bipolar plate with gas flow channels on it, which can reduce the machining cost of the bipolar plate. If thermoplastic resins are selected, an additional advantage can still be gained for their recuperability. Because most polymer resins intrinsically have low-electrical conductivity, higher loading fillers must be added in order to improve the conductivity and meet the requirements of the bipolar plate ($>100 \text{ S cm}^{-1}$ [3]). The filler content must be limited otherwise it can lead to poorer mechanical properties of the bipolar plates.

PPS resin is a semi-crystalline thermoplastic polymer with high degree of chemical resistance. The superior chemical resistance, coupled with excellent mechanical properties, dimensional stability, and high-temperature resistance, makes the PPS resin one of the ideal choices for the composite bipolar plates [4]. Mighri and Huneault [5] applied injection and compression molding methods to fabricate bipolar plates with carbon-filled polyphenylene sulfide. By adding up to 60 wt% graphite, conductive carbon black and carbon fibers, the volume resistivity of the bipolar plate attained around $0.06 \Omega \text{ cm}$.

* Corresponding author. Tel.: +86 531 88392439; fax: +86 531 88392439.
E-mail address: liaiju57@sina.com (A.-j. Li).

Radhakrishnan et al. [6] used PPS resin and natural graphite powder to prepare bipolar plate by high-pressure compaction. Resistance values of 0.1Ω were achieved in their studies. Huang et al. [4] produced bipolar plates consisting of graphite particles, PPS fibers and glass or carbon fibers by means of wet-lay process. The plates have in-plane conductivity of $200\text{--}300 \text{ S cm}^{-1}$, tensile strength of 57 MPa, flexural strength of 96 MPa and impact strength of 81 J m^{-1} .

Compared with their investigations, the PPS powder and graphite powder were directly mixed in a planetary high-energy ball miller and then a simple hot pressing was used to prepare the samples in our research. The samples are easier to fabricate as no slurry-making process and their electrical conductivity and bending strength can meet the DOE targets at the same time. This paper reports our study of the PPS/G composite bipolar plate material and gives effects of the resin content, the molding temperature and holding time on the properties of the bipolar plate material.

2. Experimental

2.1. Materials

The resin was commercial grade polyphenylene sulfide (PPS, Ryton P-6, MFI 380, ash weight 0.8%) and supplied by Chevron Phillips Chemical International Incorporation. Graphite powder, with purity $\geq 95\%$ and granularity in the range of 100–140 mesh, was obtained from Laixi, PR China.

2.2. Sample preparation

Graphite and PPS resin powders with different mixture ratios were first mixed thoroughly in a planetary high-energy ball miller for 2 h at the speed of 380 rpm and then hot-pressure molded at different temperatures under a pressure of 30 MPa for different times to obtain the composite samples.

2.3. Measurements of performance

The samples were cut into $20 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$ in size. The bending strength of the composite samples was investigated using a universal testing machine (CMT5105). The supporting span was 20 mm and the rate of displacement was 0.5 mm min^{-1} . The bulk electrical conductivity was measured by using a QJ44 type four-point probe instrument. The morphologies of the samples were observed by a JXA-8800R type electronic probe microanalyzer (EPMA). The degree of the PPS resin crystallization was characterized by an X-ray diffraction instrument.

3. Results and discussion

3.1. The effect of PPS resin content on the properties of the composite bipolar plate

Keeping the molding temperature and holding time constant, the samples with different PPS resin contents were prepared under the pressure of 30 MPa and the effects of PPS resin con-

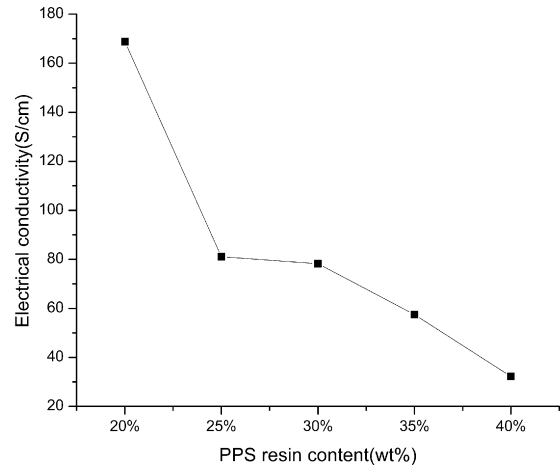


Fig. 1. Effect of PPS resin content on conductivity of the composite.

tent on the electrical conductivity and bending strength of the composite were investigated (Figs. 1 and 2). It can be seen that the conductivity of the composite decreases with increase in PPS resin content, but the bending strength of the composite increases firstly, then decreases and finally increases again. The electrical conductivity of the composite can reach its maximum value (168.8 S cm^{-1}) when the PPS resin content is 20%, while the bending strength of the composite can attain 41.3 MPa. And the bending strength of the composite can reach its maximum value (49.5 MPa) and minimum value (26.1 MPa) when the PPS resin content is 25% and 35%, respectively.

The electrical conductivity can be explained by two mechanisms: inter-particle conductivity and intra-particle conductivity. The inter-particle conductivity is related to the connectivity by direct contact among graphite particles. The intra-particle conductivity is proportional to the conductive path length of the inside of a unit particle, or to particle size [7]. At high-filler loadings, there is no difference between the two mechanisms when graphite particles are fully compacted. The PPS resin is intrinsically insulator, which can isolate the graphite particles and then decrease the number of direct contacting particles. In consequence, less conductive networks can be formed. More-

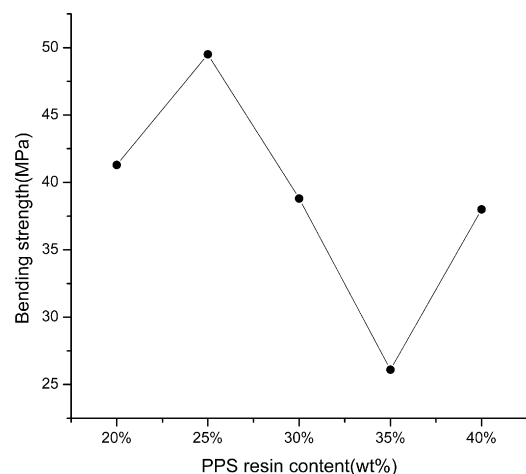


Fig. 2. Effect of PPS content on bending strength of the composite.

over, the increase of the PPS resin content means the decrease of the conductive graphite phase which can reduce the number of conducting current carrier [8]. Tunnel current may be yielded when graphite particles are isolated by thin resin layer. The resin layer spreading on the graphite particles will become thicker with increase in the resin content, which can reduce the possibility of the tunnel effect. Therefore, the conductivity of the composite decreases with the increase of the PPS resin content.

The crystallinity and grain size of the resin will have a significant effect on the properties of the composite as the PPS resin is a kind of crystalline polymer. Moreover, the distribution of the resin will also have an effect on the properties because the PPS resin is used as the adhesive in the PPS/G composite. Fig. 3 shows the X-ray diffraction patterns of the PPS/G composite with different resin contents, among which the crystal plane (200) corresponds to the intense peak in the diffraction pattern of pure PPS resin. The crystallinity and grain size of the resin in the composites can be characterized qualitatively by the crystal plane. It can be seen from the figures that when the PPS resin content is 25%, the crystallinity of the PPS resin and the average grain size calculated and demonstrated by Scherrer equation are minimum; along with the increase of the resin content up to 35%, the crystallinity of the resin increases and the grain size grows; finally, when the resin content continues to increase, the crystallinity reduces and the grain size refines. The reduction of the crystallinity and refinement of the grain size can improve the bending strength of the PPS/G composite. The fracture appearances of the PPS/G composites with different resin contents were investigated by EPMA (Fig. 4). It reveals that the resin distributes more uniformly and coats the graphite particles effectively when the resin content is 25% in Fig. 4a. The fracture of the composite exhibits a typical tearing of the resin which coated on the graphite particles. On the contrary, the resin distribution was uneven and the graphite particles aggregated in some regions when the resin content is 35% in Fig. 4b. The fracture of the composite reveals tearing along aggregated graphite lamellar. The difference between the failures leads to the variance of the bending strength.

3.2. The effects of molding temperature and holding time on the properties of the composite bipolar plate

The effects of the molding temperature and holding time on the electrical conductivity of the composite are shown in Fig. 5.

It can be seen from Fig. 5 that when the holding time is certain, the electrical conductivity decreases with the molding temperature increasing, but the conductivity curves of the holding time are different at different molding temperatures. The electrical conductivity increases firstly and then decreases with the holding time increasing at 370 °C. The electrical conductivity can reach its maximum value (168.8 S cm⁻¹) when the holding time is 90 min. The effects of the holding time on the properties of the composite are similar when the molding temperatures are 380 °C and 390 °C. The electrical conductivities decrease firstly and then increase with the increase of the holding

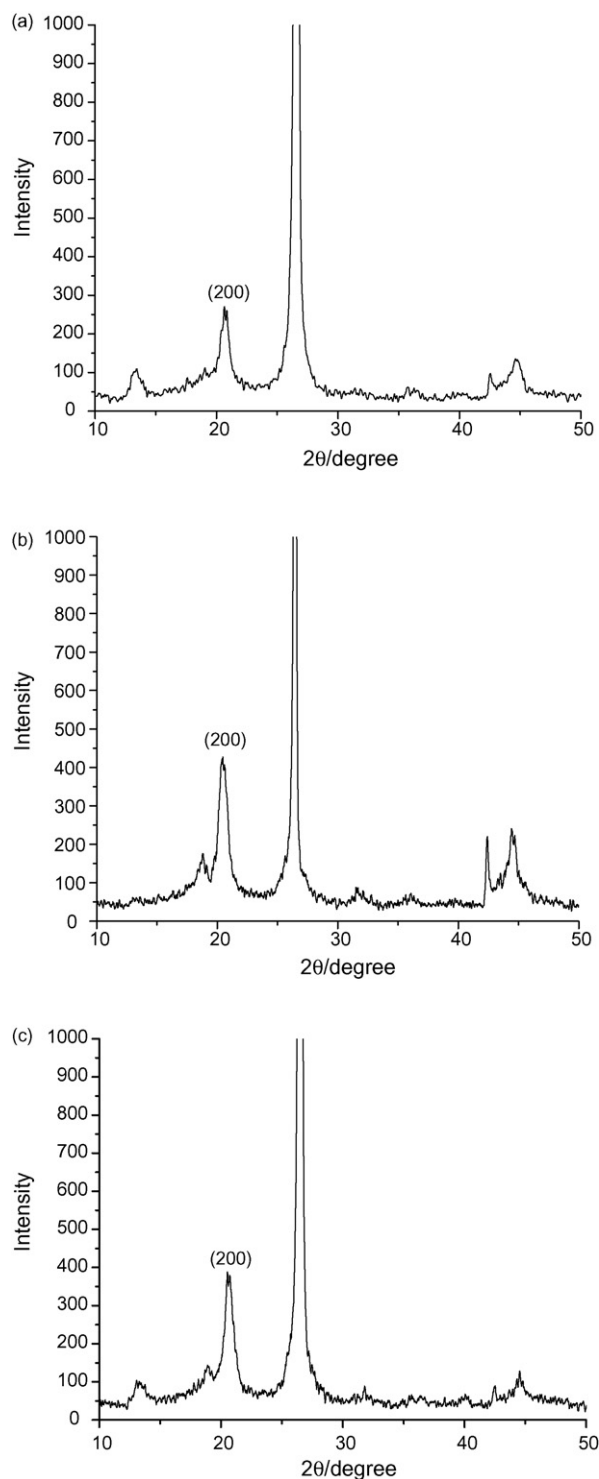


Fig. 3. X-ray patterns of PPS/G composites with different resin contents (a) 25% (b) 35%, and (c) 40%.

time, and can both reach their maximum values (118.9 S cm⁻¹ and 105 S cm⁻¹) when the holding time is 30 min in our research conditions.

The effect of the molding temperature on the electrical conductivity can mainly attribute to the following aspects. On one hand, more graphite particles are coated on by the resin evenly

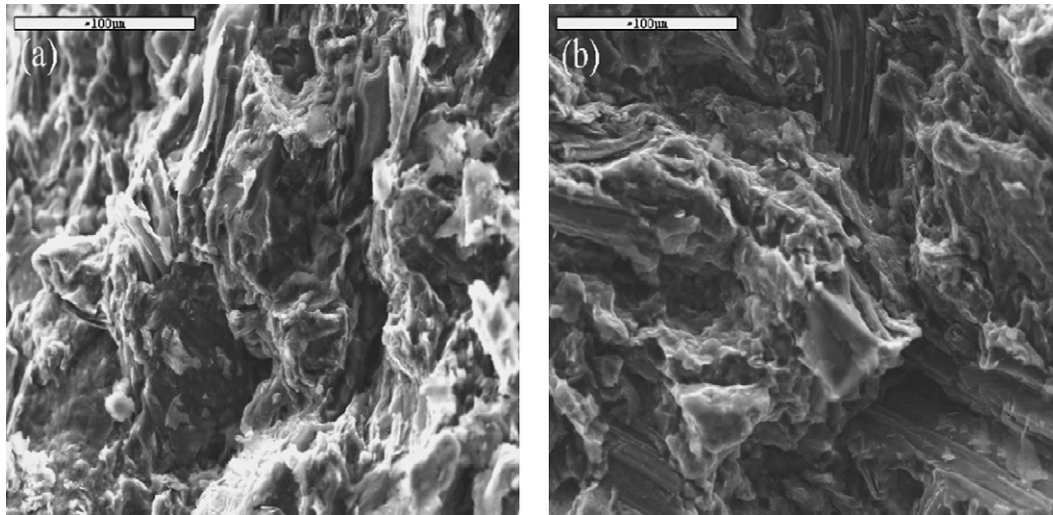


Fig. 4. Fracture appearance of PPS/G composites by SEM (a) 25% PPS and (b) 35% PPS.

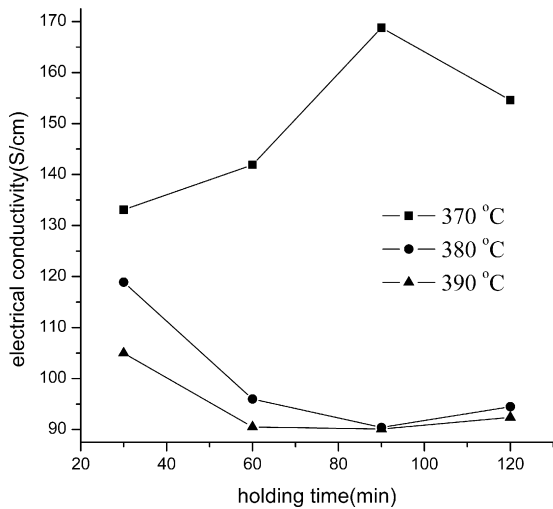
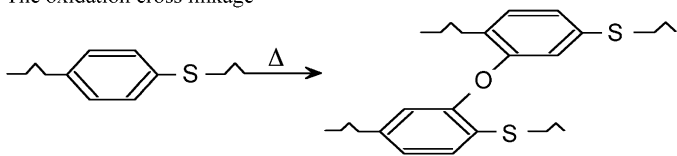


Fig. 5. Effects of holding time on electrical conductivity of the composite at different molding temperatures.

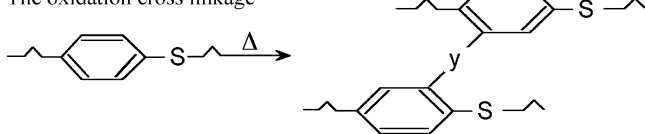
and furthermore isolated as the fluidity of the resin increases with the temperature increasing. As a result, the electrical conductivity is reduced. On the other hand, the chain link increment of the resin will take place [9]:



The oxidation cross linkage



The oxidation cross linkage



will also occur [9]. Therefore a three-dimensional network structure is formed, which will baffle the flow of the conducting current carrier and then reduce the electrical conductivity of the composite. The effect of the holding time on the conductivity of the composite may be explained in two aspects. Firstly, the graphite particles are getting more isolated because of the better infiltration of the resin which will make the conductivity decrease with the increase of the holding time. Secondly, the resin layer will become thinner with the holding time increasing, which will do help to the increase of the conductivity. When the holding time is below 90 min at 370 °C, the second aspect plays a more important role and consequently the conductivity increases with the holding time increasing; reversely, the first aspect plays a more important part when the holding time is above 90 min, and this is why the conductivity reduces later. In addition, the degree of cross-linkage of the PPS resin may increase along with the holding time increasing, which will baffle the flow of the conducting current carrier and induce the composite to reveal a dropping tendency of the conductivity. Along with the molding temperature increasing up to 380 °C and 390 °C, the effect of increasing the molding temperature is similar to the effect of increasing the holding time, the first aspect plays a more important role and the conductivity of the composite tends to decrease. At higher temperature with the increase of the holding time, the resin layer becomes much thinner and makes the conductivity exhibit an increasing tendency at the later period.

Fig. 6 shows the effects of the molding temperature and holding time on the bending strength of the composites.

It can be seen from Fig. 6 that the bending strength increases with the molding temperature increasing when the holding time is certain and the bending strength curves of holding time are also different at different molding temperatures. The bending strength curve of the holding time is similar to the conductivity one at 370 °C. The bending strength of the composite can reach its maximum value (41.3 MPa) when the holding time is 90 min. When the molding temperatures are 380 °C and 390 °C, the bending strength curves of different holding time are similar. With the increase of the holding time, the bending strengths

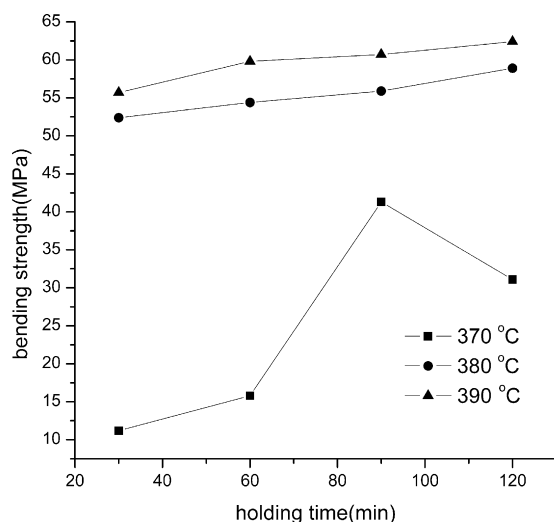


Fig. 6. Effects of holding time on bending strength of the composite at different molding temperatures.

of the composites increase and can both reach their maximum values (58.9 MPa, 62.4 MPa) when the holding time is 120 min. It should be pointed out that when the holding time is 30 min at 380 °C and 390 °C, the bending strengths of the composites are 52.4 MPa and 55.7 MPa, when the electrical conductivities of the composites are 118.9 S cm⁻¹ and 105 S cm⁻¹, respectively, which can meet the requirements of DOE standard in which the PEMFC bipolar plate material should have the properties of electrical conductivity >100 S cm⁻¹ and bending strength >50 MPa.

It can be explained by the following: more graphite particles are infiltrated and bonded much more thoroughly because the fluidity and the cross-linkage of the resin increase with the temperature increasing, and this is why the bending strength of the composite increases. That the bending strength curve of the composites possesses a tendency of rising up first and then falling down at 370 °C can be explained as the infiltration and spreading of the PPS resin on the graphite particles get more uniform with the increase of the holding time, which will improve the bending strength of the composites firstly. The degree of cross-linkage of the resin may be another reason for improving the bending strength of the composites. Because of the density difference between the PPS resin and graphite particles and plenty of pores among their particles, the PPS resin tends to flow down and up vertically under the action of the gravity which may make the resin distribute uneven and as a result the bending strength of the composite decreases subsequently. When the molding temperature is up to 380 °C and 390 °C, the bending strength tends to increase because of better fluidity of the PPS resin. Moreover, with the increase of the molding temperature and holding time, a three-dimensional network structure will be well established which will make the bending strength increase.

Moreover, it also can be seen from Figs. 5 and 6 that when the molding temperature varies from 370 °C to 380 °C and the holding time is 30 min, the electrical conductivity of the composite falls down the slowest and the bending strength rises

the fastest. However, the electrical conductivity falls down the fastest and the bending strength rises the slowest when the holding time is 90 min. The variations of the electrical conductivity and bending strength reveal opposite tendencies when the molding temperature varies from 380 °C to 390 °C. It can be explained as following: the effect of the molding temperature on the properties of the composites is mainly the increasing of the fluidity of the PPS resin when the holding time is shorter, but when the holding time is longer, the effect is mainly the increasing of the degree of cross-linking.

4. Conclusions

- (1) A kind of PPS/G composite for bipolar plate was prepared by simple hot pressing. The mechanical and electrical properties of the composite can meet the requirements of DOE at the same time.
- (2) The electrical conductivity of the composite decreases with increase in the resin content, but the bending strength increases firstly, then decreases and finally increases again; when the holding time is certain, the conductivity of the composite decreases and the bending strength increases with the increase of the molding temperature. At different molding temperatures, the effect of the holding time on the properties of the composite is different. The electrical conductivity and bending strength of the composite increase firstly and then decrease with the holding time increasing at 370 °C. When the molding temperature is up to 380 °C and 390 °C, the conductivity decreases firstly and then increases, but the bending strength tends to increase.
- (3) The optimum resin content is 20%; the electrical conductivity and bending strength of the composite with 20% PPS resin content, molded at 380 °C for 30 min, are 118.9 S cm⁻¹ and 52.4 MPa, respectively; when the composite is molded at 390 °C for 30 min, the electrical conductivity and bending strength can attain 105 S cm⁻¹ and 55.7 MPa, respectively.

Acknowledgement

The authors would like to thank Chevron Phillips Chemical International Incorporation for supplying us free polyphenylene sulfide sample.

References

- [1] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47.
- [2] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Appl. Electrochem. 30 (1) (2000) 101–105.
- [3] T. Wu, Y.-P. Zheng, Z.-H. Huang, et al., J. Mater. Sci. Eng. 23 (2) (2005) 196–199.
- [4] J. Huang, D.G. Baird, J.E. McGrath, J. Power Sources 150 (2005) 110–119.
- [5] F. Mighri, M.A. Huneault, Polym. Eng. Sci. 44 (9) (2004) 1755–1765.
- [6] S.B.T. Radhakrishnan, S. Ramanujam, et al., J. Power Sources 163 (2) (2007) 702–707.
- [7] S.I. Heo, J.C. Yun, K.S. Oh, K.S. Han, Adv. Compos. Mater. 15 (1) (2006) 115–126.
- [8] R.C. Talar, S. Rabii, Phys. Rev. B 25 (6) (1982) 4126–4141.
- [9] T. Zhang, X.-H. Wang, Z.-M. Zhang, New Chem. Mater. (2) (1996) 13–17.