

New Polymer Bipolar Plates for Polymer Electrolyte Membrane Fuel Cells: Synthesis and Characterization

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ABSTRACT: Carbon black (CB) and polyvinylidene fluoride (PVDF) composites were obtained and subsequently characterized, both microstructurally (DSC and DMA) and electrically. In addition, the electrochemical performance of these materials was tested in the form of bipolar plates, expressly manufactured for this purpose and incorporated in a conventional fuel cell. The results obtained allow for the conclusion that CB incorporation into PVDF yields polymer composite materials with electrical conductivity of about 2.4 S/cm, which may be thermally processed and given any convenient shape with the means conventionally applied in the field of polymer technologies. It was found that CB concentration slightly affects the microstructural parameters of the composites (melting temperature, glass-transition temperature, Avrami kinetic parameters, etc.). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2817–2822, 2002; DOI 10.1002/app.10257

Key words: DSC; DMA; electrical conductivity; electrochemical performance; fuel cell; polymer electrolyte membrane fuel cells

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFC) have been developed as an alternative power source for both stationary and mobile applications because of their high power density and low operating temperatures.¹ Their acceptability in the future, especially for transportation applications, will depend on the ability to develop systems, which are competitive in price to that of the internal combustion engine. Typical stack costs today range between \$2000 and \$5000/kW, whereas the ultimate goal to replace the internal combustion engine² is \$20–\$50/kW. To achieve this tar-

get significant cost reductions of fuel cell stack components like membrane/electrode assemblies and bipolar plates have become key aspects of research and development. To date, the bipolar plate is the most problematic and costly component of PEMFC's stack.³

The bipolar plate is a multifunctional component within the PEMFC stack. Its primary function is to supply reactant gases to the gas diffusion electrode by a flow field in the surface. It must also provide series electrical connection between the individual cells and effectively remove product water. To satisfy these requirements, the base material for bipolar plates requires certain properties. An ideal bipolar plate would be high in electrical conductivity and corrosion protection, of low density but with mechanical strength, impermeable to reactants, chemically inert, and allow

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Table I Thermal Data of the Different Samples

Sample	Composition PVDF/CB (wt %)	T_g (K)	T_c (K)	T_m (K)	n	$\log K$ (min ⁻ⁿ)
BP-41	100/0	228.5	423	448.3	2.1	-0.981
			424	447.8	2.3	-1.429
			425	447.7	2.6	-2.117
BP-42	80/20	233.4	424	448.0	2.4	-1.231
			425	447.8	2.3	-1.475
			426	448.3	2.3	-1.894
BP-43	70/30	234.1	424	447.9	1.4	-1.192
			426	449.4	2.4	-0.557
			427	449.4	2.3	-0.924
BP-44	60/40	236.7	424	447.2	2.1	-1.101
			425	447.2	1.9	-1.218
			426	447.2	1.8	-1.356

for ease of manufacture.⁴ To attain the suggested cost target of \$20–\$50/kW for transport applications a lightweight, robust, low-cost plate material is required.

Nowadays, the most commonly used bipolar plate material is graphite. Advantages of graphite are its excellent resistance to corrosion, its low bulk resistivity, its low specific density, and its low electrical contact resistance with electrode backing materials. Disadvantages of graphite are its cost, the difficulty of machining it, and its brittleness.⁵ Because of the brittleness of graphite, bipolar plates need to have a thickness in the order of several millimeters, which makes a fuel cell stack heavy and voluminous.

Pure metals and stainless steel,^{6–8} either with or without a protective and conductive coating, are being researched as possible bipolar plates. However, the use of metals has shown problems associated with a possible corrosion in the fuel cell environment.

In light of these difficulties, much of the recent work on fuel bipolar materials has been concentrated on graphite/polymer composites.^{9,10} Composite materials offer advantages of low cost, low weight, and easier manufacturing over the above-mentioned materials (graphite, metal, stainless steel).

At the present state of the art the successful procurement of these systems (polymer composites filled with conducting additives) depends on the adequate choice of the polymer system. Contrary to the predominant opinion some years ago, the polymer matrix is not just the network supporting the filler; it plays an essential role in many other aspects conditioning the performance

of the end material. It favors particle interconnectivity (percolation); it provides for electrical conductivity through a tunnel-type mechanism in the event of deficient percolation; it tolerates the incorporation of large amounts of additive with no deterioration of its mechanical properties, thus favoring both the conducting mechanisms and the dimensional stability of the resulting composite.

In this research polyvinylidene fluoride (PVDF) blends were used, incorporating varying amounts of carbon black. The composites thus obtained are characterized from a microstructural (T_g , crystallization kinetics, etc.) and electrical point of view to know their ability to be used as bipolar plates in polymer fuel cells.

EXPERIMENTAL

The materials used were polyvinylidene fluoride (PVDF) Solef 6010 (Solvay) and carbon black (CB) Isaf N200 (Cabot Laboratories) in powdered form (20 nm) and density 1.8 g/cm³.

Blending of components was carried out in an internal mixer (Haake torque rheometer type); chamber temperature was set to 200°C and the rotor rate fixed at 45 rpm; blends remained in the chamber for 15 min, once the torque had stabilized. The composition of the obtained samples can be seen in Tables I and II.

Bipolar plates (0.3 cm thickness and 50 cm² area) were formed in a Collin hydraulic press for thermoplastics.

Dynamic mechanical analyses of the different samples were carried out on a dynamic mechanical thermal analyzer DMTA MKII from Polymer

Table II Conductivity of the Samples at Different Temperatures

Sample	Composition PVDF/CB (wt %)	<i>T</i> (°C)	σ (S cm ⁻¹)
BP-42	80/20	20	0.30
		30	0.29
		50	0.29
		70	0.28
		90	0.23
		110	0.22
BP-43	70/30	20	0.39
		30	0.38
		50	0.37
		70	0.35
		90	0.31
		110	0.28
BP-44	60/40	20	2.31
		30	2.36
		50	2.21
		70	2.14
		90	1.94
		110	1.87

Laboratory (UK) at 3, 10, and 30 Hz over a temperature range from -140 to 140°C and a heating rate of $2^\circ\text{C}/\text{min}$.

Glass-transition temperatures and isothermal crystallization of the samples were analyzed by means of a Mettler TA 4000 differential scanning calorimeter. Samples were heated above their melting point (260°C) and then held at that temperature for 5 min to delete their thermal history. For glass-transition temperature measurements the samples were quenched to -100°C at a rate of $100^\circ\text{C}/\text{min}$. Glass-transition temperature was defined as the temperature corresponding to the medium point of the increment in the specific heat generated during the transition. The crystallization thermogram was recorded at a rate of $10^\circ\text{C}/\text{min}$ until the crystallization temperature of choice was reached. Subsequently, the samples underwent a controlled heat-treatment program ($10^\circ\text{C}/\text{min}$) up to 260°C , in which the respective melting thermograms were likewise recorded.

Conductivity measurements of the samples were carried out using the two-probe technique with a Hewlett–Packard 6614C dc power supply (Hewlett–Packard, Palo Alto, CA) and two Hewlett–Packard 34401A multimeters controlled by a computer. The amplitude of the applied dc signal was 0.1 V. Samples were painted with Ag thin film (Ceramic Lustre 200 in xylene; Emet-

ron), to optimize the electrode–electrolyte interface, and sandwiched between two brass-blocking electrodes in the cell measurement. The samples (1 cm^2 surface and 0.1 mm thick) were placed in an Oxford Instrument DN 1710 cryostat provided with a liquid nitrogen chamber, specially designed for measurements at variable temperature (between 20 and 110°C).

The fuel cell employed for this work was a commercial single cell (Electrochem) with a 50-cm^2 active area. This fuel cell consisted of a Nafion 117 as electrolyte and porous gas diffusion electrode $1\text{ mg Pt}/\text{cm}^2$ loading (20 wt % Pt/C) and gas pressure used was $1\text{ kg}/\text{cm}^2$. This membrane electrode assembly (MEA) was sandwiched between two graphite bipolar plates using a hot-pressing procedure. Each graphite plate included a thermocouple well, a connector for accurate temperature and voltage measurement. Finally, the resulting cell was sandwiched between two copper ends, through which the current was collected.

Three polymer composite materials were studied as bipolar plates. The composite material replaced the graphite bipolar plate on the anode side. The experiments were conducted by analyzing the behavior of the MEA, which was operated between a graphite plate on the cathode side and composite material on the anode side. The behavior of the MEA between graphite plates was taken as reference.

Characterization of the single cell was evaluated by measuring the voltage and temperature with a varying resistive load (HP 6060B) under operating conditions. The cell resistance was measured by a milliohmeter (HP 4338B). The tests were carried out at 60°C , atmospheric pressure, 70°C for the anode humidifier, 65°C for the cathode humidifier, hydrogen as fuel, and oxygen or air as oxidant.

RESULTS AND DISCUSSION

Microstructural Analysis

Taking into account that we are dealing with semicrystalline composites, their microstructural characterization was conducted in the amorphous zone (assessing the effect produced by carbon black on the glass-transition temperature), as well as in the crystalline zone (analyzing the changes produced in the crystal structure resulting from CB incorporation).

For glass-transition temperature (T_g) analysis two different techniques, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), were applied to compare test reproducibility. Figure 1(A) shows the effect of carbon black on composite T_g obtained through DSC. As can be observed, T_g increases noticeably as a function of the CB portion in the composite, which suggests a crosslinking effect,¹¹ interfering with polymer backbone movement in the matrix of the material. Hence the T_g of filler-free PVDF is consistently lower than that of PVDF containing any CB concentration. Figure 2 shows the dynamic mechanical spectra (by DMA) of all samples.

Structural analysis of the crystalline zone of the composites was carried out by determining their crystallization kinetics, that is, the variation of the fraction of crystallized material χ_t as a function of time t . The kinetics of isothermal crystallization were analyzed by means of the Avrami equation¹²:

$$(1 - \chi_t) = \exp(-Kt^n)$$

where n is the Avrami exponent, a numerical value that provides information on the type of nucleation and the geometry of the growing crystals; and K is the rate constant. The Avrami exponent n , the rate constant K , the crystallization temperature T_c , and the melting point temperature T_m of the isothermally crystallized compos-

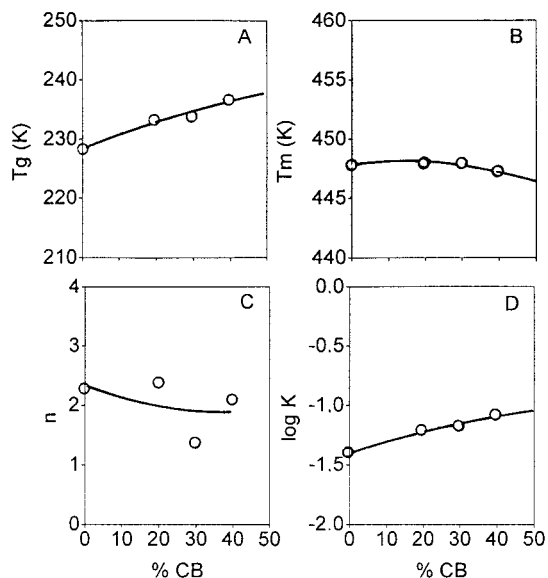


Figure 1 Microstructural (A) and kinetic (B, C, and D) parameters of PVDF/CB composite.

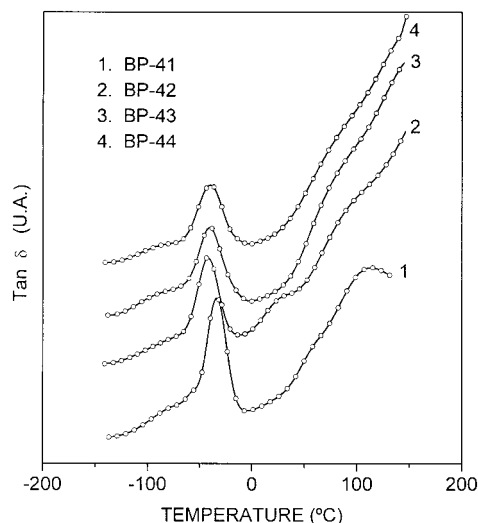


Figure 2 DMA analysis of the samples.

ites are shown in Table I. The graphs of these parameters are shown in Figure 1. CB incorporation into PVDF matrices affects each of the parameters governing the crystallization kinetics in a different way. Thus, from the perspective of growth geometry of the crystalline PVDF entities, whose significance is interpreted through the value of Avrami's exponent n , Figure 1(C) shows that the value of n (measured at a crystallization temperature of 174°C) tends to basically diminish with increasing CB portion. This fact can be interpreted as a transition from a hybrid two- and three-dimensional growth geometry toward a pure three-dimensional one, exclusively attributed to the effect of CB concentration. The growth rate, as represented by the rate constant K , is likewise influenced by CB concentration [Fig. 1(D)]. The crystal growth rate increases at any crystallization temperature, as a consequence of the physical nucleating effect exerted by CB particles on the growth of PVDF spherulites. The melting temperatures of the composites, however, do not significantly vary and hence prove to be independent of CB concentration. This is indicative of the fact that, under experimental conditions, the crystallization process yields crystal sizes of approximately the same dimensions as those of our four samples.

Conductivity Analysis

The conductivity of the samples was measured as a function of temperature, according to the procedure described in the experimental part of this

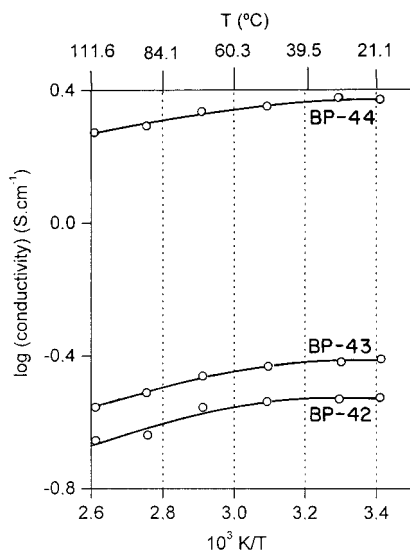


Figure 3 Effect of the temperature on the conductivity of the samples (Arrhenius coordinates).

work. The respective data are compiled in Table II and the conductivity plots against temperature on Arrhenius coordinates are shown in Figure 3. Conductivity proves to diminish slightly with temperature, thus displaying the typical behavior of an electronic conducting metallic material. The maximum value obtained was 2.36 S/cm, corresponding to sample BP-44 (40%CB) and 30°C.

Figure 4 shows conductivity (measured at 90°C) plotted against CB content. When the CB content changes from 30 to 40% a sudden rise is observed, with the percolation threshold appearing just in this range. Higher CB concentrations

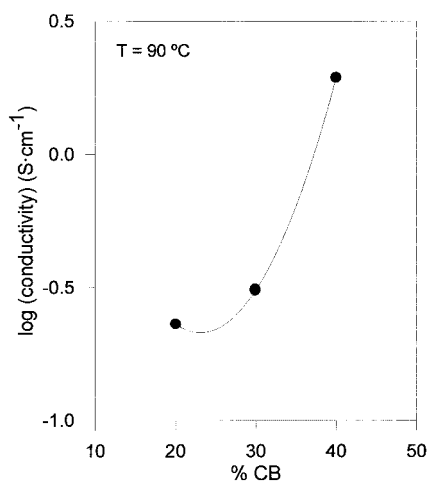


Figure 4 Effect of the CB concentration on the conductivity of the PVDF.

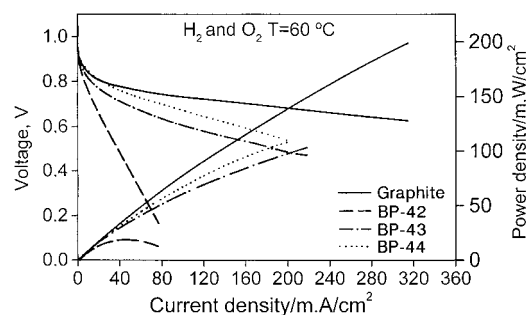


Figure 5 Polarization curves for new bipolar plates based on PVDF/CB and graphite plates with oxygen as oxidant.

could not be tested because of the difficulty of incorporating CB into the PVDF matrix.

Electrochemical Performance of Materials

Figure 5 shows the single-cell polarization curves for each of the bipolar plate composite materials with oxygen as a reactant. The results obtained with graphite (reference material 0.5 mΩ) are also displayed for comparison. The results show a lower performance than that of the reference cell. One reason could be the high internal resistance of the new composites, which are one order higher than the reference data for BP-44 (4.2 mΩ) and two orders higher for BP-42 (25 mΩ) and BP-43 (33 mΩ). The best behavior was observed for the composite material BP-44, with a power density of 100 mW/cm² at 200 mA/cm². On the other hand, the lowest performance level was recorded for BP-42, probably the result of the high value of internal resistances.

The polarization curves obtained with air as an oxidant are displayed in Figure 6. The performance of BP-44 and BP-43 was very similar and

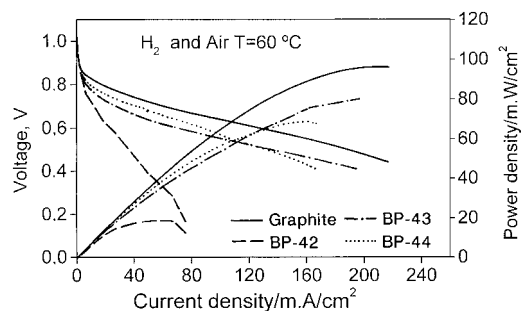


Figure 6 Polarization curves for new bipolar plates based on PVDF/CB and graphite plates with air as oxidant.

close to the commercial value; with BP-43 it was possible to achieve 75 mW/cm^2 at 200 mA/cm^2 . The performance of BP-42, however, showed a poor behavior. Once again this is likely to be attributable to the high value of internal resistances.

Figures 5 and 6 exhibit the effect of oxygen and air as oxidants on the performance of the single cell. Results improved with oxygen as the oxidant. This behavior may be explained in terms of a greater degree of mass transport limitations, when air is used as the oxidant, instead of oxygen.

Present results obtained with BP-44 and BP-43 qualifies these materials as promising candidates for PEMFC bipolar plates. Even though a further reduction of material resistances could enhance cell performance, the materials tested appear to be a good choice for high-performance and cost-efficient PEMFC bipolar plates.

CONCLUSIONS

These new polymer composites may be thermally processed and given the convenient form to be used as bipolar plates.

Conductivity results indicate that these materials possess an electronic conductivity up to $0.2.4 \text{ S/cm}$ ($\%CB = 40\%$ and $T = 30^\circ\text{C}$), which diminishes slightly with increasing temperature, thus displaying the typical behavior of an electronic conducting metallic material.

The electrochemical performance of these materials was tested in the form of bipolar plates in a conventional fuel cell. The best results were obtained when using oxygen as oxidant and the

material with the highest CB concentration (100 mW/cm^2 at 200 mA/cm^2). However, the results show in all cases a lower performance than that of the reference cell and indicate that further research has to be done to reduce the internal resistance of the composites.

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