

Development of bipolar plates for fuel cells from graphite filled wet-lay material and a thermoplastic laminate skin layer

Brent D. Cunningham*, Jianhua Huang, Donald G. Baird

Chemical Engineering and Macromolecules and Interfaces Institute Virginia Tech, Blacksburg, VA 24061, United States

Received 7 August 2006; received in revised form 8 December 2006; accepted 11 December 2006

Available online 28 December 2006

Abstract

In this paper, a method with the potential to rapidly produce thermoplastic polymer composite bipolar plates with improved formability and through-plane conductivity is described. In our earlier work, it was reported that composite bipolar plates made with graphite filled wet-lay materials exhibited excellent mechanical properties and in-plane electrical conductivity. However, the through-plane conductivity and formability of the materials needed improvement. In this work, laminate polymer composite plates consisting of a wet-lay based core and a fluoropolymer/graphite skin layer are manufactured in an effort to improve formability and through-plane conductivity. These plates are characterized by their through-plane and in-plane conductivity, half-cell resistance, and mechanical properties at ambient and elevated temperatures. The laminate plates with PPS based wet-lay core exhibited bulk conductivities of above 300 S cm^{-1} , tensile strength of up to 34 MPa, and flexural strength of up to 54 MPa. Compared to the bipolar plates consisting of wet-lay material only, the bipolar plates with laminate structure exhibited an increase in through-plane conductivity of 25–35%, as well as a decrease in half-cell resistance by a factor of up to 5. The laminate bipolar plates can be manufactured in several ways with two of them being discussed in detail in the paper.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fuel cell; Bipolar plate; Laminate; Wet-lay composite; Graphite composite

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have drawn attention as alternative sources of energy for use in stationary and automotive applications. Bipolar plates are by weight, volume, and cost one of the most significant parts of a fuel cell stack. Bipolar plates must exhibit excellent electrical conductivity, adequate mechanical stability, corrosion resistance, and low gas permeability. Furthermore, bipolar plates must be amenable to a rapid, low cost processing methodology if they are to be widely used in the automotive industry.

The endeavor to develop a suitable material for bipolar plate production is based on the following requirements:

- Electrical conductivity ($>100 \text{ S cm}^{-1}$)¹,
- low permeability ($<2 \times 10^{-6} \text{ cm}^3 (\text{cm}^2 \text{ s})^{-1}$)¹,

- corrosion resistant ($<16 \text{ mA cm}^2$)¹,
- tensile strength ($>41 \text{ MPa}$)²,
- flexural strength ($>59 \text{ MPa}$)²,
- high thermal conductivity ($>10 \text{ W (m K)}^{-1}$)²,
- chemical and electrochemical stability,
- low thermal expansion,
- efficient processability.

The electrical conductivity target is specified as bulk, or in-plane conductivity. Although no target has been specified for through-plane conductivity, it is thought to be an important measurement because the through-plane direction is the route that electrons travel in an operating fuel cell. Corrosion resistance is mainly a concern with metal plates and metal-coated fibers, but it can also apply to polymer systems that may dissolve electrochemically in a fuel cell. The mechanical targets are specified for ambient temperature, while targets at elevated temperatures have not yet been specified. Efficient processability incorporates

* Corresponding author. Tel.: +1 540 231 7870; fax: +1 540 231 2732.

E-mail addresses: brcunni1@vt.edu (B.D. Cunningham), jianhua@vt.edu (J. Huang), dbarid@vt.edu (D.G. Baird).

¹ Department of Energy (DOE) & FreedomCAR specified targets [1].

² Plug Power targets [2].

several factors, including material and production costs and the ability to be rapidly manufactured.

Traditional materials for producing bipolar plates are sintered graphite and metal. Graphite plates have been used because they possess high electrical conductivity, corrosion resistance, and a lower density than that of metals [3]. Problems with graphite plates include brittleness and the cost associated with machining channels into the surface. Because the material and machining cost of graphite plates are exorbitant, at least for the automotive industry, the development of a more suitable material has drawn extensive research. Metal bipolar plates such as stainless steel, aluminum, and titanium have gained attention for their high electrical conductivity, mechanical strength, and negligible gas permeability [3–5]. The main advantage with metal plates is that channels can be embossed or etched into the surface, relieving much time and cost associated with machining. However, because metals are subject to corrosion and leaching of ions, a coating must be applied to the surface to provide a protective layer. Unfortunately, the protective layer can be highly electrically insulating, drastically reducing the bulk conductivity of the plate. Additionally, metal plates contribute a significant amount of weight to the overall fuel cell stack. Therefore, it is desired to make the metal plates very thin.

In an effort to improve on sintered graphite, researchers at Oak Ridge National Laboratory (ORNL) have developed carbon/carbon composite bipolar plates by slurry molding carbon fiber and phenolic resin [6]. ORNL researchers claim that the plates have high electrical conductivity and adequate mechanical stability. However, the manufacturing step in the production of carbon/carbon plates is complex and expensive due to a chemical vapor infiltration (CVI) process. CVI operates at very high temperatures for extended times, sealing the carbon/phenolic resin preforms by depositing carbon onto the surface. Unfortunately, channels must still be machined into the surfaces of the carbon/carbon plates.

Graphite-based polymer composite bipolar plates have shown to potentially meet target requirements. They offer advantages such as lower cost, higher flexibility, and are lighter in weight when compared to metallic and graphite plates. The gas flow channels can be molded directly into the surfaces of the plate,

eliminating the need for a costly machining step. Researchers at Los Alamos National Laboratory (LANL) have developed a bipolar plate based on a vinyl ester thermosetting polymer resin and graphite powder [2,7]. Bulk conductivities were measured to be as high as 85 S cm^{-1} , with tensile and flexural strength at 25 and 38 MPa, respectively which are still lower than the specified targets. A compression molding process was used for producing the bipolar plates in which channels were formed in less than 10 min [8,9]. The advantage in using a thermosetting polymer is that when the polymer is heated and compression molded, the plate cures and does not require subsequent cooling. Therefore, the plate can be immediately released from the mold. However, a postcure may be necessary, and can take as long as 1 h to complete [8]. Blunk and coworkers [10] have developed an epoxy-based system using expandable graphite that has exhibited low resistances. However, the flexural strength of the plates did not reach the target value. Although the graphite filled epoxy system has shown potential for use in bipolar plate production, the generation of the epoxy bipolar plates requires a 20 min curing time and the expandable graphite is anticipated to be expensive to manufacture. The epoxy-based bipolar plates also require the machining of channels. Poly(vinylidene fluoride) (PVDF), a thermoplastic fluoropolymer matrix, has been used with graphite particles and carbon fiber to produce bipolar plates [11]. Bulk conductivity values have reached 109 S cm^{-1} , exceeding the DOE target. However, the flexural strength was only 42.7 MPa, lower than the goal of 59 MPa. Liquid crystalline polymer/graphite mixtures have been considered for bipolar plate production because of their ability to be injection molded due to the low viscosity of the polymer [12]. The injection molding process allows for a relatively short cycle time of 30 s. Bulk conductivities have reached as high as 100 S cm^{-1} , just reaching the minimum target, but no mechanical properties or through-plane conductivities were reported, and it is anticipated that the mechanical properties may not reach the targets.

Huang and co-workers [13,14] reported the development of conductive polymer composite materials generated by means of a wet-lay process. The wet-lay materials were compression molded to form highly conductive and strong bipolar plates. Bulk conductivities (in-plane) and mechanical properties of the plates

Table 1
Comparison of conductive and mechanical properties for several polymer composite materials used in the production of bipolar plates

Source	Polymer	Graphite/glass or carbon reinforcing fiber (w/w%)	Conductivity (S cm^{-1})		Mechanical strength (MPa)	
			In-plane	Through-plane	Tensile	Flexural
Target			$>100^a$	–	41.0 ^b	59.0 ^b
GE [21]	PVDF	80/0	119	–	–	30.0
GE [11]	PVDF	64/16 CF	109	–	–	42.7
LANL [8]	Vinyl Ester	68/0	60	–	23.4	29.6
BMC [22,23]	Vinyl Ester	70/0	95	50	30.3	38.6
Plug Power [2]	Vinyl Ester	68/0	55	20	26.2	40.0
Patent [24]	Epoxy	90/0	3	–	–	–
DuPont [25]	–	–	–	25–33	25.1	53.1
Virginia Tech [13]	PET	65/7 GF	230	18–25	36.5	53.0
Virginia Tech	PPS	70/6 CF	271	19	57.5	95.8

^a DOE target for conductivity [1].

^b Plug Power targets for mechanical strength [2].

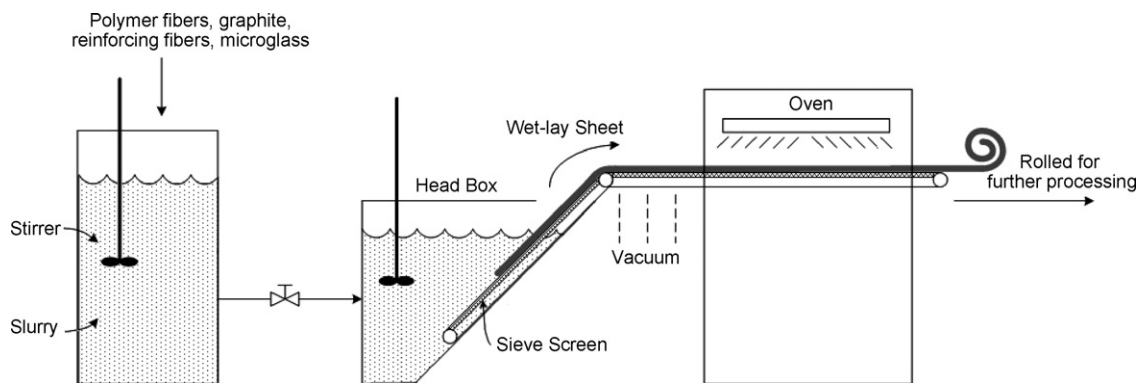


Fig. 1. The process to develop wet-lay polymer composite sheets.

were higher than that of any other polymer composite plates (see Table 1). However, the through-plane conductivity, half-cell resistance, and formability of the plates needed further improvement. Considering that the half-cell resistances were previously measured on monopolar plates (i.e. single-sided plate), the values are expected to be even higher for the double-sided bipolar plates if no further improvements are made for the materials.

In this paper, a laminate structure is proposed to improve the formability and through-plane conductivity of the bipolar plates. The bipolar plates with wet-lay material in the core and thermoplastic (e.g. PVDF)/graphite composite powders on the outer layers are generated by two methods. One is to put composite powders on the surfaces of the wet-lay sheet stacks and compression mold at a temperature to melt the polymer which is called the one-step molding method. The other is to generate a consolidated wet-lay composite plaque first, followed by the addition of composite powders on the surfaces of the flat plaque and compression mold the composite (at a temperature sufficient to melt the polymer in the surface only). This is called the two-step molding method. We will assess the bipolar plates made by the two different methods and discuss the advantages and disadvantages of the processes. The evaluation will be focused on the electrical conductivity and mechanical properties of the composites, as well as the half-cell resistance and appearance of the bipolar plates. Instead of single-sided bipolar plate as used previously, bipolar plates with gas flow channels on both sides will be generated and used in the evaluation. It turns out to be important to generate and evaluate bipolar plates under conditions as close as possible to those experienced by the bipolar plate under fuel cell operating conditions.

2. Experimental

2.1. Materials

Two thermoplastics used in the form of fibers were poly(ethylene terephthalate) (PET) (6 mm long) and poly(phenylene sulfide) (PPS) (6 mm long) at levels in the range of 13–40 wt%. Conoco carbon fibers (nominal length 1/2") or E-glass fibers were used as reinforcing fibers in the range of 6–9 wt%. Timrex[®] KS-150 and Timcal[™] TC-300 graphite particles were used as the conductive filler in the range of

50–80 wt%. Microglass (1 wt%) was also added to help particle retention. PVDF (Kynar 761 from Arkema Inc.) was used in combination with TC-300 graphite powder as the laminate material.

2.2. Production and molding of wet-lay composite sheet material

In Fig. 1 is shown the scheme for production of the wet-lay composite materials and bipolar plates. Wet-lay sheets containing a thermoplastic fiber, reinforcing fiber, conductive graphite particles, and microglass were generated with a slurry-making process on a Herty papermaking machine donated by DuPont. The slurry contained 1 wt% solids in water. First, the cut thermoplastic fibers were added to the water in a pulper and agitated for 10 min. Next, the cut reinforcing fibers, graphite particles, and microglass were added and mixed for 3–6 min. The slurry was then pumped into a head box containing a sieve screen, generating a sheet of porous material. The sheet was continuously rolled through an oven at the melting point of the polymer to continue drying and partially melt the thermoplastic fibers.

The procedure carried out by Huang and co-workers [13,14] for making a test sample or bipolar plate from wet-lay material was followed in this work. The material was cut to fit the shape of a mold and stacked to provide a desired thickness. The mold was then placed between platen heaters of a hydraulic press set at approximately 20 °C above the melting point of the thermoplastic fiber (277 °C for PET based composites, 305 °C for PPS based composites). The material was compression molded for 7–10 min at a constant compaction load of 10,000 pounds. The platen heaters were turned off and the mold was allowed to cool to 30 °C while still under pressure. The mold was then removed from the press and the flat plaque or bipolar plate was taken out of the mold. Although a batch process was used in this work, a continuous process is envisioned in the future.

2.3. Novel laminate approach

In this paper are described two methods to produce laminate bipolar plates. The first, called the one-step method, was begun by covering the bottom surface of the mold with a desired amount of PVDF/graphite mixture and spreading it evenly over the sur-

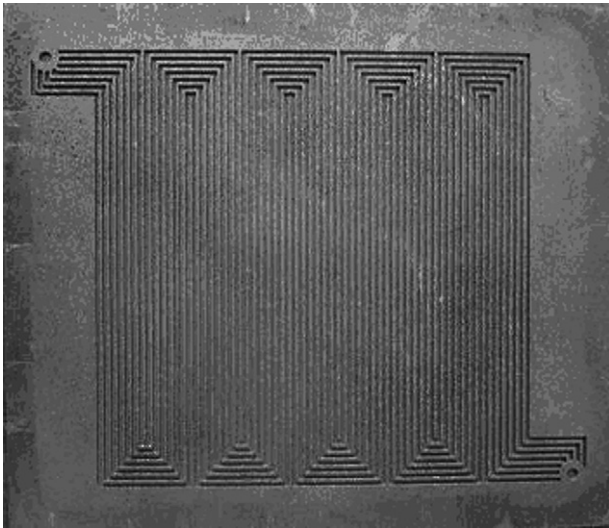


Fig. 2. One side of a laminate polymer composite bipolar plate showing the 7-channel parallel serpentine style design. Plate dimensions are 4.75 in. \times 5.5 in. Channel dimensions are 0.8 mm \times 0.8 mm.

face. Next, a pre-determined number of wet-lay sheets were stacked on top of the PVDF/graphite mixture. Finally, another layer of PVDF/graphite (same amount as placed in the bottom of the mold) was spread evenly on top of the wet-lay sheets. The mold was closed and placed into a heated press for compression molding. The molding temperature for this method was based on the polymer with the higher processing temperature (i.e. using a PPS based wet-lay core this is about 300 °C). Upon compression molding, the PVDF/graphite powder penetrates into the porous wet-lay material (>50% voids) to help bond the skin layer to the core material. The second process is called the two-step method. First, the wet-lay sheets by themselves were placed into a heated mold and compression molded to form a pre-consolidated flat plaque. After being removed from the mold, PVDF/graphite was added to the bottom surface of the mold and on top of the flat plaque similar to the one-step method. The mold was closed and placed into a heated press for compression molding. The molding temperature for this method was set at approximately 200 °C. A lower processing temperature was used because the wet-lay material was already consolidated, and only the PVDF required processing. In the two-step method the sole form of bonding between the skin layer and the wet-lay core was adhesion between the surfaces. The level of PVDF/graphite powder added to the surfaces of the wet-lay material was varied from 15 to 33 vol% (on each side) to evaluate how differences in the level of laminate layer would affect the composite properties. In Fig. 2 is shown a picture of a compression molded laminate bipolar plate of dimensions 4.75 in. \times 5.5 in. with 0.8 mm \times 0.8 mm parallel serpentine style channel design.

2.4. Measurement of mechanical properties

The tensile and flexural tests were performed on an Instron 4204 at room temperature in accordance with ASTM D638 and D790 standards, respectively. The mechanical tests were also performed at 80, 100 and 120 °C to evaluate the strength

in an environment that more accurately reflects that found in PEM fuel cells. The specimens sizes were approximately 76.2 mm \times 8.5 mm \times 3.0 mm ($L \times W \times T$) and were cut from a flat plaque.

2.5. Measurement of in-plane and through-plane conductivity

In-plane (bulk) conductivities were measured according to ASTM Standard F76–86. Current contacts were placed at the four corners of the plaque allowing for a constant current to pass through the specimen. The voltage drop was measured across the specimen with a Keithley 2000 digital multi-meter at ambient conditions. Two characteristic resistances, R_A and R_B were measured. The plaque resistance, R_S , is obtained by 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 specimen. The volume conductivity, σ_B , is defined as $1/\rho$.

Through-plane conductivities were measured based on a method proposed by Landis et al. [15]. A 76.2 mm \times 76.2 mm plaque was placed between gold plated copper electrodes. Between the electrodes and sample was placed a piece of carbon paper (Toray TGP-H120) to improve electrical contact between the electrodes and sample. The system was placed under a compaction force of 2000 pounds (approximately 1000 psi) and the resistance was measured. The sample was removed, and the resistance of the test cell (including carbon paper) was measured again under the same conditions to obtain a “baseline” resistance. The sample resistance could then be calculated by subtracting the baseline resistance from the total resistance. The resistivity of the material was calculated by:

$$\rho = \frac{[(R_T - R_{\text{baseline}})A]}{L} \quad (2)$$

where ρ is the resistivity, A the cross-sectional area of sample, L is the thickness of sample, and R_T and R_{baseline} are total resistance and baseline resistance, respectively. The through-plane conductivity, σ_τ , was then calculated as $1/\rho$.

2.6 Measurement of half-cell resistance

To measure the half-cell resistance of a bipolar plate, an apparatus was set up similarly to the one used to measure through-plane conductivity. A bipolar plate having dimensions 12.2 cm \times 14.0 cm \times 0.3 cm and an active area of 100 cm² was placed between the gold plated copper electrodes. Carbon paper (Toray TGP-H-120) was placed on both sides of the bipolar plate, and hence, in between the sample and electrodes. The size of the carbon paper was 10 cm \times 10 cm in order to completely cover the active area. The sample was placed under a compaction force of 2000 pounds (approximately 130 psi) while a constant current of 250 mA was passed through the sample. The potential was measured between the collectors and the half-cell resistance was calculated based on Ohm’s law. The bipolar plate was removed,

and the potential across the electrodes and carbon paper was measured to produce a baseline resistance. The baseline resistance, that is the resistance of the testing circuit excluding the bipolar plate but including carbon papers and electrodes, was measured after 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 total half-cell resistance.

3. Results and discussion

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

The initial idea to produce bipolar plates from wet-lay generated material was based on the desire to overcome the restriction on adding high levels of fillers (>50%) to a polymer matrix while allowing the material to flow and fill the cavity of a mold. When a slurry was produced with thermoplastic fibers, reinforcing fibers, and conductive graphite particles, filler loading levels >80% have been successfully reached while allowing the material to be compression molded [13,16].

PET was the initial thermoplastic fiber used for the development of wet-lay material. Because PET may not be the ideal polymer matrix for bipolar plates due to hydrolytic degradation, we turned our attention to the modification of the PET based material.

3.2. Production of laminate composite materials and bipolar plates

It was found that a mixture of chemical resistant polymer and graphite particles could be used to form a protective layer for the PET composite plate [13,17]. The conductive polymer mixture that forms the skin layer should meet several requirements, including excellent chemical and electrochemical resistance, high electrical conductivity, and formation of a composite with good adhesion at the interfaces. PVDF (Kynar 761) meets these requirements, and also possesses a broad processing temperature range (from 175 to 300 °C) that overlaps with the molding temperature of PET [18]. Therefore, the outer layer consisted of a 20/80 wt% ratio of PVDF/graphite. The ratio was chosen in order to maintain a consistent level of filler concentration throughout the skin layer and wet-lay core.

While concerns still remain for using PET based material in a fuel cell environment, an alternative thermoplastic matrix was investigated. PPS is a semi-crystalline polymer with a melting temperature of 285 °C and a high degree of chemical resistance. The highly stable chemical bonds of its molecular structure impart a remarkable degree of molecular stability toward both thermal degradation and chemical reactivity, making it an improved matrix over PET [19]. It is regarded as second only to polytetrafluoroethylene (PTFE) in overall chemical resistance [20]. Furthermore, results have shown (Table 1) that PPS based wet-lay composites exhibit comparable conductivity and superior mechanical properties relative to PET based wet-lay composites [13]. Therefore, it was believed that using PPS based wet-lay material in the core of a bipolar plate could provide suf-

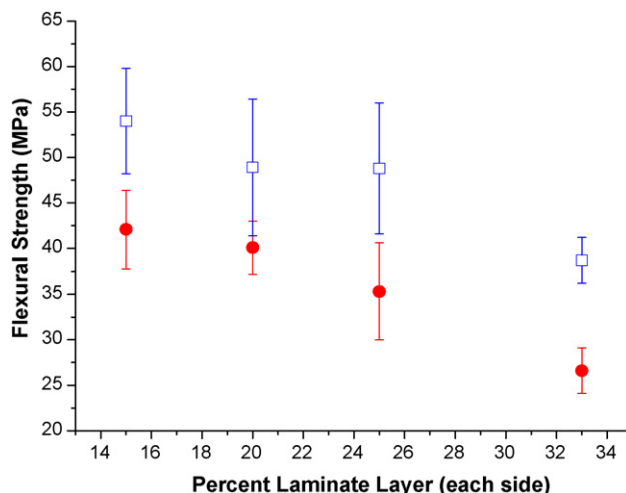


Fig. 3. Flexural strength of various volume percents of skin layer on the surfaces of a PPS-TC70 core material processed by the one-step (□) and two-step (○) methods at ambient conditions. Error bars indicate 1 S.D.

ficient strength, while the PVDF in the laminate layer could be used to promote improved formability when compression molded and the possibility for a significant reduction in the heating/cooling cycle of the molding process.

The volume percent of laminate material for a given plate was varied to obtain a balance of conductivity, mechanical strength and complete formation of gas flow channels into the PVDF/graphite powder. Based on formability observations, 20 vol% PVDF/graphite on each surface was found to be the minimum level that still allowed for complete formation of channels into the PVDF/graphite powder using our specific channel design. Dropping below 20 vol% did not provide sufficient laminate material for channel formation with our channel design, while increasing the laminate content above 20 vol% had a negative effect on overall mechanical properties as shown in Figs. 3 and 4. The wet-lay core material typically contained 70–0 wt% graphite particles. Therefore, for this paper a nomen-

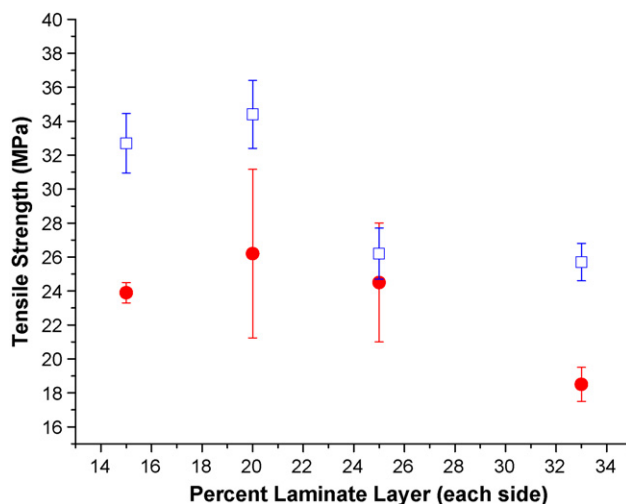


Fig. 4. Tensile strength at various volume percents of skin-layer on the surfaces of a PPS-TC70 core material processed by the one-step (□) and two-step (○) methods at ambient conditions. Error bars indicate 1 S.D.

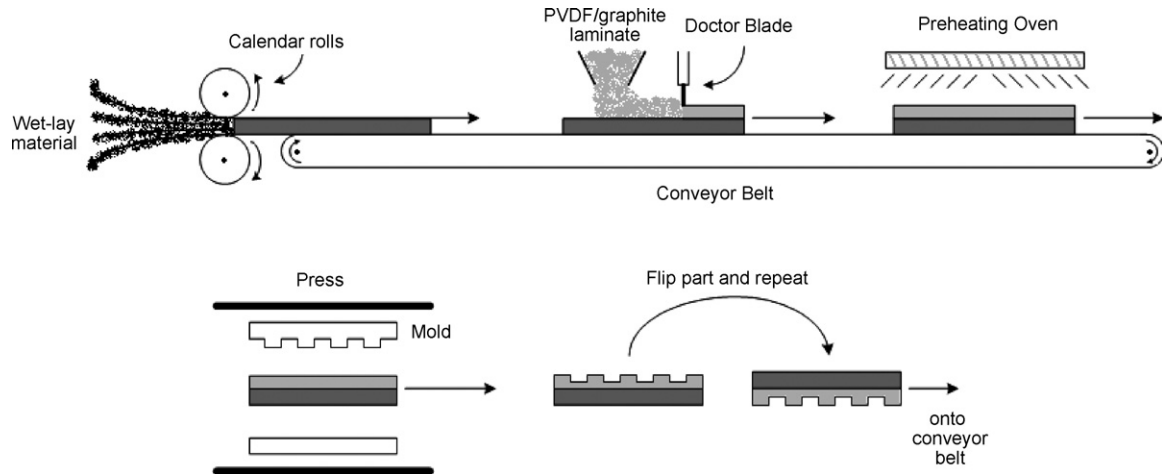


Fig. 5. Envisioned process for the continuous manufacturing of laminate polymer composite bipolar plates by pre-consolidating the wet-lay core material.

clature of 20Lam80PPS designates that the entire laminate plate consists of 20 vol% of PVDF/graphite mixture on each surface, with the wet-lay core consisting of a PPS matrix with 80 wt% conductive graphite particles.

As stated in Section 2.3, the laminate plates were produced by either the one-step or two-step molding method. Potentially there could be differences in the mechanical strengths of plates produced by the two methods because of differences in adhesion of the outer layer to the core composite material. Furthermore, processing schemes will be different because in the one-step method the entire part has to be heated, whereas in the two-step method only the surfaces have to be heated. In the one-step method, the laminate powder was added to the surfaces of sheets of porous wet-lay material. Unfortunately, the porous wet-lay material typically exhibited a significant amount of loft. When a number of wet-lay sheets were stacked, loft was further enhanced. It was difficult to manually spread the laminate powder evenly over a non-uniform surface such as the porous wet-lay sheets. The two-step method offered an advantage over the one-step method. It was found to be significantly easier to evenly spread the laminate powder over a solid, flat surface. Therefore, it may be possible to continuously manufacture bipolar plates by the two-step method as shown in Fig. 5. In this process, sheets of wet-lay material may be continuously rolled through a calendar creating a compacted blank plaque. The laminate powder can be metered onto the surface while being continuously rolled to other parts of the processing line. The potential disadvantage in this process is the

possibility for de-lamination to occur due to poor adhesion of the laminate layer onto the pre-consolidated wet-lay core material.

3.3. Electrical conductivity of laminate composite materials

Electrical conductivity is one of the most important properties of bipolar plates. Huang et al. [13] reported the electrical properties of wet-lay based composites compared to other polymer composite materials (see Table 1). PET and PPS based wet-lay composites have exhibited in-plane (bulk) conductivities higher than 200 S cm^{-1} , well exceeding the DOE target of 100 S cm^{-1} . These values were also higher than any other polymer composite material with similar graphite loadings.

In Table 2 are shown electrical conductivity results for the laminate flat plaque test specimens. The laminate plaques exhibit improved in-plane and through-plane conductivities when compared to plaques generated from wet-lay material only. Laminate plaques exhibit bulk conductivities above 300 S cm^{-1} , with through-plane conductivities as high as 50 S cm^{-1} . Both of these values represent significant improvements achieved by the laminate structure. When materials of similar compositions differing only by processing method are compared, plates produced by the one-step method exhibit slightly higher conductivities, especially in the through-plane direction. This may be expected because when the material is compression molded via the one-step method, PVDF/graphite powder penetrates into the porous wet-lay material. Therefore, a more conductive network may

Table 2

Conductivity results of laminate flat plaque test specimens consisting of an 80/20 ratio of graphite/PVDF laminate layer on each side, as a function of graphite type, graphite concentration, and processing method

Material designating the amount and type of graphite contained in the wet-lay core	Processing method	In-plane conductivity (S cm^{-1})	Through-plane conductivity (S cm^{-1})
Laminate with 70% TC-300 graphite in core	One-step	209–325	17–32
Laminate with 70% TC-300 graphite in core	Two-step	203–350	14–24
Laminate with 70% KS-150 graphite in core	One-step	166–238	16–24
Laminate with 70% KS-150 graphite in core	Two-step	147–178	16–17
Laminate with 80% KS-150 graphite in core	One-step	164–226	18–26
Laminate with 80% KS-150 graphite in core	Two-step	186–251	15–23

Plaques consisted of 20 vol% laminate layer on both sides.

be generated in the through-plane direction using the one-step molding method. When comparing the graphite type at the 70 wt% level, it appears that the TC-300 type graphite provides the composite material with higher in-plane and through-plane conductivity than those generated using KS-150 graphite. Unfortunately, no data has been obtained for composites generated with 80% TC-300 graphite particles in the wet-lay material.

It is important to realize that graphite filled polymer composite plates may have different properties and performances in different directions. It is apparent from Tables 1 and 2 that the through-plane conductivities for all wet-lay and laminate-based composites are significantly lower than the in-plane conductivities. This may be attributed to several possible factors. First, the graphite particles are not spherical, but rather elongated platelets that may orient in a plane perpendicular to the direction of the compaction force during molding. This plane is designated as the X–Y (in-plane) direction as shown in Fig. 6. Furthermore, when forming the wet-lay sheets, the thermoplastic and reinforcing fibers also align in the X–Y direction and may help induce the graphite particles to orient in the same direction. 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 conductivity. This might explain why composites generated from wet-lay and laminate material with TC-300 graphite (greater aspect ratio), have a higher ratio of in-plane to through-plane conductivities when compared to composites generated with KS-150 graphite (smaller aspect ratio) (see Table 2). Although the use of a more spherically shaped graphite particle reduces the in-plane to through-plane ratio, it might not necessarily improve the through-plane conductivity.

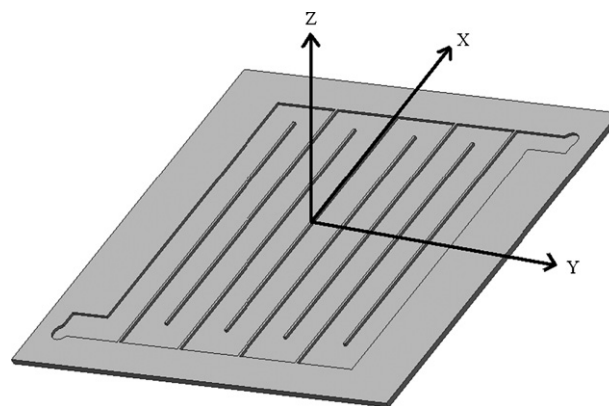


Fig. 6. Laminate plate representation showing the direction of the X–Y plane and Z plane.

3.4. Mechanical properties of wet-lay composite materials

In addition to electrical conductivity, the bipolar plates should also have adequate mechanical properties to be used in fuel cell stacks where they would be subjected to a constant compressive load. However, for polymer composites doped with high levels of conductive particles and/or fibers, it is difficult to obtain high conductivity and sufficient mechanical properties simultaneously. As a result the mechanical properties of most composite materials used to produce bipolar plates are still lower than the target values with the exception being the PPS based wet-lay composites (see Table 1).

Laminate plates produced using a PPS based wet-lay core have potential to meet electrical and mechanical properties simultaneously. In Figs. 3 and 4 are shown the flexural and tensile

Table 3
Comparisons of mechanical properties of laminate flat plaque test specimens consisting of a PPS based wet-lay core containing 70 and 80 wt% graphite, and compression molded at different temperatures using the one-step and two-step methods

Material	Testing temperature (°C)	Processing method	Flexural modulus (GPa)	Flexural strength at break (MPa)	Tensile modulus (GPa)	Tensile strength at break (MPa)
20Lam70PPS	20	One-step	7.238	48.9	15.765	34.4
	80		3.571	36.9	14.023	25.7
	100		3.416	37.7	14.231	27.7
	120		2.659	34.3	7.817	25.4
20Lam70PPS	20	Two-step	6.090	40.1	14.037	26.2
	80		3.400	41.2	14.165	27.8
	100		2.890	40.1	9.506	30.4
	120		2.605	35.5	7.416	25.0
20Lam80PPS	20	One-step	6.630	30.6	10.855	25.0
	80		3.940	28.2	8.401	17.8
	100		3.394	32.2	9.447	14.2
	120		2.922	34.8	8.132	18.5
20Lam80PPS	20	Two-step	5.530	29.9	11.624	15.2
	80		3.432	27.7	6.601	16.7
	100		2.863	31.6	9.105	15.0
	120		2.471	27.2	5.885	18.1
15Lam70PPS	20	One-step	8.089	54.0	16.048	32.7
15Lam70PPS	120	One-step	2.900	44.7	9.561	29.1
25Lam70PPS	20	One-step	8.156	48.8	16.228	26.2
25Lam70PPS	120	One-step	2.950	34.1	10.083	23.2

Plaques consisting of 15, 20, and 25 vol% laminate layers are compared.

strengths of laminate plates at various vol% of PVDF/graphite using a PPS based wet-lay core and their dependency on the production method. The laminate plates exhibit lower strength than wet-lay composite material as reported in Table 1. A decrease in mechanical properties is expected with the laminate plates because the surfaces are comprised of the relatively weaker PVDF matrix. However, due to the presence of wet-lay in the core, the mechanical strengths of the laminate plates still compared well to the vinyl ester and PVDF based polymer composite materials, even at high loading levels of the laminate layer (33 vol% on each side). Composite materials generated by the one-step method generally show a 30–0% increase in flexural and tensile strengths. This increase may be attributed to the penetration of the outer skin layer into the porous wet-lay sheets when compression molded, thus creating a stronger network throughout the entire plate than those generated by the two-step method in which the outer layer contains only PVDF and graphite.

In Table 3 are shown the tensile and flexural strengths and moduli of various compositions of laminate plates using the one-step and two-step methods tested at different temperatures. Mechanical properties are evaluated at elevated temperatures typical of fuel cell operation (80, 100 and 120 °C). The moduli show a significant decrease when temperature is elevated. The decrease in modulus is expected, especially because the testing temperatures are near or above the T_g s of PPS (~88 °C) and PVDF (~–30 °C). The flexural and tensile strengths exhibit a significant dependency on the processing method at ambient temperature. However, at elevated temperatures there appears to be less dependency on the processing method. Although the fuel cell operation temperatures are above the T_g s of both PPS and PVDF, it is believed that the laminate composite bipolar plates will be able to withstand the constant compressive forces of a fuel cell stack because both polymers possess high degrees of crystallinity.

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

Although electrical conductivity of the materials used to produce bipolar plates is important, the performance of the bipolar plate in a fuel cell is the defining characteristic. A bipolar plate may have electrical properties that drastically differ from flat plaque test specimens because of the molded gas flow channels in the surfaces. Additionally, interfacial resistance between bipolar plates and the membrane electrode assembly, gas diffusion layer, etc. also contribute to the total resistance. To evaluate their contribution to the electrical properties of the bipolar plates, half-cell resistance tests were conducted. In addition to measuring the resistance of the entire assembly, the resistance of the electrodes and carbon paper was measured to produce a baseline resistance. The measurement of a baseline was found to be important because the contact resistance between current collectors and carbon paper could differ dramatically depending on the specific collectors used.

Half-cell resistances measured on bipolar plates can exhibit significant differences than those measured on monopolar plates of similar compositions. Half-cell resistances for wet-lay based bipolar plates are measured to be 0.11–19 $\Omega \text{ cm}^2$ (see Fig. 7).

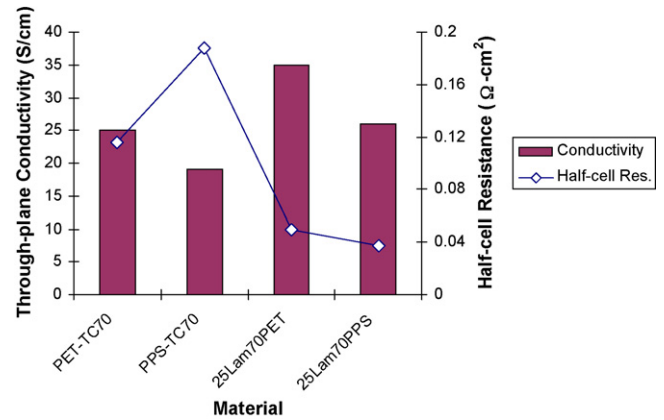


Fig. 7. Through-plane conductivity and half-cell resistance comparisons for compression molded wet-lay material and laminate plates.

Huang et al. [13] reported half-cell resistances for wet-lay based monopolar plates less than 0.03 $\Omega \text{ cm}^2$. It is expected that the half-cell resistance for wet-lay based bipolar plates would measure twice as high as monopolar plates of the same composition because of reduced contact area. However, the half-cell resistances of wet-lay based bipolar plates exhibit a four-fold increase over that of wet-lay based monopolar plates of the same composition. This may be due to several factors. First, when the wet-lay material is compression molded into a monopolar plate, the material exhibits poor flowability in the rib area of the mold. The situation may be worse when using a double-sided mold instead of a single-sided mold. Second, due to the anisotropy of the wet-lay material there may not be uniform pressure over the plate when compression molding. Because monopolar plates typically had a thickness of 2.4 mm while the bipolar plates had a thickness of 3.6–8 mm, there may be a larger number of voids present in the bipolar plate. Last, the active areas for measuring the half-cell resistance of a monopolar plate was 100 cm^2 (channel side) and 168.5 cm^2 (flat side), whereas the active areas for measuring the half-cell resistance of a bipolar plate was 100 cm^2 on both sides. Because a smaller total active area was used for the bipolar plates, and that bipolar plates contain double-sided features, they are likely to exhibit a higher half-cell resistance than that of monopolar plates.

In Fig. 7 are presented comparisons of the through-plane conductivities for wet-lay material and laminate composite materials, as well as their respective half-cell resistance of a bipolar plate generated from material of similar compositions. The through-plane conductivities increase with the addition of PVDF/graphite on the surfaces by 25–5%. Furthermore, the laminate plates exhibit a decrease in half-cell resistance by a factor of up to 5. An increase in through-plane conductivity is expected for the laminate plates, but it is surprising to see a greater change in the half-cell resistance. The dramatic decrease in half-cell resistance using the laminate structure is believed to be due to several factors. First, bipolar plates generated by wet-lay material do not have surfaces as smooth as that of laminate bipolar plates as suggested in Fig. 8. As a result, the wet-lay based plates have higher contact resistance between the plate and carbon papers and, thus, higher half-cell resistances. Second, the difference

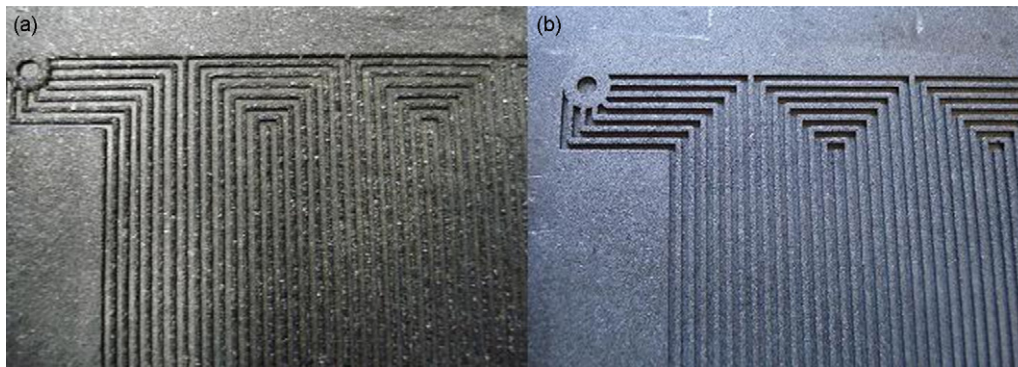


Fig. 8. (a) Expanded view of a bipolar plate generated by wet-lay material and (b) expanded view of a laminate bipolar plate showing improved channel formation.

of through-plane conductivities for wet-lay and laminate bipolar plates may be greater than that of flat samples used in the conductivity test. While poor formability of wet-lay sheets may not influence the formation of flat samples, it can have a great impact on the formation of double-sided bipolar plates and lead to lower through-plane conductivity (due to uneven compaction pressures of the materials) in comparison with the flat samples. For laminate bipolar plates, there is no such difference due to improved material formability. Third, when compressed with a bipolar plate mold, the graphite particles in the PVDF matrix (outer layers of laminate bipolar plate) in the rib area may align more in the Z direction compared to that in the wet-lay sheets, resulting in higher through-plane conductivity of the laminate plates.

4. Conclusions

A new method has been developed to produce cost-effective bipolar plates with high electrical conductivity, good mechanical properties and potential rapid manufacturability. Composite sheets consisting of graphite particles, PPS or polyester and carbon fibers were first generated by means of a wet-lay process. The porous sheets were then stacked and covered with fluoropolymer/graphite particles and compression molded to form layered composite bipolar plates with gas flow channels. Compared to the bipolar plates consisting of wet-lay composite materials only, the bipolar plates with laminate structure have improved formability, higher in-plane and through-plane conductivities and significantly lower half-cell resistance. The shape and definition of the gas flow channels have also been improved by the laminate structure. Although the mechanical properties of the laminate plates are not as high as that of the wet-lay based plates, they are still higher than that of other polymer composite bipolar plates due to the presence of a strong wet-lay material in the core. While the one-step method is good for batch production of laminate bipolar plates with desired mechanical and electrical properties, the two-step method may be chosen for continuous mass production of the plates. It has been shown that the mechanical properties of the laminate plates decrease with temperature. However, it is believed that because PPS and PVDF both possess relatively high degrees of crystallinity, the laminate bipolar plates will still be able to perform well in a

fuel cell stack. The mechanical properties of the laminate bipolar plates may be improved further by using a thermoplastic with higher strength (such as PPS instead of PVDF) in the skin layer. Teflon[®] is another possible thermoplastic matrix which can potentially improve mechanical properties. Although the T_g of Teflon[®] is close to that of PVDF ($<0^\circ\text{C}$), Teflon[®] has an extremely high degree of crystallinity (95%). It is also believed that reducing the channel depth could provide improvements by allowing for a thinner plate to be made and potentially lowering the half-cell resistance of the bipolar plate.

Acknowledgements

The financial support for this work was provided by the Department of Energy (#DE-FG02-05ER86254) through a STTR grant to Nanosonic, Inc. and is gratefully acknowledged.

References

- [1] K. RoBberg, V. Trapp, in: H.A.G. Wolf Vielstich, A. Lamm (Eds.), Handbook of Fuel Cells-Fundamentals Technology and Applications, John Wiley & Sons, Ltd., 2003, pp. 308–314.
- [2] J.G. Clulow, F.E. Zappitelli, C.M. Carlstrom, J.I.L. Zemsky, D.N. Busick, M.S. Wilson, AIChE Spring National Meeting, New Orleans, LA, 2002.
- [3] G.O. Mepsted, J.M. Moore, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), Handbook of Fuel Cells-Fundamentals Technology and Applications, John Wiley & Sons, Ltd., 2003, pp. 286–293.
- [4] J. Wind, A. LaCroix, S. Braeuningner, P. Hedrich, C. Heller, M. Schudy, in: H. Wang, Sweikart, Mary Ann, Turner, A. John (Eds.), Handbook of Fuel Cells-Fundamentals Technology and Applications, John Wiley & Sons, Ltd., 2003, pp. 295–307.
- [5] H. Wang, M.A. Sweikart, J.A. Turner, J. Power Sources 115 (2003) 243–251.
- [6] T.M. Besmann, J.W. Klett, J.J. Henry Jr., E. Lara-Curzio, J. Electrochem. Soc. 147 (11) (2000) 4083–4086.
- [7] D.N. Busick, S. Wilson, Mater. Res. Soc. Symp. Proc. 575 (2000) 247–251.
- [8] M.S. Wilson, Busick, N. Deanna, Composite Bipolar Plate for Electrochemical Cells, The Regents of the University of California, USA, 2001, p. 12.
- [9] D.N. Busick, S. Wilson, Fuel Cells Bull. 2 (5) (1999) 6–8.
- [10] R. Blunk, et al., J. Power Sources 156 (2) (2006) 151–157.
- [11] E. Balko, N. Lawrance, J. Richard, Carbon Fiber Reinforced Fluorocarbon-Graphite Bipolar Current Collector-Separator, General Electric Company, USA, 1982, p. 10.
- [12] M.K. Bisaria, P. Andrin, M. Abdou, Y. Cai, US 6,379,795 (2002).
- [13] J. Huang, D.G. Baird, J.E. McGrath, J. Power Sources 150 (2005) 110–119.

- [14] B.D. Cunningham, D.G. Baird, Review of Materials and Processing Methods in the Production of Bipolar Plates for Fuel Cells, 52(1), 2007.
- [15] L. Landis, J.L. Tucker, Bipolar Plate Components Move to the Forefront, R&D Magazine, 2002, pp. 36–38.
- [16] K.W. Tucker, G.P. Weeks, Wet-Laid Sheet Material and Composite Thereof, E.I. Du Pont de Nemours and Company, USA, 1997, p. 10.
- [17] D.G. Baird, J. Huang, J. McGrath, Compression Moldable Composite Bipolar Plates with High Through-Plane Conductivity, 2005.
- [18] Kynar® and Kynar Flex® PVDF Technical Brochure, Elf Atochem North American Inc.
- [19] http://www.cpchem.com/enu/ryton_pps_p-what_is_pps.asp.
- [20] J.W. Gardner, P.J. Boeke, in: I.I. Rubin (Ed.), Handbook of Plastic Materials and Technology, Wiley, New York, 1990, p. 423.
- [21] R.J. Lawrance, Low Cost Bipolar Current Collector-Separator for Electrochemical Cells, General Electric Company, USA, 1980, p. 10.
- [22] <http://www.matweb.com/search/SpecificMaterial.asp?bassnum=PPTSM029>.
- [23] BMC Inc. Briefs, Editor: Grapevine Marketing, 13(2) (2001) 2–4.
- [24] A. Pellegrini, Spaziante, M. Placido, Bipolar Separator for Electrochemical Cells and Method of Preparation Thereof, Oronzio deNora Impianti Elettrochimici S.p.S, USA, 1980, pp. 1–8.
- [25] <http://www.dupont.com/fuelcells/pdf/plates.pdf>.