

Development of fuel cell bipolar plates from graphite filled wet-lay thermoplastic composite materials

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Abstract

A method with the potential to produce economical bipolar plates with high electrical conductivity and mechanical properties is described. Thermoplastic composite materials consisting of graphite particles, thermoplastic fibers and glass or carbon fibers are generated by means of a wet-lay (paper-making) process to yield highly formable sheets. The sheets are then stacked and compression molded to form bipolar plates with gas flow channels. Poly(phenylene sulfide) (PPS) based wet-lay composite plates have in-plane conductivity of 200–300 S cm⁻¹, tensile strength of 57 MPa, flexural strength of 96 MPa and impact strength (unnotched) of 81 J m⁻¹ (1.5 ft-lb in.⁻¹). These values well exceed industrial as well as Department of Energy requirements or targets and have never been reached before for composite bipolar plates. The use of wet-lay sheets also makes it possible to choose different components including polymer, graphite particle and reinforcement for the core and outer layers of the plate, respectively, to optimize the properties and/or reduce the cost of the plate. The through-plane conductivity (around 20 S cm⁻¹) and half-cell resistance of the bipolar plate indicate that the through-plane conductivity of the material needs some improvement. © 2005 Elsevier B.V. All rights reserved.

Keywords: Fuel cell; Bipolar plate; Conductive materials; Wet-lay composite; Carbon composite

1. Introduction

The significant and growing interest in fuel cells for stationary power and transportation has been demonstrated by the attention these technologies are receiving from both government and industries, especially the automotive sector. As one of the key components of polymer electrolyte membrane (PEM) fuel cells, bipolar plates must have high electrical conductivity, sufficient mechanical integrity, corrosion resistance, low gas permeability, and low-cost as a result of both material selection and processing methodology if they are to be widely used in the automotive industry [1].

Historically graphite bipolar plates have been used in PEM fuel cells for space, military and other special applications. Graphite plates have good electrical conductivity, excellent

corrosion resistance, and a density lower than that of metal plates. The problems with graphite plates are their brittleness and porous structure, and the cost associated with machining the gas flow channels into the plates. In addition, post-processing (such as resin impregnation) is needed to make the plate impermeable to the fuel and oxygen [2]. Because the material and manufacturing costs of the graphite plates are prohibitive for at least automotive applications, extensive efforts have been made to develop alternative materials and bipolar plates, including metallic and graphite-based composite bipolar plates. Materials for metallic plates include stainless steel, titanium, and aluminum with stainless steel being considered most promising for commercialization [3]. Metallic bipolar plates usually have high bulk electrical and thermal conductivities, good mechanical properties and negligible gas permeability. New techniques such as continuous rolling or batch stamping have also been developed to facilitate the mass production of metallic bipolar plates. However,

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because metals have low corrosion resistance, a conductive and low-cost coating must be applied to the surfaces of the plates to form a protective layer, which has been found to be very difficult to accomplish [3]. In addition, the weight of metal plates is a disadvantage, especially in transportation applications.

Graphite-based composite bipolar plates are made from a combination of graphite or carbon powder filler and a polymer resin with conventional polymer processing methods like compression molding or injection molding. They offer the advantages of lower cost, higher flexibility and greater ease of manufacturing than graphite plates. They are also light in weight compared to metallic and graphite plates. The gas flow channels can be molded directly into the plate, eliminating the need for the costly machining step. Both thermoplastic and thermosetting resins have been used to fabricate the plate [4–6].

Ideally the composite plates should meet the following requirements:

- high electrical conductivity (DOE target [5]: $>100 \text{ S cm}^{-1}$);
- good mechanical properties (PlugPower's targets [7]: tensile strength $>41 \text{ MPa}$, flexural strength $>59 \text{ MPa}$, impact strength $>40.5 \text{ J m}^{-1}$ ($0.75 \text{ ft-lb in.}^{-1}$); DOE target [5]: crush strength $>4200 \text{ kPa}$);
- thermal stability at fuel cell operating temperature (-40 to $120 \text{ }^\circ\text{C}$ for fuel cell driven vehicles);
- chemical stability in the presence of fuel, oxidant and product water, which may be slightly acidic (down to pH 4) (DOE target [5]: corrosion $<16 \mu\text{A cm}^{-2}$);
- low permeability to fuel and oxidant (DOE target [5]: H_2 permeability $<2 \times 10^{-6} \text{ cm}^3 (\text{cm}^2 \text{ s})^{-1}$);
- low thermal expansion;
- high thermal conductivity (PlugPower's target [7]: $>10 \text{ W (m K)}^{-1}$);
- rapid processability.

Thermoplastic resins such as poly(vinylidene fluoride) (PVDF), liquid crystalline polymer (LCP), poly(phenylene sulfide) (PPS), and thermosetting resins such as phenolics, epoxies and vinyl esters have been used in fabricating composite bipolar plates [5]. In all cases, excessive carbon or graphite fillers ($>60 \text{ wt\%}$) have to be incorporated into the composite to meet the minimum requirement on electrical conductivities. Some typical conductivity values reported for polymer/graphite materials are 100 S cm^{-1} in the in-plane direction and 20 S cm^{-1} in the through-plane direction. Various mechanical properties (flexural, tensile, and impact strength, et al.) have been reported for composites which depend on the type of polymer resins and reinforcing fibers used, but all composites fail to meet the industrial target values as mentioned above. In fact, the mechanical strength of the bipolar plate is more important than originally believed. 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 weight and volume of the fuel cells (very important for use in vehicles) would also be reduced accordingly. The problem is that it is difficult to increase the electrical conductivity and mechanical properties further for polymer composite plates.

Recently researchers at Oak Ridge National Laboratory (ORNL) developed carbon/carbon composite bipolar plates and claimed that the plates had high electrical conductivity and excellent physical properties [8]. The manufacturing process consists of multiple steps, including the production of carbon fiber/phenolic resin preforms (by slurry-molding process) followed by compression molding, and the pyrolysis and densification by a chemical vapor infiltration (CVI) process. The technology was reportedly under scale up by Porvair Fuel Cell Technology. However, the process is likely too complicated and costly to be applied in civil applications such as automotive.

In 1997, a new technology for making conductive materials was reported by Tucker and Weeks [9]. They made wet-lay sheet materials (mats consisting of graphite particles, thermoplastic fibers and glass or carbon fibers) using a slurry-making process and then compression molded them to form conductive composite plaques. The composites containing 50 wt% graphite, 10 wt% glass, and 40 wt% poly(ethylene terephthalate) (PET) were reported to have a volume electrical conductivity of 100 S cm^{-1} and tensile strength of 51 MPa. The objective of this work is to determine whether the wet-lay sheets can be used to form bipolar plates with well-defined gas flow channels by mean of compression molding and whether the plates will exhibit high through-plane electrical conductivity and mechanical toughness required for bipolar plates.

2. Experimental

2.1. Production of wet-lay composite sheet materials

Wet-lay sheets containing graphite particles, thermoplastic (PPS or PET) fibers, and carbon or glass fibers were generated with a slurry-making process on a Herty papermaking machine donated by DuPont. First the cut thermoplastic fibers were mixed with water, and the suspension was agitated in a pulper for 10 min. The cut carbon fibers and graphite particles were added next and mixed for about 3–6 min. The slurry was then diluted with re-circulating water and fed to the forming box of the machine at a constant rate. The collected sheet material was then conveyed through an oven set at the melting point of the thermoplastic fibers to evaporate the water and partially melt the thermoplastic fibers. The porous sheet materials were then rolled for later use.

2.2. Compression molding of wet-lay composite plates

2.2.1. Direct molding

The sheets were cut according to the mold size and stacked in the mold. The assembly was then placed in a hydraulic

press and pressed at 270–285 °C for PET based composites and 305–310 °C for PPS based materials for about 10 min. The typical pressure used was 6.89 MPa (1000 psi). The platen heaters were then turned off and the mold was allowed to cool. The pressure was maintained until the mold temperature reached 30 °C and then the platens were released. The assembly was then removed from the press and the flat plaque or bipolar plate was removed from the mold. It should be noted that this is not the process envisioned for commercialization. Heating by the means of induction will be used for this purpose.

2.2.2. Wet/dry lay

The approach is similar to direct molding except that additional graphite particles (TIMREX provided by Timcal America Inc.) were added and sandwiched between porous sheet materials before they were stacked in the mold. As a result, the compression-molded plates had a graphite loading higher than the wet-lay sheet materials.

2.2.3. Skin-core laminate

This method was the same as the direct molding or wet/dry lay process mentioned above, except that the wet-lay sheet stacks were covered with a mixture of poly(vinylidene fluoride) (Kynar 761 provided by Atofina Chemicals) and graphite particles before the mold was closed. The molded plates, thus, had a skin layer formed by poly(vinylidene fluoride)/graphite mixture and a core layer the same as that made from wet-lay sheets through direct or wet/dry lay molding.

2.3. Measurement of in-plane electrical conductivity

The in-plane bulk conductivities were measured according to ASTM Standard F76-86. The test method A (for Van der Pauw specimens) or B (for parallelepiped specimens) of the standard was used in accordance with the sample shapes. In case that the samples were circular or square plaques (Van der Pauw specimens), the sheet resistance, R_S , was obtained from the two measured characteristic resistances R_A and R_B by numerically solving the Van der Pauw equation:

$$\exp\left(\frac{-\pi R_A}{R_S}\right) + \exp\left(\frac{-\pi R_B}{R_S}\right) = 1 \quad (1)$$

The resistivity, ρ , is given by $\rho = R_S d$, where d is the thickness of the specimen. The volume conductivity, σ , is $1/\rho$. For samples cut from a compression-molded plaque with size of 76.2 mm × 76.2 mm × 2 mm, test method B was used. The measurement was made for each specimen in the following way. The current contacts covering the entire end of the specimen were connected to a dc source to allow a constant current to pass through the specimen. The voltage drop was measured across the specimen with a Keithley 2000 digital multi-meter. The conductivity values for eight specimens were then averaged to give the final conductivity value of the sample. All specimens were tested at ambient conditions.

2.4. Measurement of through-plane electrical conductivity

The through-plane conductivities were measured based on the method proposed by L. Landis and J.L. Tucker with some modifications [10]. A composite sample with length and width of 25.4 mm and thickness of 2–3 mm was cut and placed between two gold-plated copper test electrodes. Between the electrode and sample a gas diffusion layer (GDL) paper was added to improve electrical contact of the sample with the electrode. The test cell was placed under pressure to simulate conditions more similar to those in a fuel cell. The system was initially preconditioned at a pressure of 10.3 MPa (1500 psi) for three cycles, then the resistance of the test cell was measured five times at 6.89 MPa (1000 psi) and the average value calculated. The sample was removed, and the resistance of the test cell (including GDL papers) was measured again under the same condition to obtain the “base” resistance. Subtracting the base resistance from the total gave the sample resistance. The resistivity or conductivity of the sample was determined by the following equation:

$$\rho = R_S \frac{A}{L} = \frac{(R_T - R_B)A}{L} \quad (2)$$

$$\sigma = \frac{1}{\rho} \quad (3)$$

where ρ is resistivity, A the cross-sectional area of the sample, L the thickness of the same, R_T , R_B and R_S are total resistance, baseline resistance and sample resistance, respectively.

2.5. Measurement of mechanical properties

The tensile and flexural (three-point bending) tests were performed on an Instron 4204 Tester at room temperature (23 °C) in accordance with ASTM D638 and D790 standards, respectively. The specimen sizes were 76.2 mm × 7.7 mm × 2.0 mm ($L \times W \times T$) for the tensile test, and 76.2 mm × 12.7 mm × 3.2 mm for the flexural test. The Izod impact test (unnotched) was performed on a Tinius Olsen 92T Impact Tester based on ASTM D-256. The sample had a size of 64.0 mm × 12.7 mm × 3.3 mm. Dynamic mechanical properties of the wet-lay composite as a function of temperature were measured on a Rheometrics RMS-800 at frequency of 10 rad s⁻¹ and shear strain of 0.1%. The temperature scan was performed from ambient temperature to 250 °C with a heating rate of 2 °C min⁻¹. The expansion of the sample during the test was recorded to evaluate the thermal expansion coefficient of the sample.

2.6. Measurement of half-cell resistance of the bipolar plates

To measure the half-cell resistance, an experimental apparatus similar to that used in the through-plane conductivity test was established. A single-sided bipolar plate with size of

12.1 cm × 14.0 cm × 0.32 cm and active area of 100 cm² was placed between two pieces of carbon paper (TORAY TGP-H-120), each of which was in contact with a gold-plated copper plate (current collector) on the opposite side. The size of carbon papers is 10 cm × 10 cm on the channel side and 12.1 cm × 14.0 cm on the flat side of the plate (this is actually a mono-polar plate). While a constant current (typically 250 mA) was passed through the current collectors, the potential drop between the collectors was measured. The half-cell resistance was then calculated based on Ohm's law. The measurements were made with a 1-ton load or 1.0 MPa (145 psi) on the channel side, a typical clamp pressure used in the actual PEM fuel cell stacks. The baseline of resistance, that is the resistance of the testing circuit excluding the bipolar plate but including carbon papers and everything else, was measured every time after the testing of the plate. This was done to ensure the stability of the baseline of the instrument and to evaluate the contribution of the bipolar plate to the whole half-cell resistance.

3. Results and discussion

3.1. Production of wet-lay composite materials and bipolar plates

The scheme for production of the wet-lay composite materials and bipolar plates is shown in Fig. 1. The composition of the wet-lay composite sheet materials produced and used in this work is listed in Table 1. Note there are two kinds of PET based wet-lay sheets used in this work. One is SC500 with fixed composition of 50 wt% graphite particles, 40 wt% polyester fibers and 10 wt% glass fibers, which was a development grade material provided by DuPont. The other one as well as the all the PPS based wet-lay sheets were fabricated at Virginia Tech with a Herty papermaking machine donated by DuPont (see Fig. 2). In the initial stage of this study, the SC500 wet-lay sheets were the only conductive wet-lay composites available to us and were, therefore, used to test the feasibility of using wet-lay sheets as bipolar plate materials. Because the SC500 sheets contain 50% graphite only, a dry-lay method was used to add more graphite to the porous sheets before the compression-molding process to increase the conductivity of the plate. The product was, there-

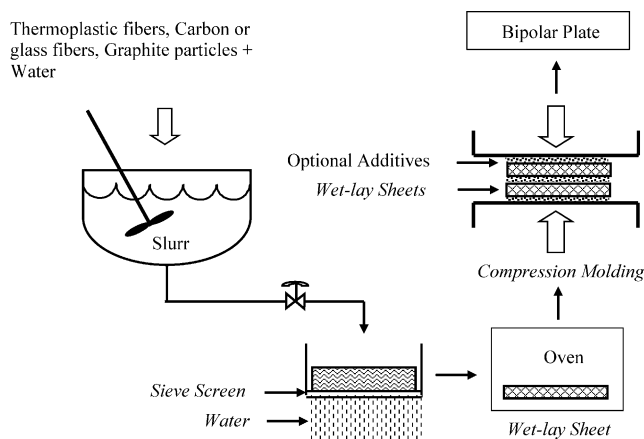


Fig. 1. Schematic diagram of manufacture of wet-lay composite sheets and bipolar plates.

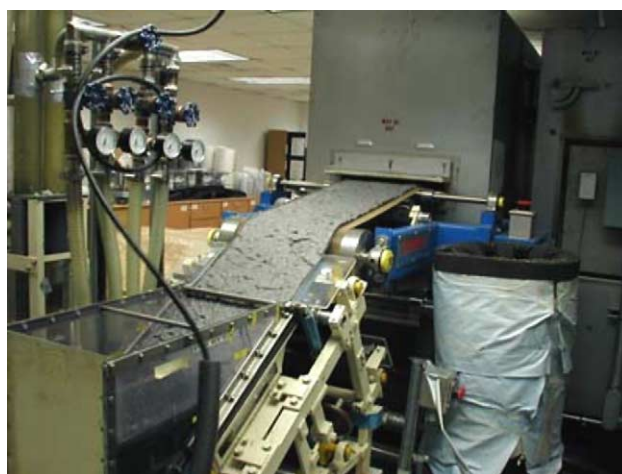


Fig. 2. Picture showing the manufacture of wet-lay sheets on a Herty paper-making machine.

fore, called wet/dry lay composite or bipolar plate. While PET may not be an ideal matrix for bipolar plate applications in the fuel cell environment, our preliminary result showed that the wet-lay composites could be very promising materials for producing bipolar plates. We then turned our attention to the modification of the PET based material to address the hydrolysis issue of polyesters, and the production of a new wet-lay composite with more stable polymers.

Table 1
Compositions of wet-lay composite materials

Name	Polymer		Graphite			Reinforcement
	Wet-lay	Dry-lay	Wet-lay	Dry-lay	Total (%)	
WDL-65	PET, 40%		TC300, 50%	KS150	65	Glass fiber
WDL-65/F2G8	PET, 40%	PVDF, 20%	TC300, 50%	KS150	66.5	Glass fiber
WDL-75/F1G9	PET, 40%	PVDF, 10%	TC300, 50%	KS150	78	Glass fiber
PPS-TC70	PPS, 23%		TC300, 70%		70	Carbon fiber
PPS-KS70	PPS, 23%		KS150, 70%		70	Carbon fiber
PET-TC70	PET, 23%		TC300, 70%		70	Carbon fiber
PET-KS70	PET, 23%		KS150, 70%		70	Carbon fiber

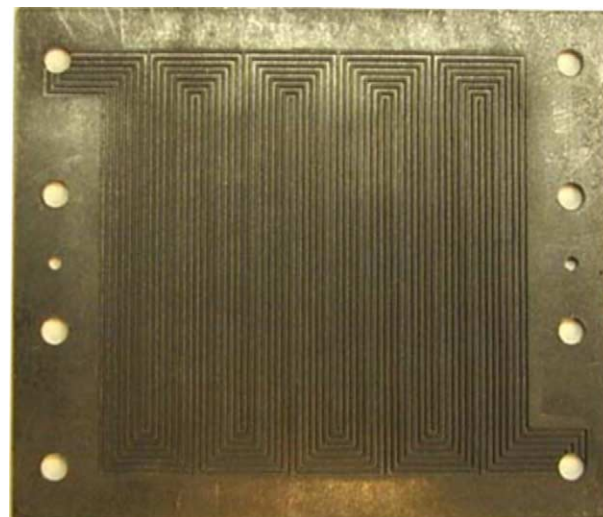
The effort to address the hydrolysis of the PET composite lead to the finding that a mixture of chemical resistant polymers and graphite particles could be used to form a protective layer for the PET based composite plate. The polymer to be used in the skin layer should meet a number of requirements, including excellent chemical resistance, moldable at a temperature matching that of PET (note: the PET-based wet-lay material is used in the core), excellent electrical conductivity after doped with graphite fillers, and formation of a composite with good adhesion at the interfaces. Considering that poly(vinylidene fluoride) (PVDF) has these properties [11], as well as a broad processing temperature range (from 175 °C to above 300 °C [12]) that overlaps with the molding temperature of PET, we chose Kynar 761, a powder form of PVDF produced by Atofina Chemicals for the skin layers. The processing and compression molding conditions for laminate bipolar plates are basically the same as the wet/dry lay composite plates as was described above.

An alternate thermoplastic used in making the wet-lay composite sheets is poly(phenylene sulfide) fibers. PPS is a semi-crystalline polymer with a melting point of 280 °C and a high degree of chemical resistance. It is generally regarded as second only to polytetrafluoroethylene (PTFE) in overall chemical resistance [13]. The superior chemical resistance of PPS, coupled with excellent mechanical properties, dimensional stability, and high temperature resistance, makes it one of the ideal matrices for the composite bipolar plates.

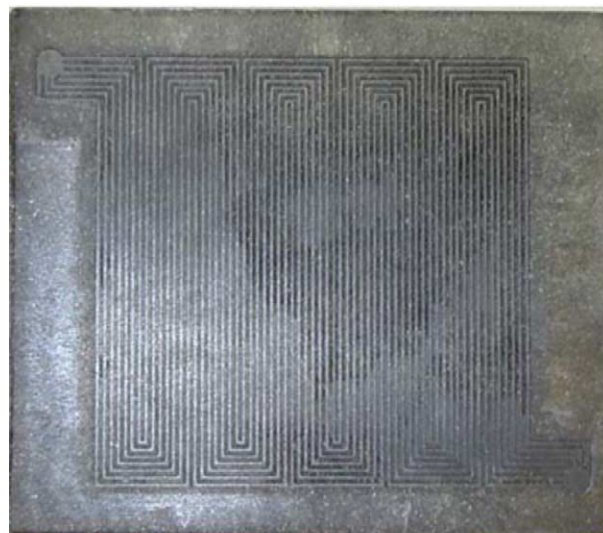
To make composite bipolar plates with gas flow channels molded into the plate, the composite material must have good formability. This is because the flow channels in bipolar plates are usually densely spaced, and are narrow and relatively deep (say 0.8 mm or 1/32 in. in width and depth). For the wet-lay composite sheets, we needed to know whether they were deformable enough in the compression molding process to form the channels and other features of the bipolar plates. If not, the flow channels would have to be machined instead of molded. To evaluate the formability of the wet/dry lay composite, we designed and fabricated a standard (7-channel) bipolar plate mold and used it in the compression molding process. In Fig. 3 are presented the compression-molded bipolar plates produced with this mold and wet-lay composite materials (we note that these are really mono-polar plates as the channels have been molded into one side of the plate initially). It can be seen that the composites could be molded to form well-defined gas flow channels. The formability of the wet-lay composites is good enough to produce bipolar plates with good shape and definition. In addition, these materials have the potential to be rapidly heated and molded by means of the compression molding process. The detail of the fabrication scheme will be described in a later paper.

3.2. Electrical conductivity of wet-lay composite materials

Electrical conductivity is one of the most important properties of bipolar plates. Moreover, it is important to realize that



(A)



(B)

Fig. 3. Pictures of compression-molded composite bipolar plates (single-sided) from PET (A) and PPS (B) based wet-lay composite sheets.

the graphite filled polymer plates may have different properties and performance in different directions. More specifically, if the length direction of the plate is designated as X , the width direction as Y , and the thickness direction as Z , then the properties in the X – Y plane and along the Z direction (the same as the compaction direction of the compression molding in general) may be quite different. A measurement made in and through the X – Y plane is, therefore, needed to evaluate the properties of the plate comprehensively. Technically, the measurement of through-plane conductivity is difficult to obtain compared to the in-plane conductivity measurement. This is probably why the earlier literature reported the in-plane conductivity of the bipolar plates only. In fact, because the electrons need to pass through the bipolar plate, the through-plane conductivity is obviously more important than the in-plane conductivity for a bipolar plate.

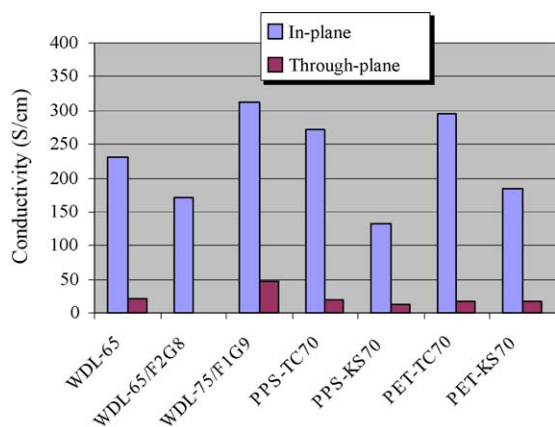


Fig. 4. Electrical conductivity of wet-lay composite materials.

In Fig. 4 are presented the bulk conductivities (in-plane and through-plane) of wet-lay composite materials. Most of the plates have in-plane conductivities higher than 200 S cm^{-1} , well exceeding the DOE target value (100 S cm^{-1}) for composite bipolar plates [5]. The values are also higher than those of the other polymer composite bipolar plates with similar graphite loadings (see Table 2). It is noted that the carbon/carbon composite bipolar plates developed by the Oak Ridge National Laboratory have an electrical conductivity of $200\text{--}300 \text{ S cm}^{-1}$ [8]. However, because they must use pyrolysis and chemical vapor infiltration (CVI) processes (which represent over 70% of total cost of C/C plates [8]) in making the bipolar plates, one should be able to manufacture the wet-lay bipolar plates at much less cost compared to the carbon/carbon bipolar plates.

Also included in Fig. 4 are the through-plane conductivities of the wet-lay composites. It is apparent that the through-plane conductivities for all wet-lay composites are significantly lower than the in-plane conductivities. This difference was also observed for other compression molded bipolar plates (see Table 2). The degree of the anisotropy is, however, not as high as what we saw for the wet-lay composites. This might be attributed to the following possible factors. First, the

graphite particles may orient in a plane perpendicular to the direction of the compaction force during molding. This possibility exists in all polymer/graphite systems as long as the aspect ratios of the graphite particles are not unity. Second, when forming the wet-lay sheet materials, the thermoplastic fibers and reinforcing fibers will orient in the sheet plane direction (perpendicular to the thickness direction) and might induce the graphite particles to orient in the same way. Third, the graphite particles used in the wet-lay may have a higher aspect ratio than that used in other composite plates. It is believed that for compression-molded composite bipolar plates, the higher the aspect ratio of the graphite used, the greater the ratio of in-plane to through-plane conductivities. This might also explain the fact that PPS-70TC, the wet-lay composites with TC300 graphite (with greater aspect ratio), have a higher ratio of in-plane to through-plane conductivities compared to PPS-70KS, the one with KS150 graphite (with smaller aspect ratio) (see Fig. 4). Fig. 4 also shows that the PPS-70TC and PPS-70KS wet-lay composites have similar through-plane conductivities. This suggests that although the use of more spherically shaped graphite could reduce the in-plane to through-plane conductivity ratio, it might not necessarily help in improving the through-plane conductivities of the composites. This matter is, however, subject to further investigation.

3.3. Mechanical properties of wet-lay composite materials

In addition to the electrical conductivity, the bipolar plates should also have adequate mechanical properties to be used in the fuel cell stacks. For example, the target values for flexural, tensile and impact strengths are 59 MPa, 41 MPa and 40.5 J m^{-1} , respectively [7]. However, for polymer composites doped with conductive particles or fibers, it is difficult to get high conductivity and sufficient mechanical properties at the same time. As a result, the mechanical properties (such as flexural, tensile and impact strengths) of composite bipolar plates available today are still significantly lower than the target values (see Table 2).

Table 2
Properties of polymer composite bipolar plates

Manufacturer	Polymer	% Graphite + fibers	Conductivity (S cm^{-1})		Mechanical strength	
			In-plane	Through-plane	Tensile (MPa)	Flexural (MPa)
GE [11]	PVDF	74	119			36.2
GE [14]	PVDF	64 + 16 CF	109			42.7
LANL [15]	Vinyl ester	68	60		23.4	29.6
Premix [15]	Vinyl ester	68	85		24.1	28.2
BMC [15]	Vinyl ester	69	30		26.2	37.9
Commercial [15]			105		19.3	20.7
BMC 940 [16]	Vinyl ester		100	50	30.3	40.0
Plug Power [7]	Vinyl ester	68	55	20	26.2	40.0
DuPont [17]				25–33	25.1	53.1
SGL [18]			100	20		40.0
H ₂ Economy [19]			67			29.4
Virginia Tech [20]	PET	65 + 7 GF	230	18–25	36.5	53.0
Virginia Tech	PPS	70 + 6 CF	271	19	57.5	95.8

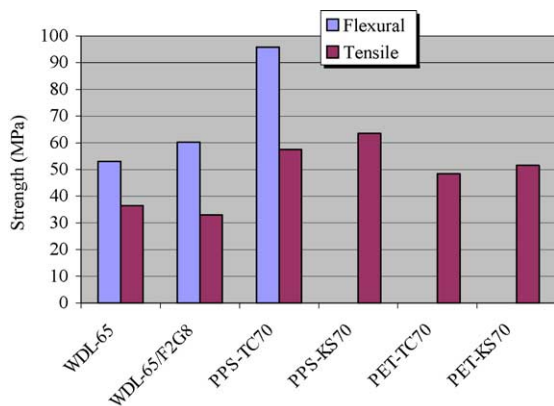


Fig. 5. Tensile and flexural strength of wet-lay composite materials.

In Fig. 5 are presented the tensile and flexural strength of wet-lay composite plates. The flexural and tensile strengths of all wet-lay composites are higher than those of other polymer composite plates with the same or similar graphite loadings. Among these wet-lay composites, the PPS based composites have the best mechanical properties, with both flexural and tensile strengths being significantly higher than Plug Power's target values. If a comparison is made between PPS based wet-lay composites with different graphite particles, one can find that the one with KS150 graphite has higher strength and modulus. This may be attributed to the fact that the dispersion of KS150 graphite in the composite is better than that of TC300 graphite. For the skin-core laminate composite materials, because the skin layers consisting of PVDF and graphite are not as strong as the PET based wet/dry lay materials (core material), lower mechanical properties are expected for the laminate composite compared to the wet/dry lay composite. From Fig. 5, one can see that the skin-core composites do lose some tensile strength. For flexural properties, however, no degradation in flexural strength is observed after the skin layer was added. This result suggests that a skin layer of 10–20% of the plate thickness has only minor, if any, influence on the mechanical properties of the composite materials.

The skin-core wet-lay composite plate has advantages over the composite plate consisting of PVDF (Kynar) and graphite (the same components used in the skin layers) only [21]. As can be seen from Table 3, the Kynar/graphite composite (26/74) developed by GE has an electrical conductivity of 119 S cm^{-1} and flexural strength of 37.2 MPa. After carbon fiber was used (Kynar/graphite/carbon fiber = 20/64/16), the flexural strength rose to 42.7 MPa while the electrical con-

Table 3
Property comparisons for composite bipolar plates

Binders	Fillers (wt%)	In-plane conductivity (S cm^{-1})	Flexural strength (MPa)	Source
Kynar	74% graphite	119	37.2	US 4,214,969
Kynar	74% (graphite + CF)	109	42.7	US 4,339,322
Kynar + PET	66.5% graphite skin/core = 10/90, Kynar/graphite = 20/80	171	60.2	Present work
Kynar + PET	68% graphite skin/core = 20/80, Kynar/graphite = 20/80	163	54.4	Present work

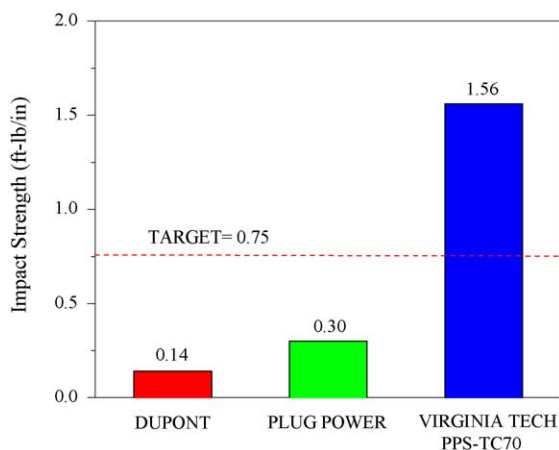


Fig. 6. Impact strength (unnotched) of composite bipolar plates.

ductivity decreased to 109 S cm^{-1} [14]. In comparison, our skin-core composite plate has higher electrical conductivity and mechanical properties. In addition, the laminate composites should have a lower raw material cost, as the price of PET is much lower than that of PVDF.

It is noted that Besmann et al. [8] reported a flexural strength of 175 MPa for their carbon/carbon plates. However, because the property was obtained by means of a biaxial flexure test, not the standard three-point flexure as defined by ASTM D790, it is difficult to compare their results with other reported strength data.

The wet-lay composite bipolar plates have also excellent impact strength. In Fig. 6 are presented the Izod impact strength (unnotched) of the PPS-TC70 composite plate. The value is two times higher than the target value, five times higher than that of Plug Power's plates [7] and over 10 times higher than that of the DuPont's plates [17]. These are the only companies who reported impact strength data for their plates.

It is not clear why the wet-lay composite plates have such excellent mechanical properties. One possible answer could be the unique structure of the wet-lay sheet materials. Traditionally, for making polymer composite bipolar plates, the thermoplastics in powder form were used to allow for more uniform blending with the graphite particles or other fillers and then used in compression molding. Although these polymer particles might bind the whole composite together after being heated and compression-molded, there are actually weld lines everywhere inside the composite. The situation is worse considering that a relatively low molding tempera-

ture has to be used to get as high electrical conductivity as possible. This is why most of the graphite composite bipolar plates, including those containing carbon fibers [14] or glass and graphite fibers [1], have inadequate mechanical properties. In contrast, the wet-lay composite materials have a much different structure. The base materials for compression molding are porous sheets consisting of fine thermoplastic fibers and reinforcing fibers. The web-like structure makes the molded composites much stronger than that made from the mixture of the graphite and thermoplastic powders. In addition, the reinforcing fibers (carbon or glass fibers) with length of 2.54 cm can be used in the wet-lay process without any difficulties. The use of carbon fiber reinforced PPS makes the composite even stronger.

3.4. Thermo-mechanical properties

In Fig. 7 are presented the dynamic mechanical properties of the wet-lay composite materials as a function of temperature, from which the thermo-mechanical properties of the material can be estimated. At 80 °C (a typical running temperature for PEM fuel cells), the PPS-TC70 wet-lay composite has a value of G' of 6.43 GPa, which is about 97% of that at ambient conditions (6.63 GPa). Even at 150 °C, the composite still retains 57% of G' at room temperature. Plug Power has reported a storage modulus (flexural or three-point bending) of 5.51 GPa at 150 °C for their bipolar plate, whereas their target is 8.27 GPa. Because the magnitude of the flexural modulus is typically three times as large as that of the shear modulus, our bipolar plate at 150 °C should have a flexural modulus of over 11 GPa, which is significantly higher than Plug Power's target values.

From dynamic mechanical temperature analysis (DMTA) testing, the thermal expansion ($\Delta L/L$) of the sample as a function of temperature can be obtained at the same time. The thermal expansion coefficient can be determined from the $\Delta L/L-T$ plot. The result indicates that

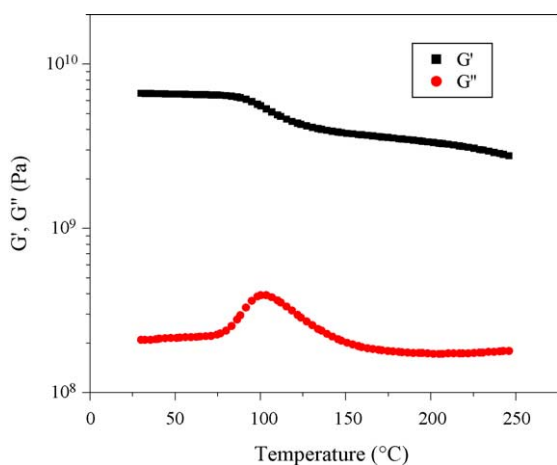


Fig. 7. Dynamic mechanical properties of PPS based wet-lay composite materials as a function of temperature at frequency of 10 rad s⁻¹.

the composite has a low thermal expansion coefficient ($5.23 \times 10^{-5} \text{ cm (cm } ^\circ\text{C)}^{-1}$ at 80 °C), as does the pure PPS polymers ($4.9\text{--}5.9 \times 10^{-5} \text{ cm (cm } ^\circ\text{C)}^{-1}$ at 20 °C). This is also an advantage of the PPS based composite bipolar plates, as a low thermal expansion coefficient is desired for bipolar plates [3].

3.5. Half-cell resistance of wet-lay composite bipolar plates

While electrical conductivities (in- and through-plane) are important in characterizing the materials used in the manufacture of bipolar plates, the performance of the bipolar plate itself is needed. Due to the differences in the molds and the polymer flow patterns, the compression molded bipolar plates may have properties quite different from those of the flat plate test specimens. In addition, the contact resistance between bipolar plates and gas diffusion layers also contribute to the total resistance. To evaluate these important properties of the bipolar plates, a test termed the half-cell resistance test was found to be useful. In Fig. 8 are presented the configuration we used in the test. The method is similar to that reported by others, except that the baseline resistance (i.e. the resistance of testing circuit excluding the bipolar plate but including carbon papers and anything else) test is performed following half-cell testing. The test of baseline resistance was found important because the contact resistances between current collector (such as gold-plated copper plates) and carbon papers (usually inserted between the collector and bipolar plate) could differ dramatically depending on the specific collectors used.

In Fig. 9 are presented the half-cell resistances of the wet-lay composite bipolar plates and the corresponding baseline resistances. The data for the POCO AXF-5Q graphite plate (with the same design and geometric size) are also included for comparison. It can be seen that, while the baseline resistances in all cases are almost the same (about $0.01 \Omega \text{ cm}^2$), the bipolar plates made from different materials have much different half-cell resistances. The PPS based wet-lay composite plate (PPS-TC70) and PET based one (WDL-65) have similar half-cell resistances ($\sim 0.039 \Omega \text{ cm}^2$). The resistance of the plates is, thus, close to $0.029 \Omega \text{ cm}^2$. Comparatively, the POCO graphite plate has a much lower half-cell resistance

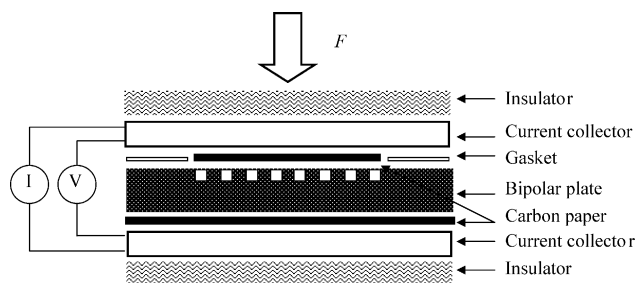


Fig. 8. Schematic diagram of testing cell used in the half-cell resistance measurement.

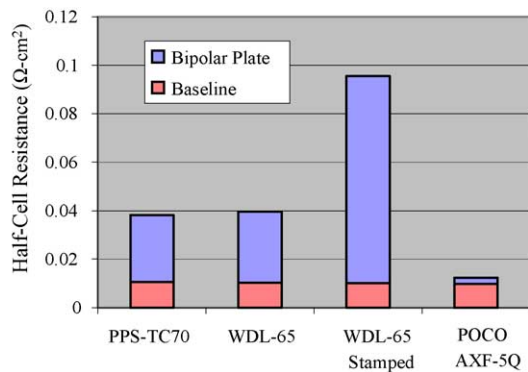


Fig. 9. Half-cell resistance of bipolar plates at room temperature (23 °C).

(about 1/3 of the wet-lay composites). Considering the baseline resistance, the resistance of the graphite plate is more than 10 times smaller than that of the composite plates. This is reasonable considering the large difference in the through-plane conductivities of the materials (about 680 S cm^{-1} for graphite versus 20 S cm^{-1} for wet-lay composites). Obviously, the electrical conductivity of the composite bipolar plates is not as good as the graphite plate. Improvement of the through-plane conductivity of the wet-lay composites is needed.

Fig. 9 also shows the half-cell resistance of the compression molded wet-lay composite plate labeled as WDL-65S. The plate was made in two steps. First, a flat panel was compression-molded from a stack of porous wet-lay sheets. The flat panel was then used in compression molding (stamping with the bipolar plate mold) to form a single sided bipolar plate. It was found that the plate had also a good shape and high definition gas flow channels and looked as good as the directly molded WDL-65 plates (refer to Fig. 3). However, this result showed that the molded and then stamped plate had a higher resistance compared to the conventional plates. This may be attributed to the fact that in the stamping process, the flowability of the graphite particles is lower than that of molten polymers in the composite, resulting in the formation of resin-rich zones or layers in the rib area of the bipolar plate. This may be an issue to be addressed when one tries to develop a commercial fabrication process for the bipolar plates.

There are reports showing that the half-cell resistance or the fuel cell I - V (current-voltage) performance of the composite plates could be very close to that of the graphite bipolar plates even though the composite has a through-plane conductivity significantly lower than that of the pure graphite (see, for example, Refs. [22,23]). This fact seems to suggest that the composite plates actually have performances close to the graphite plate. This may not be true, however. For example, Cho et al. [22] found that, under a pressure of 180 N cm^{-2} , their pure graphite, composite A and composite B, plates have half-cell resistances of 30.2, 31.7 and $33.4 \text{ m}\Omega \text{ cm}^2$, respectively, while the bulk conductivities of the plates are 593.5 , 76.3 and 66.0 S cm^{-1} . They attributed

these results to the fact that by compressing the carbon composites, carbon powders formed a compact network of carbon powders. However, we believe that the results are related to the high baseline resistance. Theoretically, the graphite plate and composite plate (with bulk resistance much higher than that of graphite) could have similar half-cell resistance when the baseline resistances are different, or the baseline resistances are much higher than the bulk resistance of the composite plate. In the latter situation, the baseline resistance is so large that the difference between bulk resistances of graphite and composite plates is nearly negligible. Therefore, the similarity in half-cell resistances does not necessarily mean the performance (in conducting electricity) of the bipolar plates is similar. It can, thus, be concluded that it makes little sense to compare half-cell resistances of bipolar plates without the baseline information. Even if the baselines are the same, the magnitude of baselines is also needed to make a proper judgment. The same issue should also exist in the fuel cell test, especially the single cell test in which the ratio of baseline and half-cell resistances is probably greater than that of the stacks. Effort should be made to measure the baseline or contact resistance between the current collector and GDL papers.

4. Conclusions

This work shows that graphite filled wet-lay composite sheets may be used to produce bipolar plates with high electrical conductivity, high corrosion resistance, excellent mechanical properties, and potentially rapid manufacturability. The sheets consisting of graphite particles, thermoplastic fibers and reinforcing fibers are generated by means of a wet-lay process and are highly formable. The porous sheets together with optional additives are then stacked and compression molded to form bipolar plates with gas flow channels. The use of the wet-lay composite in the formation of bipolar plates has multiple advantages. First, it increases in-plane conductivities of the composite plate significantly while maintaining the through-plane conductivity. Second, it dramatically increases the mechanical properties of the composites. The PPS based composite bipolar plate is the first polymer composite bipolar plate that meets industrial requirements (targets) for tensile, flexural and impact strengths. Third, one can use different components including polymers, graphite particles and reinforcement for the core and outer layers of the plate, respectively, and optimize the properties and/or reduce the cost of the plate. Moisture sensitive polymers like PET can be used for bipolar plates as long as a chemically stable polymer is used to form a protective layer. The half-cell resistances of the wet-lay composite plates were also determined to evaluate the performance of the plates. It is pointed out that the measurement of the baseline resistance is important in interpreting the half-cell resistances of bipolar plates. The through-plane conductivity (around 20 S cm^{-1}) and half-cell resistance of the bipolar plate indicate that the through-plane conductivity of the material needs some improvement.

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