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Polymer composites bipolar plates for PEMFCs

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Abstract

In order to improve their commercial liability, many scientific and technological efforts are being performed on fuel cell systems. The bipolar plates represent a major part of the stack with about 80% of the total weight and 30 to 40% of cost. On the technical point of view, bipolar plates should fulfill functional challenges besides ensuring the mechanical strength of the stack. As a result an optimal material for bipolar plate application should present an unusual balance of properties, essentially high electrical conductivity and good mechanical strength. To date, many different materials for bipolar plates have been investigated and an alternative solution consists in polymer composite that combine the processability and mechanical properties of the polymeric phase and the conductivity of the carbon fillers. This communication provides a state-of-the-art review of the current development, manufacturing and structure-property relationship of polymer composites designed for bipolar plates applications. Both thermoset resins and thermoplastics were considered and combined to many different carbon fillers: graphite, carbon fibers, carbon black, carbon nanotubes. The interests and limitations of these formulations are presented in terms of processability and most relevant properties. A debate on the optimization of electrical and mechanical properties is presented.

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1. Introduction

Fuel cells are expected to play a major role in the economy of this century. In order to reduce the impact of our energy consumption on the environment, fuel cells represent an attractive solution, for instance addressing the issue of intermittent behavior of renewable sources. The proton exchange membrane fuel cells (PEMFCs) convert hydrogen and oxygen (or air) into electricity at low operation temperature (< 100°*C*[29]). In order to improve their commercial liability, some applications as for automotive application may require better volumetric and gravimetric power density (> 1kW/L and 1kW/kg)[16, 32, 46]. But

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cost and durability remain the major parameters to improve for the extensive use of fuel cells. Many efforts are therefore performed not only on membrane electrode assemblies (MEA), but also on bipolar plates (BPPs) which constitute the backbone of a fuel cell stack[32].

BPPs represent one of the most important of the stack with about 80% of total weight [32] and 30 to 40% of cost [16, 32]. BPPs should fulfill many functions : (*i*) homogeneously distribute gases over the area of the cell, (*ii*) separate the fuel and oxidant gases and prevent gas leakage, (*iii*) collect the current produced in the electrochemical reactions, (*iv*) discharge the water produced, and (*v*) ensure the mechanical strength of the stack.

On the material stand point, BPPs application should thus present a balance of various physical and chemical properties. These specificity requirements on which the development of BPPs is based are issued by the Department of Energy (DOE) and several companies[33]. The most relevant properties are the electrical and the mechanical properties and their durability. Theses are characterized by[33, 56]: in plane electrical conductivity larger than 100 S.cm⁻¹, flexural strength above 59 MPa, high corrosion resistance and low interfacial contact resistance close to 20 m Ω .cm² at 140 N.cm⁻².

To date, different materials for BPPs have been investigated, but non porous graphite is the reference material in terms of durability and performance, thanks to its electrical conductivity and corrosion resistance. Its porous structure induces however a brittle behavior and allows gas permeation through the channels formed after machining. Post processing, such as resin impregnation is an efficient way to fill the holes[33], but it further increases the price of the products. Extensive efforts have been made to develop alternative materials, essentially metallic and composite bipolar plates.

Materials used for metallic plates are generally based on stainless steel, titanium[32]. Theses metallic bipolar plates present high bulk and thermal conductivities, good mechanical properties and negligible gas permeability. However metals lack of corrosion resistance[33] and the cations resulting from electro-corrosion are likely to act as membrane contaminant, altering the performance and durability of the systems[3, 27]. Considerable attempts have been made using noble metals, stainless steel and various coated materials (nitride - and carbide-based alloys, conducting polymer) to improve the corrosion resistance of the metals. But, to date the corrosion resistance obtained with these materials remain lower than the BPPs requirement and the processing of BPPs with these materials is often expensive[56].

An alternative solution exists thanks to polymer composite combining the processability and mechanical properties of the polymeric phase to the conductivity of the carbon fillers. In order to reach the targets presented above, an unusually large amount of loading is generally employed. Many attempts have been described in the literature giving rise to interesting and complementary results. In this review we will first describe the common formulations tested. Both thermoset resins and thermoplastics were considered and combined to many different carbon fillers : graphite, carbon black, carbon fiber, carbon nanotubes. The interests of these formulations are presented in terms of processability and most relevant properties (electrical and mechanical properties). In the second part, different combinations are suggested in order to reach the two main requirements of the materials used for the fabrication of bipolar plates. In addition, a debate on the optimization of electrical and mechanical properties is presented.

2. Materials

This section is devoted to the presentation of the individual materials, it will first concern the carbon fillers and the polymeric hosts.

2.1. Fillers

Polymers are commonly electrical insulators, but some conductivity may be obtained by the additive fillers. Two types of fillers may be considered, either based on metallic conductors, or the derivatives of carbon. Although the metallic conduction may be very high, most of studies in the literature are concerned with carbon fillers. Few studies concern BPPs based on polymer metal composite[32, 56](and references therein) and this can be explained by the fact that this solution could hardly compete for this application, combining the limitations of metal and composites.

2.1.1. Graphite (Gr)

Graphite is the most crystalline form of carbon, apart from diamond and fullerenes. It exhibits the properties both of metal such as thermal and electrical conductivity and of a non-metal such as inertness, high thermal resistance and lubricity. Usual properties of these fillers are presented in table 1. Theses micronic fillers present a low specific surface and an aspect ratio close to one and therefore induce little mechanical properties improvement. In addition, their electrical conductivity is rather high compared to others carbon fillers.

	Graphite	Carbon fibers	Carbon black	Carbon nanotubes
Density $(g.cm^{-3})$	2-2.25	1.79-1.99	1.7-1.9	2
Particle size	6-100 µm	L : 10-100 µm	14-250 nm	L : 10-100 µm
		D : 4-10 µm		D : few nm
Specific surface area (m^2/g)	6.5-20	0.27-0.98	7-560	200-250
Aspect ratio	Close to 1	6-30	Close to 1	1000-50000
Conductivity $(S.cm^{-1})$	400-1250	0.03-0.7	2.5-20	$10^{-4} - 10^{2}$

Table 1. Principal properties of fillers[51,53,63] *Aspect ratio is the ratio between the largest and the lowest dimension of the particle.

2.1.2. Expanded graphite (EG) & Graphite Nanoplatelets (GNP)

The layers in graphite are bonded by weak van der Waals forces and an intercalation of atoms and molecules is possible between the graphene plans. Natural graphite with a layered structure can be converted to graphite oxide (GO) or graphite intercalation compound (GIC) through chemical oxidation[21,60], then to expanded graphite (EG) with the action of temperature. Further exfoliation in a solvent leads to graphite nanoplatelets (GNP)[7]. The final GNP contain no functional groups on their surfaces, that is similar to graphite. For EG, the expansion induces a modification of spacing between graphite layers, inducing a reduction of the density between 10^{-3} and 10^{-2} g.cm⁻³, whereas the surface area may increase with the mean ratio aspect to $40 \ m^2.g^{-1}$ and 15 respectively[21]. Moreover the electrical properties are improved, since a conductivity of $12500 \ S.cm^{-1}$ is measured by Celzard et al.[6] with these fillers. The "paper" materials based on GNPs have been reported with conductivities as high as $350 \ S.cm^{-1}$ [8] much above the needs for the BPPs application.

2.1.3. Carbon fibers (CF)

Carbon fiber is described as a fiber containing at least 90% carbon. It is usually obtained by the controlled pyrolysis of appropriate polymeric fibers. The most prevalent precursor remains polyacrylonitrile (PAN). Carbon fibers are used in composites with a lightweight matrix. The usual properties of carbon fiber are gathered in table 1. Compared to graphite, carbon fibers, which are also micronized fillers, present a high aspect ratio highly desirable for strength and stiffness, to the expense of a lower intrinsic conductivity.

2.1.4. Carbon black (CB)

Carbon black is a generic term for a large variety of products used principally for the reinforcement of polymer, as black pigment, and for electrical conductivity. Although based on carbon, carbon black differs from graphite and carbon fibers because it is composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions. The primary dispersible unit of carbon black is referred to as an "aggregate" that is a discrete, rigid colloidal entity. The aggregate is composed of spheres, which are generally called primary "particles" ou "nodules". These nodules are composed of many tiny graphite-like stacks[22]. The main properties of carbon black are observable in table 1. Compared to graphite or carbon fibers, carbon black present a complex morphology that could fill the holes left with the previous fillers. Its intrinsically relatively low conductivity and large specific area are the drawbacks of this filler.

2.1.5. Carbon nanotubes (CNT)

The carbon nanotubes are nanoscopic particles constituted by a tubular structure of carbon atoms. They present a diameter between 1 and 50 nm for a length commonly of one micrometer up to few centime-ters[43]. Consequently, their aspect ratio can be very large, table 1. Carbon nanotubes can be found now in a commercial form of multiwall (MWNT) or in the laboratories as single wall (SWNT)[67]. Since their discovery, the nanotubes have induced a very large scientific interest because of their unique physical properties. The main properties of these fillers are presented in table 1. With a very large elastic modulus, carbon nanotubes are known as effective reinforcing agent. Depending on their molecular structure, carbon nanotubes with a small diameter show either semi-conducting or metallic behaviour, table 1.

2.2. Polymers

From the previous discussion, it seems that electrical performance of composite BPPs is determined by the conductive fillers added to the formulations. However, the polymer matrix also influences the electrical behavior of the composite. Both thermoplastic and thermosetting resins may be employed [16, 32]. Regardless of the nature of the polymer, the preparation of BP requires a fairly large proportion of fillers, and will eventually cause wetting problem[26]. If the difference in the surface energies between the polymer and the fillers is low, then the polymer should efficiently wet the fillers, allowing an increase in the filler concentration, before porosity appears in the composite. Dhakate et al. [21] also proposed that in contrast polymers with polar groups favoured the conductive paths, enhancing the electrical conductivity of the composite.

2.2.1. Thermosetting resins

Various types of thermosetting resins have been studied as possible matrix for composite bipolar plates. There are a number of benefits in using thermosets. During processing, their viscosities are low and they thus can be loaded with high level of conductive fillers. These materials also have a low density and a good corrosion resistance combined with a dimensional and thermal stability.

Three types of thermosets are mostly described in the literature for the fabrication of BPPs : epoxy[23, 40], phenolic[21] and vinylester[36, 39, 42] resins. The same fillers are commonly incorporated in the formulations : expanded graphite, natural and synthetic graphite, carbon black, carbon fiber and carbon nanotubes. Theses thermosets can be liquid (vinylesters in styrene solution[36, 39, 42] or others resins dissolved in a solvent[21, 23]) or solid under powder form (epoxy[40], phenolic novolac[21]). These different natures enable various method of processing, each system presenting its benefits and disadvantages. The use of liquid resin enables the incorporation of high filler content, nevertheless the use of solvent is a disadvantage for processing conditions and thus for the industrialization. In the case of the powder form, no solvent is used but the obtained compound is often very powdery and thus its molding is difficult. Another disadvantage is the time cycle, which can be very long, because a post-curing is often necessary to reduce the residual solvent content.

2.2.2. Thermoplastics

Many authors also investigate the use of thermoplastics for this application. At first glance, these materials seem less competitive because they commonly can incorporate fewer amount of filler than thermoset resins. A short cycle time associated with solvent free process may however overcome this drawback. Different thermoplastics have been tested for BPPs application and the most used is polypropylene (PP)[24,42,47]. It combines a low cost, good processing conditions and mechanical properties. Polyvinylidene fluoride (PVDF) is also envisaged[2, 20, 61, 62] because it shows a serie of unusual properties of interest for the application: good barrier properties, chemical inertness, good mechanical properties and moisture resistance. Some studies concern poly(phenylene)sulfide(PPS) [9–11, 17, 18, 64], which has good mechanical properties and may be prepared with high filler contents. As for thermoset resins, the most used preparation process remains the compression[25, 42, 47], even if the injection molding seems under development[47, 65, 66]. One of the drawbacks of injection molding is that the maximal filler content, that can be incorporated in the formulation, is lower than for a formulation for compression. In addition, the final properties are strongly dependent on the processing conditions and particularly on the flow direction in the mold.



Fig. 1. In plane conductivity versus carbon filler content for several composites filled graphite (Gr), low structure carbon black (LSCB), high structure carbon black (HSCB), carbon fiber (CF), carbon nanotube (CNT) and carbon black (CB)

3. Electrical and Mechanical properties

3.1. Electrical properties

Besides BPPs application, many studies have been conducted to develop composites with high electrical conductivity. When conductive fillers are incorporated in a polymer phase, a low increase in the conductivity of the composite can be noticed for the low filler contents. Nevertheless, for a critical filler content named percolation threshold ϕ_c , the conductivity increases sharply of several orders of magnitude. As shown in figure 1, the evolution of the conductivity versus filler content usually exibits a typical S-shaped dependency with three regions (dielectric, transition, conductive). From these curves, it is possible to deduce the percolation thresholds ϕ_c for each composites presented. The examples presented in figure 1 show that the low size (CB, CNT), the high aspect ratio (CNT) and the high specific surface (CB, CNT) increase the probability of particle-particle contact, reducing the percolation threshold[1, 6, 41, 49]. As shown in table 2, this general trend is confirmed with other systems. Moreover several studies of Sumita et al.[48, 55] demonstrated that ϕ_c also depends on the polymer species and tends to increase with the surface tension of polymer.

The most difficult requirement for composites BPPs is the high electrical conductivity. Conductivity is directly calculated from resistance measurements of the composite plates. The two types of resistance measurements generally performed for BPPs are in plane or bulk, *i.e.* along the surface, and through plane, *i.e.* perpendicular to surface. Although much more difficult to develop on the technical point of view, through plane resistance is directly related to the operating conditions and should be preferred[19,31]. Approximate knowledge of ϕ_c of the different carbon fillers can be useful to determine the maximal filler content because these two parameters appear roughly to vary proportionately. This can be shown in table 2 and in figure 2, which presents the maximal conductivity σ_{max} obtained for different systems versus filler content. Due to its high ϕ_c close to 50wt% [25](figure 1), graphite is thus an interesting filler, because it can be incorporated at high filler content in the formulation. Moreover, the highest conductivities are obtained for Gr and EG, figure 2 and table 2. For few composites, this property is even above the DOE requirement. The composites filled CF or CB or CNT or GNP have intermediate electrical properties. This seems to be in agreement with filler conductivity, since EG and Gr are very conductive fillers, table 2. In addition, even if the polymer matrix can alter the electrical properties[48], it seems that this factor plays a less important role than the filler nature and content.

Matrix polymer	Filler type	References	ϕ_c	ϕ_m	σ_{max}	$\sigma_{flexion}$	Process
			wt%	wt%	$S.cm^{-1}$	MPa	
PODS	EG	[54]	45	50	130	32	Solution blending
Phenolic Novolac	EG	[21]	5	90	1000	13	compression
Phenolic Novolac	EG	[21]	-	50	100	54	Compression
HDPE	Gr	[57]	50	75	11	-	Compression
PP	Gr	[42]	-	80	131	24	Compression
Phenolic Resol	Gr	[45]	45	81	141	-	Compression
Epoxy	Gr	[5]	-	81	1	-	-
Epoxy	Gr	[40]	-	91	73	18	Compression
Epoxy	Gr	[36]	-	77	50	30	Compression
Vinylester	Gr	[36]	-	77	50	38	Compression
Phenolic Resol	Gr	[36]	-	77	130	38	Compression
Phenolic novolac	Gr	[36]	-	77	130	60	Compression
PP	Gr	[24]	-	80	7	-	Melt compounding
PP	Gr	[24]	-	80	23	-	Solution blending
Epoxy	CF	[52]	1.5	4	0.0002	-	Compression
HDPE	CF	[57]	7.5	20	11	-	Compression
EO Rubber	CF	[26]	18	41	1	-	Compression
Epoxy	CB	[28]	0.04	1.34	11	-	Compression
HDPE	CB	[57]	15	35	2	-	Compression
EO Rubber	HSCB	[26]	26.1	47	1	-	Compression
EO Rubber	LSCB	[26]	58	71	0.1	-	Compression
Epoxy	CNT	[4]	0.04	0.6	8	-	-
HDPE	CNT	[68]	4	6	0.01	-	-
Polyaniline doped	GNP	[50]	0.7	10	522	-	-
PMMA	GNP	[50]	0.7	10	1	-	-
PP	GNP	[50]	0.7	10	0.005	-	-

Table 2. Values of electrical percolation thresholds ϕ_c and maximal electrical conductivities σ_{max} with corresponding filler content ϕ_m , flexural strength $\sigma_{flexion}$ and the used process for composites filled with different carbon fillers: expanded graphite EG, graphite Gr, carbon black CB, carbon fiber CF, carbon nanotube CNT, graphite nanoplatelets GNP



Fig. 2. Maximal conductivity σ_{max} obtained for different composites filled with one type of carbon fillers: expanded graphite EG, graphite nanoplatelets GNP, graphite Gr, carbon fiber CF, carbon black CB and carbon nanotube CNT as a function of carbon filler content



Fig. 3. a) In plane conductivity versus carbon filler content for composites filled graphite (Gr) or expanded graphite (EG), b)In plane conductivity versus graphite content for composites filled with different types of carbon fillers

The influence of graphite content on the conductivity of the composite is presented in figure 3 a). The addition of graphite in large quantity in a composite enables to improve electrical properties, but the conductivity level required by the application is often not reached. The use of EG enables to obtain similar conductivity level with lower filler content than that of Gr filled composites. For Gr filled epoxy [40], a critical graphite content can be observed, above that the electrical conductivity decreases rapidly with increasing Gr content. It is concluded that an insufficient amount resin might prevent full wetting of the graphite particles and induces porosity in the composite.

Polymer composites containing carbon based fillers have been studied in the literature. The use of combination of different carbon fillers would be a good way to get balanced properties [15, 58, 59]. In fact some polymer-base composite containing two or three different carbon fillers (Gr, EG, CB, CF, CNT) have been investigated and a sum-up of the obtained electrical properties is presented in figure 3 b) and table 3. For most of materials presented, it is found that upon addition of complementary carbon fillers (CB, CF, CNT) to Gr, up to a critical value, electrical conductivity increases. Upon further increases of complementary carbon filler content, conductivity decreases. It seems that composites with an optimal of complementary carbon filler content provide higher conductivity, up to three times higher than with only Gr in composites. This indicates that others carbon fillers (CB, CNT, CF) formed an additional conductive network in composites. The reduced size of CB and CNT allows for filling voids between Gr particles, thus increasing the number of conductive paths and the bulk electrical conductivity of the composite[14]. This is not unexpected because the intrinsic conductivity of EG and Gr is much larger than that of CB or CF or CNT. It means that other carbon fillers further reveals the conductivity of graphite[15]. As shown in figure 3 b), this synergistic effect is less significant for PP/Gr-CB[24] and Ph resol/Gr-CF[45]. Due to difficult processing conditions (high filler content, high viscosity of the compounds for thermoplastic), the filler dispersion is certainly poor hindering the electrical properties.

3.2. Mechanical properties

A proper balance between the electrical conductivity, mechanical properties and processing characteristics is an important requirement for the design of conducting polymer composites. In order to reach electrical properties required by the application of BPPs, a large amount of carbon filler content is required, the impact of mechanical properties is now presented. The flexural strength versus graphite content for different Gr filled composites is presented in figure 4 a). An important decrease in the flexural strength is observed with increasing graphite content for all materials presented, even at low filler content. The mechanical properties

Matrix polymer	Filler type	References	ϕ_m	$\phi_{CB/CF/CNT}$	σ_{max}	$\sigma_{flexion}$	Process
			wt%	wt%	$S.cm^{-1}$	MPa	
Phenolic novolac	EG-CB	[21]	55	CB=5	280	52	Compression
Epoxy	Gr-CB	[40]	84.4	CB=4.5	150	20	Compression
Epoxy	Gr-CB	[36]	75.8	CB =25	80	44	Compression
Vinylester	Gr-CB	[36]	75.8	CB=20	250	55	Compression
Ph resol	Gr-CB	[36]	75.8	CB=25	250	50	Compression
Ph novolac	Gr-CB	[36]	75.8	CB=25	330	75	Compression
PP	Gr-CB	[24]	80	CB=25	36.4	-	Melt compounding
PP	Gr-CB	[24]	80	CB=5	27.3	-	Solution blending
Phenolic Resol	Gr-CB	[45]	80	CB=19	344	-	Compression
Epoxy	Gr-CF	[40]	84.4	CF=6.3	235	55	Compression
Phenolic Resol	Gr-CF	[45]	81	CF=0.9	118	-	Compression
Epoxy	Gr-CNT	[40]	70.6	CNT=0.6	740	42	Compression
PP	Gr-CNT	[42]	80	CNT=1	750	41	Compression
Phenolic Resol	Gr-CB-CF	[45]	81.4	CB =19 CF=3.8	333	51	Compression

Table 3. Values of maximal electrical conductivities σ_{max} with corresponding total carbon filler content ϕ_m , and CB or CF or CNT content $\phi_{CB/CF/CNT}$ added in the formulation, flexural strength $\sigma_{flexion}$ and the used process for composites filled with a mix of carbon fillers: Gr-CB, Gr-CF, Gr-CNT, Gr-CF.

remain lower than that required by the application. For low filler content, the properties are dominated by the resin content, consequently the bending strength is relatively stable or slightly increases with increasing filler content. At higher Gr or EG content, properties are mostly dominated by the filler content and in this case, composites become brittle[34, 35]. When mixing polymer with the conductive fillers, besides an increase in conductivity, an increase in Young's modulus and tensile strength is observed, accompanied by a lower elongation at break and reduced toughness of the material [12, 13]. At higher filler content, processing of the material becomes difficult, because of the increase in viscosity. As showed by Chodak et al. [12, 13], a significant decrease in the elongation at break occurs within the content range around the conductivity percolation threshold. The formation of the conductive network, leading to a substantial increase in conductivity, has a pronounced effect on the mechanical properties via a formation of a more or less continuous filler phase. This can be mainly explained by porosity in highly filled composites. In fact, porosity is linked to filler dispersion in the polymer phase and to the polymer-filler wetting: the apparent density of a composite versus filler content reaches a maximum^[44]. Above this critical value, the apparent density decreases with the filler content, because of the bad wetting of polymer inducing porosity formation. As for cements and concretes, the mechanical strength in tensile test and in flexion decreases with increasing porosity volume fraction[30, 38]. One way to limit the porosity is to add in the formulation a mix of particles with different sizes, in order to obtain a high compaction[37].

The flexural strength of composites filled with different combinations of carbon fillers (Gr-CB, Gr-CF or Gr-CNT) versus Gr content are presented in then figure 4 b). For Gr-CB filled composites, different variations can be observed: the addition of CB can induce an increase (Vinylester/Gr-CB [36]) or a decrease (Epoxy/Gr-CB [40])in flexural strength with an increasing CB content. These contradictory effects suggest that mechanical properties are strongly dependent on the processing conditions and it seems that the CB addition in Gr filled composites does not improve the flexural properties. Nevertheless, there is a critical content of CF or CNT, which induces an optimal flexural strength, figure 4 b). Since these fillers are fibers with a high aspect ratio, they act as reinforcing agent and thus enhance the mechanical properties as well as electrical properties.

4. Conclusions

In order to optimize the two main requirements (electrical and mechanical properties) of composites used for the fabrication of bipolar plates, the flexural strength has been represented as a function of the in-plane conductivity, figure 5. Most of studied composites have electrical properties required by the application. Nevertheless, the mechanical properties mostly remain below the set of requirements. Consequently it seems to be difficult to obtain a good balance of electrical and mechanical properties. The first way to improve the electrical properties of these composites is to increase the carbon filler content. This strategy is however limited by the wetting problem and the loss in flexural strength that accompanies it. Nevertheless there is



Fig. 4. a) Flexural strength versus carbon filler content for composites filled graphite (Gr) or expanded graphite (EG), b)Flexural strength versus graphite content for composites filled with different types of carbon fillers



Fig. 5. Flexural strength versus in plane conductivity for different composite systems

another way sparsely studied in the literature, which consists in optimizing the mix of carbon fillers in the composite. This solution seems to give interesting results since the composites filled with different carbon fillers (Gr-CB, Gr-CF, Gr-CNT, Gr-CB-CF) have better mechanical properties than the others composites filled with one carbon filler (Gr), figure 5.

For this type of composites, the graphite must be incorporated as a primary component, because of its high electrical conductivity. In addition, due to its micronic size, low specific surface area and an aspect ratio close to one, it can be incorporated at high filler content. Then another carbon fillers can be added to the formulation. Because of the pore formation in the accumulation of one kind of fillers, the pore volume can be reduced by adding smaller particles. This way enables to increase the conductive paths and the composite become less resistive, but the porosities formation is limited, inducing an improvement of mechanical properties. Carbon black, carbon fibers or carbon nanotubes can be added in addition to graphite, the last two also giving an inducing a better improvement of mechanical properties. These systems are today sparsely studied and an optimization of these formulations and more particularly of the carbon filler choice and their respective proportions will be necessary to reach the two main requirements of bipolar plates.

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References

- Renato A. Antunes, Mara C.L. de Oliveira, Gerhard Ett, and Volkmar Ett, Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: A review of the main challenges to improve electrical performance, Journal of Power Sources 196 (2011), no. 6, 2945 –2961.
- [2] T Arai, Y Tominaga, S Asai, and M Sumita, *Study on correlation between physical properties and interfacial characteristics in highly loaded graphite-polymer composites*, J. Polym. Sci., Part B: Polym. Phys. **43** (2005), no. 18, 2568–2577.
- [3] C. Bas, L. Flandin, A.-S. Danerol, E. Claude, E. Rossinot, and N. D. Alberola, *Changes in the chemical structure and properties of a perfluorosulfonated acid membrane induced by fuel-cell operation*, J. Appl. Polym. Sci. 117 (2010), no. 4, 2121–2132.
- [4] Wolfgang Bauhofer and Josef Z. Kovacs, A review and analysis of electrical percolation in carbon nanotube polymer composites, Compos. Sci. Technol. 69 (2009), no. 10, 1486 –1498. CNT-NET 07 Special Issue with regular papers.
- [5] Michael Blaszkiewicz, David S. McLachlan, and Robert E. Newnham, The volume fraction and temperature dependence of the resistivity in carbon black and graphite polymer composites: An effective media-percolation approach, Polym. Eng. Sci. 32 (1992), no. 6, 421–425.
- [6] A Celzard, JF Mareche, G Furdin, and S Puricelli, *Electrical conductivity of anisotropic expanded graphite-based monoliths*, J. Phys. D: Appl. Phys. 33 (2000), no. 23, 3094–3101.
- [7] Guohua Chen, Dajun Wu, Wengui Weng, and Cuiling Wu, Exfoliation of graphite flake and its nanocomposites, Carbon 41 (2003), no. 3, 619–621.
- [8] Haiqun Chen, Marc B. MÃijller, Kerry J. Gilmore, Gordon G. Wallace, and Dan Li, *Mechanically strong, electrically conductive, and biocompatible graphene paper*, Advanced Materials 20 (2008), no. 18, 3557–3561.
- [9] S.G. Chen, M.Y. Shih, and Y.G. Li, Study of the effect on conductivity and its uniform distribution in injection molded composite polymer bipolar plate, Epolymers 143 (2007).
- [10] Shia-Chung Chen, Rean-Der Chien, Ping-Hwei Lee, and Jeng-Sheng Huang, Effects of molding conditions on the electromagnetic interference performance of conductive abs parts, J. Appl. Polym. Sci. 98 (2005), no. 3, 1072–1080.
- [11] EA Cho, US Jeon, HY Ha, SA Hong, and IH Oh, *Characteristics of composite bipolar plates for polymer electrolyte membrane fuel cells*, J. Power Sources **125** (2004), no. 2, 178–182.
- [12] I. Chodak and I. Krupa, Percolation effect and mechanical behavior of carbon black filled polyethylene, J. Mater. Sci. Lett. 18 (1999), 1457–1459. 10.1023/A:1006665527806.
- [13] Ivan Chodak, Maria Omastova, and Jurgen Pionteck, Relation between electrical and mechanical properties of conducting polymer composites, J. Appl. Polym. Sci. 82 (2001), no. 8, 1903–1906.

- [14] Shen Chunhui, Pan Mu, and Yuan Runzhang, *The effect of particle size gradation of conductive fillers on the conductivity and the flexural strength of composite bipolar plate*, International Journal of Hydrogen Energy **33** (2008), no. 3, 1035–1039.
- [15] Matthew L. Clingerman, Erik H. Weber, Julia A. King, and Kirk H. Schulz, Synergistic effect of carbon fillers in electrically conductive nylon 6,6 and polycarbonate based resins, Polym. Compos. 23 (2002), no. 5, 911–924.
- [16] B. D. Cunningham, J. Huang, and D. G. Baird, Review of materials and processing methods used in the production of bipolar plates for fuel cells, Int. Mater. Rev. 52 (2007), no. 1, 1–13.
- [17] Brent Cunningham and Donald G. Baird, *The development of economical bipolar plates for fuel cells*, J. Mater. Chem. 16 (2006), no. 45, 4385–4388.
- [18] Brent D. Cunningham, Jianhua Huang, and Donald G. Baird, Development of bipolar plates for fuel cells from graphite filled wetlay material and a thermoplastic laminate skin layer, J. Power Sources 165 (2007), no. 2, 764 –773. Iba - Hbc 2006 - Selected Papers From The International Battery Association & Hawaii Battery Conference 2006 Waikoloa, Hawaii, Usa 9-12 January 2006.
- [19] ______, Development of bipolar plates for fuel cells from graphite filled wet-lay material and a thermoplastic laminate skin layer,
 J. Power Sources 165 (2007), no. 2, 764 –773. Iba Hbc 2006 Selected Papers From The International Battery Association & Hawaii Battery Conference 2006 Waikoloa, Hawaii, Usa 9-12 January 2006.
- [20] C Del Rio, MC Ojeda, JL Acosta, MJ Escudero, E Hontanon, and L Daza, New polymer bipolar plates for polymer electrolyte membrane fuel cells: Synthesis and characterization, J. Appl. Polym. Sci. 83 (2002), no. 13, 2817–2822.
- [21] S. R. Dhakate, S. Sharma, M. Borah, R. B. Mathur, and T. L. Dhami, Expanded graphite-based electrically conductive composites as bipolar plate for pem fuel cell, Int. J. Hydrogen Energy 33 (2008), no. 23, 7146–7152.
- [22] JB Donnet, E Custodero, and TK Wang, Atomic force microscopy of carbon black aggregates, Kautsch. Gummi Kunstst. 49 (1996), no. 4, 274–279.
- [23] Ling Du and Sadhan C. Jana, Highly conductive epoxy/graphite composites for bipolar plates in proton exchange membrane fuel cells, J. Power Sources 172 (2007), no. 2, 734–741.
- [24] Radwan Dweiri and Jaafar Sahari, Electrical properties of carbon-based polypropylene composites for bipolar plates in polymer electrolyte membrane fuel cell (pemfc), J. Power Sources 171 (2007), no. 2, 424 – 432.
- [25] _____, Microstructural image analysis and structure-electrical conductivity relationship of single- and multiple-filler conductive composites, Compos. Sci. Technol. 68 (2008JUN), no. 7-8, 1679–1687 (English).
- [26] L. Flandin, A. Chang, S. Nazarenko, A. Hiltner, and E. Baer, *Effect of strain on the properties of an ethylene-octene elastomer with conductive carbon fillers*, J. Appl. Polym. Sci. 76 (2000), no. 6, 894–905.
- [27] L. Flandin, A. S. Danerol, C. Bas, E. Claude, G. De-Moor, and N. Alberola, *Characterization of the degradation in membrane electrode assemblies through passive electrical measurements*, J. Electrochem. Soc. **156** (2009), no. 10, B1117–B1123.
- [28] L. Flandin, T. Prasse, R. Schueler, K. Schulte, W. Bauhofer, and J.-Y. Cavaille, Anomalous percolation transition in carbonblack-epoxy composite materials, Phys. Rev. B 59 (1999Jun), no. 22, 14349–14355.
- [29] Shimshon Gottesfeld and Tom A. Zawodzinski, Polymer electrolyte fuel cells, Wiley-VCH Verlag GmbH, 2008.
- [30] A. A. Griffith, *The phenomena of rupture and flow in solids*, Philosophical Transactions Of The Royal Society Of London. Series A, Containing Papers Of A Mathematical Or Physical Character 221 (1921), no. 582-593, 163–198, available at Http: //Rsta.Royalsocietypublishing.Org/Content/221/582-593/163.Full.Pdf+Html.
- [31] P. J. Hamilton and B. G. Pollet, Polymer electrolyte membrane fuel cell (pemfc) flow field plate: Design, materials and characterisation, Fuel Cells 10 (2010), no. 4, 489–509.
- [32] A Hermann, T Chaudhuri, and P Spagnol, *Bipolar plates for pem fuel cells: A review*, Int. J. Hydrogen Energy 30 (2005), no. 12, 1297–1302. International Symposium On Solar-Hydrogen-Fuel Cell, Cancun, MEXICO, 2003.
- [33] JH Huang, DG Baird, and JE McGrath, Development of fuel cell bipolar plates from graphite filled wet-lay thermoplastic composite materials, J. Power Sources 150 (2005), 110–119.
- [34] J Jancar, J Kucera, and P Vesely, Some peculiarities in viscoelastic response of heavily filled polypropylene composites, J. Mater. Sci. Lett. 7 (1988DEC), no. 12, 1377–1378 (English).
- [35] _____, Peculiarities of mechanical response of heavily filled polypropylene composites .1. elastic-modulus, J. Mater. Sci. 26 (1991SEP 15), no. 18, 4878–4882 (English).
- [36] Biraj Kumar Kakati and Dhanapati Deka, Effect of resin matrix precursor on the properties of graphite composite bipolar plate for pem fuel cell, Energy & Fuels 21 (May 2007), no. 3, 1681–1687.
- [37] T Kauly, B Keren, A Siegmann, and M Narkis, Highly filled particulate thermoplastic composites .1. packing density of irregularly shaped particles, J. Mater. Sci. 32 (1997), no. 3, 693–699.
- [38] K. Kendall, A. J. Howard, J. D. Birchall, P. L. Pratt, B. A. Proctor, and S. A. Jefferis, *The relation between porosity, microstructure and strength, and the approach to advanced cement-based materials [and discussion]*, Philosophical Transactions Of The Royal Society Of London. Series A, Mathematical And Physical Sciences **310** (1983), no. 1511, 139–153, available at Http://Rsta. Royalsocietypublishing.Org/Content/310/1511/139.Full.Pdf+Html.

- [39] Hsu-Chiang Kuan, Chen-Chi M. Ma, Ke Hong Chen, and Shih-Ming Chen, *Preparation, electrical, mechanical and thermal properties of composite bipolar plate for a fuel cell*, J. Power Sources **134** (2004), no. 1, 7–17.
- [40] Joong Hee Lee, Yun Ki Jang, Chang Eui Hong, Nam Hoon Kim, Peng Li, and Hong Ki Lee, Effect of carbon fillers on properties of polymer composite bipolar plates of fuel cells, J. Power Sources 193 (2009), no. 2, 523 –529.
- [41] Jing Li and Jang-Kyo Kim, Percolation threshold of conducting polymer composites containing 3d randomly distributed graphite nanoplatelets, Composites Science and Technology 67 (2007), no. 10, 2114 –2120.
- [42] Shu-Hang Liao, Chuan-Yu Yen, Cheng-Chih Weng, Yu-Feng Lin, Chen-Chi M. Ma, Ching-Hung Yang, Ming-Chi Tsai, Ming-Yu Yen, Min-Chien Hsiao, Shuo-Jen Lee, Xiao-Feng Xie, and Yi-Hsiu Hsiao, Preparation and properties of carbon nanotube/polypropylene nanocomposite bipolar plates for polymer electrolyte membrane fuel cells, J. Power Sources 185 (2008), no. 2, 1225–1232.
- [43] Peng-Cheng Ma, Naveed A. Siddiqui, Gad Marom, and Jang-Kyo Kim, *Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review*, Composites Part A: Applied Science and Manufacturing 41 (2010), no. 10, 1345 –1367.
- [44] M. A. Magrupov, A. V. Umarov, K. Sh. Saidkhodzhaeva, G. A. Kasimov, and P. Curtis, *Investigation of the density of the surface layer of filler modified with heat-treated polyacrylonitrile*, Int. Polymer. Sci. Tech. 23 (1996), 77–79.
- [45] R.B. Mathur, S.R. Dhakate, D.K. Gupta, T.L. Dhami, and R.K. Aggarwal, Effect of different carbon fillers on the properties of graphite composite bipolar plate, J. Mater. Process. Technol. 203 (2008), no. 1-3, 184–192.
- [46] Viral Mehta and Joyce Smith Cooper, Review and analysis of pem fuel cell design and manufacturing, J. Power Sources 114 (2003), no. 1, 32 –53.
- [47] Frej Mighri, Michel A. Huneault, and Michel F. Champagne, Electrically conductive thermoplastic blends for injection and compression molding of bipolar plates in the fuel cell application, Polym. Eng. Sci. 44 (2004), no. 9, 1755–1765.
- [48] K Miyasaka, K Watanabe, E Jojima, H Aida, M Sumita, and K Ishikawa, Electrical-conductivity of carbon polymer composites as a function of carbon content, J. Mater. Sci. 17 (1982), no. 6, 1610–1616.
- [49] Stuart H. Munson-McGee, Estimation of the critical concentration in an anisotropic percolation network, Phys. Rev. B 43 (1991Feb), no. 4, 3331–3336.
- [50] Jeffrey R. Potts, Daniel R. Dreyer, Christopher W. Bielawski, and Rodney S. Ruoff, Graphene-based polymer nanocomposites, Polymer 52 (2011), no. 1, 5–25.
- [51] Nicolaus Probst and Eusebiu Grivei, Structure and electrical properties of carbon black, Carbon 40 (2002), no. 2, 201 205.
- [52] Z. Rimska, V. Kresalek, and J. Spacek, Ac conductivity of carbon fiber-polymer matrix composites at the percolation threshold, Polym. Compos. 23 (2002), no. 1, 95–103.
- [53] R. Saito, M. Fujita, G. Dresselhaus, and M. S Dresselhaus, *Electronic structure of chiral graphene tubules*, Appl. Phys. Lett. 60 (1992), no. 18, 2204–2206.
- [54] L.N. Song, M. Xiao, X.H. Li, and Y.Z. Meng, Short carbon fiber reinforced electrically conductive aromatic polydisulfide/expanded graphite nanocomposites, Mater. Chem. Phys. 93 (2005), no. 1, 122 –128.
- [55] M Sumita, H Abe, H Kayaki, and K Miyasaka, Effect of melt viscosity and surface-tension of polymers on the percolationthreshold of conductive-particle-filled polymeric composites, J. Macromol. Sci. Phys. B25 (1986), no. 1-2, 171–184 (English).
- [56] H. Tawfik, Y. Hung, and D. Mahajan, *Metal bipolar plates for pem fuel cell : A review*, Journal of Power Sources 163 (2007), no. 2, 755 –767. <ce:title>Selected Papers presented at the FUEL PROCESSING FOR HYDROGEN PRODUCTION SYMPOSIUM at the 230th American Chemical SocietyNational Meeting Washington, DC, USA, 28 August ãĂŞ 1 September 2005</ce:title>.
- [57] W Thongruang, CM Balik, and RJ Spontak, Volume-exclusion effects in polyethylene blends filled with carbon black, graphite, or carbon fiber, J. Polym. Sci., Part B: Polym. Phys. 40 (2002), no. 10, 1013–1025.
- [58] Wiriya Thongruang, Richard J. Spontak, and C. Maurice Balik, Bridged double percolation in conductive polymer composites: An electrical conductivity, morphology and mechanical property study, Polymer 43 (2002), no. 13, 3717–3725.
- [59] _____, Correlated electrical conductivity and mechanical property analysis of high-density polyethylene filled with graphite and carbon fiber, Polymer 43 (2002), no. 8, 2279 –2286.
- [60] Mathis Wissler, *Graphite and carbon powders for electrochemical applications*, Journal of Power Sources **156** (2006), no. 2, 142 –150.
- [61] M Wu and LL Shaw, A novel concept of carbon-filled polymer blends for applications in pem fuel cell bipolar plates, Int. J. Hydrogen Energy 30 (2005MAR), no. 4, 373–380 (English).
- [62] Man Wu and Leon L. Shaw, On the improved properties of injection-molded, carbon nanotube-filled pet/pvdf blends, J. Power Sources 136 (2004), no. 1, 37 –44.
- [63] G Wypych, Handbook of fillers (Plastics Design Library, ed.), Chem Tech Publishing, 1999.
- [64] Tao Yang and Pengfei Shi, Study on the mesocarbon microbeads/polyphenylene sulfide composite bipolar plates applied for proton exchange membrane fuel cells, J. Power Sources 175 (2008), no. 1, 390–396.
- [65] Influence of polypyrrole on electrical conductivity of injection-thermoplastic-composite bipolar plates (2009)

- [66] Rungsima Yeetsorn, Michael Fowler, Costas Tzoganakis, Wang Yuhua, and Mali Taylor, *Polypropylene composites for polymer* electrolyte membrane fuel cell bipolar plates, Macromolecular Symposia **264** (2008), no. 1, 34–43.
- [67] A. Zettl, Chapter 1 nanotubes: an experimental overview, Carbon nanotubes: Quantum cylinders of graphene, 2008, pp. 1 –27.
- [68] Qinghua Zhang, Sanjay Rastogi, Dajun Chen, Dirk Lippits, and Piet J. Lemstra, Low percolation threshold in single-walled carbon nanotube/high density polyethylene composites prepared by melt processing technique, Carbon 44 (2006), no. 4, 778 – 785.