Novel composite bipolar plates in PEM fuel cells

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Abstract: To overcome some of the traditional material’s major disadvantages, a variety of composite bipolar plates have been developed. The compound structure bipolar plates consisting a metal core layer and a conductive polymer outer layer not only utilize the metal’s advantage, but also prevent the metal from being corroded. And the flow field can be easy obtained by injection moulding. The key problem of this kind bipolar plate is how to enhance the bond between two layers. The conductive polymer bipolar plate has the specific advantage, which is coated noble metal on, can increase the conductivity remarkably. The high polymer/graphite composite bipolar plates are being improved in materials selection, formulation and preparation, the mechanical strength and the conductivity have been rised. The detail contents of some high conductivity bipolar plates are described in this paper.

Keywords: fuel cell, bipolar plate, conductive polymer, composite

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are of interest for power generation due to their high efficiency and near-zero emissions. Cost remains a key barrier to their widespread commercialization. One of the most expensive components in PEMFCs are the bipolar plates, which must perform several functions. First, it must aid in uniformly distributing the hydrogen on one side of a membrane (anode) and the oxygen on the other (cathode). This function is achieved with a pattern of grooves called “flow channels”. Next, the plates must be rigid and support the membrane in the pressurized fuel cell environment, preventing gas and liquid leaks.[1]

The bipolar plate is one of the key components of proton exchange membrane (PEM) fuel cells. The development of materials suitable for use as bipolar plates is technically challenging due to the need to maintain high electrical conductivity in both oxidizing and reducing environments, exhibit chemical compatibility with the aqueous environment and the polymer electrolyte, provide mechanical integrity, and separate/distribute anodic and cathodic reactant gas streams. A key requirement for transportation-related applications is that the material must not only be inexpensive, but must also be amenable to high volume, low cost manufacturing techniques. The U.S. Department of Energy’s Fuel Cells in Transportation Program has set a bipolar plate cost target of $10/kW, which roughly translates into a cost range of $1-2 per plate (≈ 500 cm² area).[2]

One major drawback of graphite is that the gas distribution and cooling channels must be machined, which adds considerable costs. Because of the brittleness of graphite, the bipolar plate requires a thickness of the order of several millimeters, and this cause the fuel-cell stack to be heavy and voluminous. They can represent nearly 80% of the weight of a PEM fuel cell stack.

The potential benefits of metallic bipolar plates were reduced plate thickness and weight and improved thermal and electrical conductivity. Challenges associated with metal bipolar plates are primarily associated with corrosion.

Bipolar plate based on polymer composites offer a high potential to reduce costs and enhance power density.[3] Composite materials offer advantages of low cost, low weight, and easier manufacturing over the other materials. Polymer compound material can be manufactured by injection moulding straightforward one-step process bipolar plates that does not require any perform processes.
In comparison to a similar 20-cell stack with compression moulded bipolar plates of the same materials, the stack with injection moulded bipolar plates has a higher specific electrical output and lower resistance. With the help of tailored moulds injection moulding of bipolar plates becomes price competitive even for comparatively small series in the range of several thousand plate.[4]

2. polymer/graphite composite bipolar plate


The polymer matrix is not just the network supporting the filler; it plays an essential role in many other aspects conditioning the performance of the end material. It favors particle interconnectivity (percolation); it provides for electrical conductivity through a tunnel-type mechanism in the event of deficient percolation; it tolerates the incorporation of large amounts of additive with no deterioration of its mechanical properties, thus favoring both the conducting mechanisms and the dimensional stability of the resulting composite. [6] The most widely used conductive filler in composite bipolar plates is graphite powder. Carbon black, carbon nanotubes filled polymers have relatively low-bulk electrical conductivity. [6–11].

A novel composite bipolar plate has been prepared by a bulk-moulding compound (BMC) process. When the graphite content is 75% and Graphite Powder diameter is over 177µm performance of the bipolar plates is best. The electric conducty is 114Scm⁻¹, and the flexural strength is 31.25Mpa. [12]. Some information is given in table 1.

<table>
<thead>
<tr>
<th>Table 1 Formulation of BMC process</th>
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<tbody>
<tr>
<td>Component</td>
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<tr>
<td>Vinyl ester a (wt.%)</td>
</tr>
<tr>
<td>Low profile agent (wt.%)</td>
</tr>
<tr>
<td>Styrene monomer (wt.%)</td>
</tr>
<tr>
<td>TBPB (phr) b</td>
</tr>
<tr>
<td>Zinc stearate (phr)</td>
</tr>
<tr>
<td>Magnesium oxide (phr)</td>
</tr>
<tr>
<td>Graphite powder (wt.%)</td>
</tr>
<tr>
<td>Total (wt.%)</td>
</tr>
</tbody>
</table>

a Chemical structure of phenolic-novolac, epoxy-based, vinyl ester resin is as follows:
b phr: parts per hundred parts of resin, based on amount of vinyl ester + low profile agent styrene monomer.

The $I-V$ performance of composite bipolar plate is very similar to that of the graphite bipolar plate, and so is the $I-P$ performance which is presented in Fig 1. The data indicate that the optimum composition (75 wt.%) of the composite bipolar plate provides a suitable replacement for the graphite composite plate.[13]

Fig.1. (a) Comparison of $I-V$ performance of graphite bipolar plate and composite bipolar plate (single cell test). (b) Comparison of $I-V$ performance of graphite bipolar plate and composite bipolar plate (6-cell stack test). [13]

A low cost method of fabricating bipolar plates for use in fuel cells utilizes a wet lay process for combining graphite particles, thermoplastic fibers, and reinforcing fibers to produce a plurality of formable sheets, which is presented in Fig 2. The formable sheets are then molded into a bipolar plates with features impressed therein via the molding process. The bipolar plates formed by the process have high conductivity and have sufficient mechanical strength to be used in fuel cells. The result is given in Table 2.[14]

Table.2

Fig.2 Schematic drawing of the wet-lay and compression molding processes used for generating bipolar plates. [14]
In addition to the electrical conductivity, the bipolar plates should also have adequate mechanical properties to be applied in the fuel cell stacks. Compared to the mechanical properties of wet/dry (W/D) lay material and other composite plates, the flexural and tensile strengths of W/D lay composite are 53.0MPa and 36.5MPa, respectively. Both are the highest in all polymer composite plates with the same or similar graphite loadings [14].

A microcomposite powder comprising flat graphite particles \(G_{LP}\) having sides from 50 to 1000 \(\mu\)m and a thickness from 5 to 50 \(\mu\)m, consisting of agglomerates of more elementary graphite particles joined together and superimposed so that their principal planes are mutually parallel, said particles being covered with particles of a fluoropolymer from 0.1 to 0.5 \(\mu\)m in size.

A blend of graphites \(G_{L}+G_{LP}\) was formulated with KYNAR®711 PVDF powder (KYNAR®710 in powder form having a size of between 10 and 50 \(\mu\)m). \(G_{L}\) is natural or synthetic graphite. \(G_{LP}\) is graphite flakes having sides from 50 to 1000 \(\mu\)m and a thickness from 5 to 50 \(\mu\)m, consisting of agglomerates of more elementary graphite particles joined together and superimposed. This blend was produced in a Turbula-type powder blender. The powder recovered had a composition of 87 wt% graphites \(G_{L}+G_{LP}\) and 13 wt% PVDF. This powder was pressed at 185°C and at 1t/cm\(^2\) in order prepare a plaque with a density of 2050 kg/cm\(^3\). The results are given in Table 3 [15].

<table>
<thead>
<tr>
<th>Material reference</th>
<th>Formulation process</th>
<th>Four-point conductivity on a plaque</th>
<th>Surface appearance of the plaques</th>
<th>Permeability of the plaques (m(^2)/m(^2)/P a()()/7.5 (\times) (10^{-18})</th>
<th>Processability in co-rotating twin-screw extruder</th>
<th>Transverse strength</th>
<th>Longitudinal thermal conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>87/13 (GL + G(_{LP})) micro-composite: [-87 wt%</td>
<td>130 S/cm</td>
<td>Uniform</td>
<td>—</td>
<td>Extrudable; 110 N.m torque; regular rod</td>
<td>0.51 GPa</td>
<td>10 W/m.K</td>
<td>32 W/m.K</td>
</tr>
<tr>
<td>Example 2 G(<em>{L}) + G(</em>{LP})</td>
<td>-13 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Extruder reference: RHEODRIVE5000, L/D=94 to 15, co-rotating twin-screw

**Force needed to make the material flow through a 4 mm die with a constant shear rate of 0.1 S\(^{-1}\) at 230°C

***Macroscopic surface appearance of the plaques [15]

### 3. Polymer/Metal composite Bipolar Plates

Coated or surface modified plates require high-conductivity, dense, and contiguous protective layers (no pinholes) to prevent catastrophic corrosion of the base metal and/or contamination of the electrolyte with corrosion products. The protective coating must protect all vulnerable areas including plate edges and the inside diameter of manifolds and other through-plate holes. DOE seeks development of materials and processes for fabricating full-size active area metal bipolar plates that can meet all of the DOE plate targets including the cost target of $6/kW with a reject.
rate of <5%. The processes must be scaleable to high-volume manufacturing. The materials must address corrosion issues.

Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion resistant. Unfortunately, most conventional coating methods (for metal nitrides) are too expensive for PEM fuel cell stack commercialization or tend to leave pin-hole defects, which result in accelerated pure metals and stainless steel, either with or without a protective and conductive coating, are being researched as possible bipolar plates. However, the use of metals has shown problems associated with a possible corrosion in the fuel cell environment. [16]

Methods of treating the surface of metals, such as aluminum, so that they can withstand the corrosive conditions in polymer electrolyte membrane, and still maintain a high level of electrical and thermal conductivity over extended periods of time.

A bipolar plates consisting of a core layer of aluminum, or similarly highly conductive metal such as copper or titanium, clad with and bonded to moulded, conductive plastic layers, that are inert to the environment of the cell, and which define the required flow fields. In order to maintain an adequate bond between the aluminum or other metal and the conductive polymer, means of mechanical surface treatments applied to the metal core layer. A further advantage of the bipolar plates is that it allows for sealing gaskets to be easily co-moulded on to the plate structure, thus simplifying assembly and reducing the costs of the final cell. The structure of the bipolar plates is shown in fig. 3 (a) (b) [17]

![Diagram](image)

(a) 

(b)

(c)

1. core metal. 

2. plated layer. 

3. noble metal layer. 

4. conductive polymer 

Fig. 3 The structure of the compound bipolar plates [17~18]

A conductive polymer outer layer used in combination with an intermediate layer between the conductive polymer and a core metal, that comprises a thin layer of silver, or other noble metal, at the interface between the conductive polymer and an underlying metal layer, are compatible with the requirements of PEM fuel cells. Such treated metals can be formed into bipolar plates or end plates after receiving the coatings, or the conductive polymer layer can be applied or shaped into specifically required forms, alternatively the core metal can be previously formed into the required physical form and then treated on its surfaces so as to realise the benefits of this invention. The structure of the bipolar plates is shown in fig. 3 (c) [18]

Noble metal layer can be very thin as its function is to control the impedance of the interface
and is not specifically related to protecting the core metal and its intermediate layers from corrosion. Conductive polymer is a final layer of a conductive polymer, that serves to protect the structure from corrosion while maintaining a conductive path across the plate under the operating conditions to be encountered in the cell.

4. Metal coated polymer composite

Bipolar plate based on polymer composites offer a high potential to reduce costs and enhance power density. Polymer composite was used as the raw material of bipolar plates. A bipolar plate which had a thickness less than 3mm and an active area ranging 25–50 cm$^2$ with the raw material of polymer composite was presented in Fig.4. The gas flow field with a channel structure was fabricated onto bipolar plate by injection molding, and then noble metals such as Ni and/or Pd–Ni were coated on the surface of polymer composite bipolar plate by electroplating to prevent corrosion and/or apply electrical conductivity. The electrical conductivity of polymer composite plate was $4.40 \times 10^3$ S/cm, respectively. It is considered that the plate in this work possess very superior electrical conductivity due to noble metal coating on the surface of substrate, since the target value in US DOE is set up over 100 S/cm. The average surface roughness was 0.08. The value of polymer composite plate is 10 times better than graphite plate. It is considered that the plate very superior sealing system. It is confirmed that polymer composite plate test cell has been operated favorably for 300 h without degradation of efficiency, the plates became to have better performance at high current densities. The power density is showed favorable specific power over 0.5 kW/kg used polymer composite bipolar plate.

![Fig. 4. Pd–Ni coated polymer composite bipolar plates (active area 25, 50 cm$^2$)](image)

It is believed that Pd–Ni coated polymer composite is one of the most promising candidate materials for PEM fuel cell bipolar plates with respect to electrical and physical performance characteristics including specific power, mechanical properties and manufacturing cost.

5. conclusion

Bipolar plate plays an important role as a key component of fuel cell. The cost of bipolar plate must be reduced in order to realize the industry development of fuel cells. Traditional materials for bipolar plate have some defects. Polymer material have advantages of lightweight, corrosion-resistant and can be shaped by injection moulding which can be manufactured bipolar plates with flow field directly. So the application of the conductive polymer has offered a new developing direction for bipolar plate. Higher conductivity is obtained when the graphite content is high in conductive polymer/graphite composite material. But that the graphite content is excessively high can bring certain defects. conglutinating a outer layer of conductive polymer on metal surface with the proper method can improve the ability of corrosion-resistant, reduce the cost of field processing. But the conductivity will be reduced. Coating noble metal on conductive polymer can raise conductivity but the cost increase. The novel bipolar plates above have superior performance compare to traditional ones.
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