LOW-COST COMPOSITE BIPOLAR PLATES FOR PEFC STACKS

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ABSTRACT

With the current emphasis on more economical PEFC stacks, fuel cell developers are focusing on new technologies that offer high performance as well as low cost. One component whose cost can be considerably reduced is the bipolar plate. Besides meeting economic constraints, bipolar plates must satisfy a host of other requirements, including high electronic conductivity, low gas permeability, corrosion resistance, low weight, high strength, and manufacturability. To achieve this demanding combination of properties, we are developing new material formulations for composite bipolar plates. Commercially available, corrosion resistant thermosetting resins are combined with graphite powder to produce relatively inexpensive composite materials that satisfy current performance objectives. Traditional and non-traditional fiber reinforcements and other additives further improve the properties of the material without substantially increasing cost. Some significant advantages of these composites over existing bipolar plate materials are described, particularly in the critical areas of weight, cost, and ease of manufacture.

INTRODUCTION

Background

Polymer electrolyte fuel cells (PEFCs) are under widespread development to produce electrical power for a variety of stationary and transportation applications (1). To produce useful currents and voltages, individual fuel cells are connected in series to form stacks of cells. Adjacent cells in a stack are typically separated by bipolar plates, which serve as the anode for one fuel cell and the cathode for the adjacent cell. Thus the bipolar plate must function as a current collector as well as an impermeable barrier between the gases on either side of the plate. In addition, many stack designs incorporate gas flow channels into the bipolar plate. These flow fields ideally provide uniform distribution of reactant gases over the entire area of a catalyzed proton exchange membrane. Flow fields are commonly molded or machined into both sides of a bipolar plate, with an anode flow field on one side and a cathode flow field on the other side.

To date, the bipolar plate remains the most problematic and costly component of PEFC stacks (2). The most commonly used material for single cell testing is machined graphite, which is expensive and costly to machine. The brittle nature of graphite also prevents the use of thin components for reducing stack size and weight, which is particularly important for transportation applications. Other stack designs consider the use of metal hardware such as stainless steel (2-4). But a number of disadvantages are associated with stainless steel, including high density, high cost of machining, and possible corrosion in the fuel cell...
environment. In light of these difficulties, much of the recent work on fuel cell bipolar plate materials has been centered around graphite/polymer composites (5-8). Composite materials offer the potential advantages of lower cost, lower weight, and greater ease of manufacture over traditional graphite and metal plates. For instance, flow fields can be molded directly into these composites, thereby eliminating the machining or forming steps required for graphite or metal hardware.

### Development of Novel Composite Bipolar Plates

Although polyethylene and polypropylene have also been used as matrices, most of the thermoplastic composite materials used in fuel cell bipolar plates are composed of graphite powder in poly(vinylidene fluoride) (PVDF), with or without short carbon fibers for reinforcement (5,6). Unfortunately, PVDF is relatively expensive, and any thermoplastic composite must be cooled before being removed from the mold. Thermosetting resins such as phenolics, epoxies, and polyesters generally offer shorter process cycle times than thermoplastics because, once cured, they can be removed from the mold while still hot. However, most of the documented methods of production of graphite/thermoset bipolar plates include difficult and costly steps such as extensive heat treatments and resin or metal coatings, and for phenolic resins in particular some concerns remain regarding porosity and corrosion issues (7-9).

Thus, the major challenge in developing a suitable composite bipolar plate material is to simultaneously meet cost, performance, and manufacturability objectives. To this end, the primary merit properties required of bipolar plate materials for PEFC stacks are listed in Table I.

### Table I. Desired Attributes of Bipolar Plate Materials

| Merit Property                  | Target Value                                      |
|--------------------------------|---------------------------------------------------|
| Good electrical conductivity   | > 100 S/cm bulk and/or > 200 S/cm² areal          |
| Low permeability               | << 1mA/cm² H, equivalent with ΔP = 2 atm          |
| Low production cost            | <$10/kg including materials and processing       |
| Good mechanical properties     | Sufficient strength and elasticity to allow thin plates to tolerate assembly and stack conditions |
| Corrosion resistance           | Chemical and physical stability during stack operation |
| Low weight                     | > 1 kW/kg for transportation; not as critical for stationary power |

Existing composite bipolar plate technologies are adequate in most respects, but require major improvements in cost and ease of manufacture to become feasible for consumer applications. For both thermoplastic and thermoset matrix composites, compression molding is favored over injection or transfer molding due to the high solids content required to attain high electrical conductivity. High solids loading (> 50%) results in a
thixotropic compound with poor rheology; injection molding of such a compound would be
nearly impossible due to the exceedingly high pressures that would be required to achieve
adequate fill in the mold.

If compression molding is used, cost-effective mass production appears to be more
readily achievable with thermosets than with thermoplastics based on cycle time. One
particular family of thermoset resins seems especially well-suited to bipolar plates; vinyl
esters are methacrylated epoxy difunctional polyesters, and as such are often described as a
cross between polyester and epoxy resins. These resins are highly corrosion resistant,
lightweight, strong, tough, and commercially available at low cost, making them nearly
ideal matrix material candidates for composite bipolar plates. Regardless of matrix
material, the most widely used conductive filler in composite bipolar plates is graphite
powder. It is employed in the vinyl ester composites described here as well, although the
relationship between electrical conductivity and graphite volume fraction has been found to
depend somewhat on particle size distribution. Thus we have identified a particular type of
graphite powder that offers relatively high conductivity for a given volume fraction and is
reasonably easy to combine with the liquid resin to form a homogeneous mixture.
Graphite/vinyl ester composites are very promising candidates for bipolar plates, even with
baseline formulations, but certain types of fiber reinforcement could offer even further
advantages in mechanical properties.

Selection of Reinforcing Fibers

Composite materials, including bipolar plates, are often reinforced with fibers to
provide additional strength. Traditional fiber reinforcements for structural composites
include graphite, glass, Kevlar or metal. The fibers are typically used as-is but may have
surface treatments designed to improve fiber-resin adhesion. "Sized" glass fibers, for
example, possess functional groups at the surface that improve adhesion or provide
chemical bonds to the resin. In general, these high-strength traditional fibers impart vastly
improved mechanical properties in structural composites where long fibers or fabric
rovings are used and the volume fractions of resin are typically quite high (e.g., 60% or
more). In the case of electrically conductive composites for electrochemical applications,
any fiber reinforcements that are used need to be relatively short to attain good fill, avoid
hand lay-up, and provide a relatively homogenous structure. As a result, short
"microfibers" (<1 mm) are utilized. On the other hand, the volume fractions of resin and
fiber in the conductive composite must be considerably lower than in structural composites
to accommodate sufficient graphite powder for conductivity. As such, it is difficult for a
resin to sufficiently encapsulate or adhere to the fibers to effectively utilize their superior
mechanical properties.

Improving the fiber/resin adhesion in such composites is required to adequately
capitalize upon the fiber reinforcement. One approach is to use a fiber of similar nature as
the resin such that a more compatible interface is obtained. Short polymer microfibers,
commonly referred to as "flock", could conceivably provide enhanced fiber/resin interfaces
and are readily available.

A novel method of improving the "adhesion" of the resin to the fiber is to utilize a
porous microfiber that imbibes the resin such that the resin/fiber interface is effectively
continuous. Porous, hollow fibers are widely utilized for separations, etc., but are not
readily available on a microfiber scale. Activated carbon microfibers and porous ceramic
whiskers are commonly available but adequate inclusion of the resin and cost are issues. We have found an alternative porous fiber for this purpose that is readily available and very low-cost. These fibers readily swell with resin and the cured structures thus formed effectively become micro-composite fibers that are integrally linked with the remainder of the resin matrix. At only 40,000 - 120,000 psi, these fibers do not have the tensile strength of graphite (520,000 psi) or glass (200,000 - 300,000 psi), but the direct link with the resin allows a more effective use of the fiber component.

**EXPERIMENTAL**

**Material Components**

The baseline composite material studied here comprises graphite powder encapsulated in a low-cost, corrosion resistant vinyl ester resin matrix. Catalysts and promoters/accelerators (in the present case methyl ethyl ketone peroxide and cobalt naphthenate) are added to the liquid resin solution to facilitate curing. Other liquid additives, such as antifoam agents and surface-functional additives, may be incorporated into the resin as desired to improve particle wet-out or composite surface tension. Synthetic graphite powder of a fairly narrow particle size distribution constitutes the major conductive component of the composite; other types of graphite or carbon powder may also be added to increase conductivity. Short (< 1 mm) fibers are often added to the material to provide reinforcement. These may include traditional fibers such as graphite and glass, or nontraditional, porous and/or polymeric fibers.

**Composite Compounding and Molding**

To prepare the molding compound for laboratory-scale samples, all liquid additives (accelerators, promoters, catalysts, surfactants, etc.) are thoroughly mixed into the resin solution with a hand mixer. The pre-blended solids (powders and/or fibers) are then gradually added to the formulated resin and the mixture is blended to form a stiff paste with a friable consistency. The mold is filled with a weighed charge of paste and pressed at ca. 100°C and 1000-2000 psi for 15 minutes. The hardened part is removed from the mold while hot and postcured in an 80-90°C oven, generally for 1-2 hours. Laboratory-scale molded parts take the form of either a 6 x 6 x 0.1 in. plaque or a 1 in. diameter disk (thickness dependent on charge).

**Property Characterization**

Various techniques are employed to measure the merit properties of these composite materials. Hydrogen gas permeability is measured using a filter-type permeation cell with an upstream H₂ pressure of 30 psig (ΔP_hydrogen = 2 atm) in which the volume of water in a column displaced by hydrogen permeation is measured. Bulk electrical conductivity is measured with a linear 4-point probe; to eliminate offset errors, the slope of the V/I scan is used to calculate resistance. Resin cure characteristics are evaluated through differential scanning calorimetry (DSC) to investigate the effects of material composition and processing conditions on gel time, cure time, and cure rate. The surface tension of the molded material is characterized using measurements of water droplet contact angles. Mechanical properties are evaluated by using an Instron materials testing system to conduct...
tensile tests and 3-point-bend (flexural) tests. Corrosion resistance is assessed by measuring the weight loss of samples submerged in sulfuric acid solutions of varying pH at 80°C for 1000 hours. To examine reactant gas effects, the solutions were continuously sparged with either 6% hydrogen/argon or air.

RESULTS

Preliminary Results for Small Samples

Initial development of a baseline composition with the required values of conductivity, permeability, strength, and cure rate was performed using 1 in. diameter compression molded disks. Cure profiles generated using DSC showed that, for the same catalyst concentration, raising the cure temperature from 100°C to 110°C effectively cuts cure time in half. Cure profiles for neat resin and a resin/47 wt% graphite mixture were nearly identical, providing no evidence of any effect of graphite on cure time. Hydrogen permeabilities of disks containing 40-75 wt% graphite were below the detection threshold of the apparatus (ca. 0.01 mA/cm²) and therefore well below the target maximum of 1 mA/cm².

Tests with small samples also revealed that the choice of graphite powder influences the conductivity of the molded disks. This effect appears to arise from differences in particle size and particle size distribution. 3-point bend tests were performed on samples containing about 40 wt% of the graphite which gave the best electrical conductivity for a given filler loading. Flexural strengths obtained from these tests ranged from 4200-4500 psi for samples with bulk conductivities of 50-120 S/cm. These results were quite promising in light of a target value of 4000 psi suggested elsewhere (9). The same graphite powder was incorporated into several subsequent samples to generate an empirical percolation curve, given in Figure 1. This curve shows that although a percolated conductive network is formed at less than 5 vol% graphite, 50-55 vol% (65-70 wt%) graphite is the threshold at which samples consistently have bulk conductivities greater than or equal to 100 S/cm. High resin content is desirable, since a continuous matrix lends structural integrity to the composite. With only 50-55 vol% graphite powder, short reinforcing fibers may be incorporated into the composite while maintaining a reasonably high resin content. Additionally, since flexural strengths for composites without fibers are already very close to a reasonable target value such as 4000 psi, a wise choice of reinforcement could provide sufficient improvements in strength at very low loading. Graphite and glass fibers are obvious candidates; porous and polymeric fibers are also strong possibilities. While graphite and glass fibers are not particularly susceptible to corrosion in a fuel cell environment, corrosion was a valid concern for the non-traditional fibers. Corrosion testing was performed on castings of both neat resin and resin containing a few wt% of either the porous or polymeric fibers. Samples containing fibers sustained slightly more weight loss than the neat resins, and the effect was more pronounced for the porous fibers than for the polymeric ones. Despite the measured weight loss, after 1000 hours no visible corrosion or pitting was present on the samples and the sulfuric acid solutions in which they were immersed remained clear. Therefore, it was suspected that a great deal of the weight loss could be attributed to escape of residual unreacted styrene from the resin, and that very little corrosion of the samples actually occurred. Additional corrosion and in-cell tests are planned to investigate this possibility.
Scale-up to Large Samples

To better address manufacturability issues, and to obtain standard-size mechanical test coupons, sample size was scaled up from 1 in. disks to 6 x 6 in. plates. Even though previous experience suggested that larger plates do not always reproduce the properties of smaller samples, the compositions and processing conditions of large samples were developed based on information gained from the smaller samples. One particular type of graphite powder with a "tailored" particle size distribution was used for all of the large samples based on conductivity results for the smaller samples. Processing was similar to the small sample case, and 68 wt% graphite was selected as a baseline composition for the composite based on the percolation curve shown in Figure 1. For a 3 mm thick plate, a bulk conductivity of 60 S/cm corresponds to the target value of 200 S/cm² areal conductivity; plates containing 68% graphite consistently exhibited bulk conductivities of 60 S/cm or higher.

With 6 x 6 in. plates, it was possible to generate some basic comparisons between the graphite/vinyl ester composites and other composite bipolar plate materials. Some measured mechanical properties of an unreinforced vinyl ester composite containing 68% graphite and a commercially available graphite/thermoplastic composite are listed in Table II. As shown in the table, the graphite/vinyl ester material outperformed the commercial material in each category.

|                  | Commercial Graphite/Thermoplastic Composite | LANL Graphite/Vinyl Ester Composite |
|------------------|--------------------------------------------|-----------------------------------|
| Percent strain at break | 0.24                                       | 0.34                              |
| Tensile strength (psi) | 2800                                       | 3400                              |
| Flexural Strength (psi) | 3000                                       | 4300                              |

In-Cell Testing

As part of a collaboration, Plug Power, LLC, designed and successfully used a 4 x 4 x 0.375 in. tool to mold bipolar plates with and without integral flow fields. A set of these molded plates which had machined flow fields were demonstrated in fuel cells at Plug Power and performed nearly as well as machined graphite. A thinner, more conductive set of the 6 x 6 plates molded at LANL and described above were also tested at Plug Power after being cut and machined to their specifications. These plates exhibited improved performance comparable to current baseline bipolar plate materials. Polarization curves for these plates along with similar data for stainless steel are shown in Figure 2 for comparison.
Mechanical Properties with Fiber Reinforcement

In addition to making baseline comparisons using unreinforced formulations, another objective of producing and studying large plate samples was to investigate the effects of different fiber additives on composite mechanical properties. Four types of fibers were used to generate preliminary comparisons: graphite, sized glass, polymeric fibers, and porous fibers. The tensile and flexural strengths of these four fiber reinforced materials relative to an unreinforced sample are shown in Figure 3. The data are normalized to the unreinforced material since the results from this figure and Table II were obtained at two different facilities.

Electrical conductivities were reduced for most of the fiber reinforced plates, but this is primarily because graphite powder loading was reduced slightly to accommodate the fibers. The conductivity of the graphite fiber reinforced composite was surprisingly low since graphite fibers are electrically conductive, but this phenomenon has also occurred in small samples and in other composite systems. It was assumed that the conductivity of any one of these composites could be brought up to acceptable levels by sacrificing resin rather than graphite powder to incorporate the fibers, so the relative improvements in mechanical properties offered by the various fibers were the real focus of the comparison in Figure 3. Despite the sizing of the glass fibers and the chemical compatibility of the polymeric fiber with the matrix, neither of these two reinforcements offered significant improvements in composite strength. Both graphite and porous fibers offered substantial improvements in strength -- over 50% increases in flexure -- at only 5 wt% loading. The porous fibers offered the greatest improvement in both tensile strength and flexural strength, despite the fact that this fiber has only 10-20% of the tensile strength of the graphite fibers. Presumably, this is because adhesion and wetting between the resin and graphite fibers is relatively poor, while the resin actually penetrates the porous fibers, effectively creating a continuous interphase region. The strength improvements offered by this porous fiber coupled with its low cost (a fraction of the cost of graphite fibers) rendered it the most intriguing of the four candidates, provided that adequate electrical conductivity could be achieved.

To further examine the relationship between mechanical properties and electrical conductivity in composites containing the porous fibers, an additional group of plates containing the porous fiber was fabricated. These plates were of various compositions within the range of 2-6 wt% fibers and 64-71 wt% graphite. With the exception of two plates with very high resin content, all of the new group of porous fiber reinforced plates met or exceeded the target of 200 S/cm² when conductivity was normalized to plate thickness, and all exhibited improved flexural strength over unreinforced samples. The flexural strengths and conductivities of these plates are shown in Figure 4, where the flexural strength values have again been normalized to the unreinforced formulation of Figure 3 to account for different testing equipment. A more complete characterization of the mechanical properties and corrosion resistance of the porous fiber reinforced samples is planned.

Potential Benefits of Surface Property Additives

Depending upon the approach adopted by the stack designer, hydrophobic channel walls are often desirable for effective water transport and removal within the flow fields of the bipolar plate. Surface-functional additives may be added to the resin to enhance the
surface properties of the composite. Certain fluorochemical intermediates tend to migrate to the surface of the molded part, such that additions to the resin of only a few volume percent can substantially lower the surface energy and discourage the accumulation of water in the channels. For a sample with 1.5% of a particular surface additive incorporated into the resin, water droplet contact angles increased by about 10° relative to an otherwise identical sample without the additive. These additives are expensive, however, so their relative merit continues to be evaluated.

Cost Analysis

Bulk material costs for composite bipolar plates can be readily estimated from the baseline composition, with allowances for any fiber reinforcements and/or additives that may be desired. For 1 kg of material, the projected costs are as follows:

- Resin: $1.25
- Graphite powder: $1.00
- “Expensive” fiber reinforcements (e.g., graphite): $0.75
- “Inexpensive” fiber reinforcements (e.g., glass, polymeric, porous): $0.10
- Additives (e.g., catalysts, promoters): $0.40

$2.75-3.40/kg

With a target total cost of $10/kg, this leaves about two-thirds of the target cost available for processing. We are currently working with compounders and molders to develop efficient and cost-effective processing methods to meet this goal.

ONGOING EFFORTS

Although bipolar plates must be sufficiently physically robust to withstand stack assembly and operation, specific required values of strength parameters are difficult to quantify. Bipolar plates must be able to support clamping forces of hundreds of pounds per square inch. But the plates are often subjected to additional stresses during handling and assembly. While high strength is desirable, a certain amount of flexibility/elasticity is also required, for example, for plates to tolerate slight misalignment during assembly. As such, in addition to further mechanical testing of the composite materials, we plan to more fully examine the mechanical property requirements of the plates. Creep is less problematic with thermoset resins than with thermoplastics, but the long-term effects of elevated temperature on mechanical properties of these composites also deserves some investigation.

A better understanding of the use and relevance of surface property additives is required, and could possibly be accomplished with in-cell testing. In-cell testing is also needed for fiber reinforced plates, along with corrosion testing and post-corrosion mechanical testing.

In cooperation with compounders and molding houses, we anticipate improvements in mixing and cycle time. Additionally, we are exploring the possibilities of other vinyl ester resin and/or additive systems. Alternative resin systems may offer advantages in mechanical properties or corrosion resistance, while changes in additives may offer processing improvements. The catalyst system for the results described here produces molding compounds with a shelf life of a few hours; we are exploring different catalysts.
systems that offer shelf lives of several weeks while maintaining short cycle times. The effects of certain additives on the corrosion susceptibility of the composites also need to be evaluated. Some of these additives possibly contain metal/organic salts. Therefore, we need to ascertain if metal ions can leach out of the composite plate and promote corrosion or accumulate in the proton exchange membrane.

CONCLUSIONS

Using commercially available vinyl ester resins and “tailored” graphite powder, we have developed a composite material that appears to meet the property requirements for PEFC bipolar plates, including high conductivity, low permeability, low weight, low cost, corrosion resistance, high strength, and good flexibility. The performance of these plates in fuel cells is comparable to that of machined graphite or stainless steel. Incorporating low-cost porous microfibers into the material significantly improves its mechanical properties, and other additives show promise for enhancing surface properties. Bulk raw material costs remain at about $3/kg, and forthcoming improvements in processing should keep the total materials and manufacturing cost below the $10/kg target. Hence, this material possibly offers considerable advantages over other composite bipolar plate technologies not only in cost and processing, but in performance as well.

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Figure 1. Empirical percolation curve for 1 in. diameter graphite/vinyl ester composites.

Figure 2. Polarization curves for composite and stainless steel bipolar plates. In-cell testing was performed as part of a collaboration with Plug Power, LLC.
Figure 3. Effects of different types of fiber reinforcement on composite strength.

Figure 4. Flexural strength vs. conductivity for porous-fiber reinforced composites.