

Bipolar Plates: Different Materials and Processing Methods for Their Usage in Fuel Cells

T Hickmann^{1,*} and O Zielinski¹

¹ Eisenhuth GmbH & Co. KG, Friedrich-Ebert-Straße 2013, 37520 Osterode, Germany

Abstract. Graphite composites based bipolar plates are a preferred material for stationary PEM fuel cell applications, because they are resistant against high temperatures and corrosive conditions. This chapter gives an overview about different material configurations as well as the most important parameters and characterization methods for graphite based bipolar plates. It describes the actual generation PPS based composite materials with improved long-term stability. It introduces the most common materials and gives an overview about interactions between other stack components, characterization and processing, great care should be taken in constructing the bipolar plates.

1 Introduction

Fuel cells are basically galvanic cells converting chemical energy directly into electrical energy. Depending on the specific technology, this reaction may take place at elevated temperatures, thus technical requirements for materials and components of the stack become more and more challenging.

In general, there are different types of bipolar plate technologies: one based on metal or titanium and one based on graphite as a conductive component. The latter can be pure (expanded) graphite or a graphite composite material containing a polymer binder. Metal plates offer excellent electrical and thermal conductivities and they can be processed easily. However, for PEM applications especially for long-life application, such as domestic heating, the corrosion problem of metal plates appears to be almost unsolved by now, so that graphite-based materials are the preferred material according to current state of the art. The thermal and chemical conditions for materials applied in fuel cells and electrolyzers are challenging. Fuel cells mostly operate at 80°C and electrolyzers as well. Due to the corrosive conditions of acid contact in some cases, presence of oxygen, electrochemical potential, in most applications graphite composite based bipolar plates with polymer binders are used in these fuel cells. As mentioned above, composite plates are a superior material regarding their stability under corrosive conditions. However, composites often require thicker plates than metal plates, resulting in more weight and more volume of the stack.

A common way to develop novel material solutions for polymer composites characterized by high thermal and/or electrical conductivity is the use of conductive filler up to 80-85 wt.%. Filler can be based on graphite or titanium or nickel powder. Such highly filled thermoplastic composites can be used as bipolar plates in fuel cells or as

plates in electrolyzers [1-3]. It is necessary to develop formulations with maximized conductivity and low filler content in order to improve mechanical properties and enable adequate plastics processing. A comprehensive understanding of the plastic processing system is required to adjust the conductive function of the composite. The choice of particle type and the use of hybrid filler systems can have an influence on conductivity, also for the usage in Electrolyzers [4]. Additionally, the type of thermoplastic polymer is of importance for composites. The plastic basis is often polyamide, polyethylene, polypropylene, polyvinylidene fluoride and polyphenylene sulphide. An electrical conductivity of approx. 200 S/cm and a thermal conductivity of up to 20 W/m·K could be achieved. Bipolar plates made of graphite/polypropylene composites were successfully tested in a fuel cell. Such Graphite/polymer composites were also used as plates in Electrolyzers and have the potential to replace complete titanium plates.

2 Process

As mentioned above, composite bipolar plates consist of a binder polymer which is highly filled with a conductive component. Typical compositions are > 80 % conductive filler and < 20 % binder polymer, in some cases for fuel cell applications also carbon black. [5] Compounding, processing and manufacturing is substantially different from conventional polymers due to the high content of filler material in the compound [6]. Therefore, a 3-dimensional percolating particle pack structure is required. Usually for fuel cells, the main carbon component of the plate is synthetic graphite. Due to its crystalline layer structure the graphite platelets are inherently anisotropic in their physical properties: conductivity is provided by the mobility of electrons within the graphite layers of each

* Corresponding author: t.hickmann@eisenhuth.de

platelet and not in transverse direction. Thus, the bipolar plate the manufacturing process has to 'promote' different orientations of the platelets forming isotropic physical properties of the macroscopic plate material. In order to realise this complex structure, special mixing devices such as double twin extruders with special features are installed by Eisenhuth.

In the case of the thermoplast method a thermoplastic binder with a defined degree of polymerization is compounded with the graphite material. The chemical structure of the polymer remains unchanged during compounding or moulding process. The polymer has to be selected with sufficient chemical and thermal stability (e.g. data from [7]). Several material candidates are available on the market in high quality and well-defined configurations. Typical thermoplastic polymers as binders in PEM bipolar plates are polypropylene (PP), polyvinylidene fluoride

(PVDF), polyphenylene sulfide (PPS), polyether ether ketone (PEEK) and polyphenylene sulfone (PSU and derivatives). Looking at the plastics pyramid, all of these polymers are in the upper right region of high temperature stability and semi-crystallinity. These polymers safely resist the acid and oxygen contact and provide heat deflection temperature far above the operating point of a high PEM fuel cell and electrolyzers. Within the last years, considerable effort was spent at Eisenhuth for development of innovative bipolar plate solutions. A broad variety of potential binder polymers was tested. Main results of the research activities were that semi-crystalline binders appear to be superior compared to amorphous polymers in terms of processability and mechanical properties of the plate material. Finally, the PP, PVDF and the PPS material was figured out to be the most suited polymer binder for PEM and electrolyser plated by now.

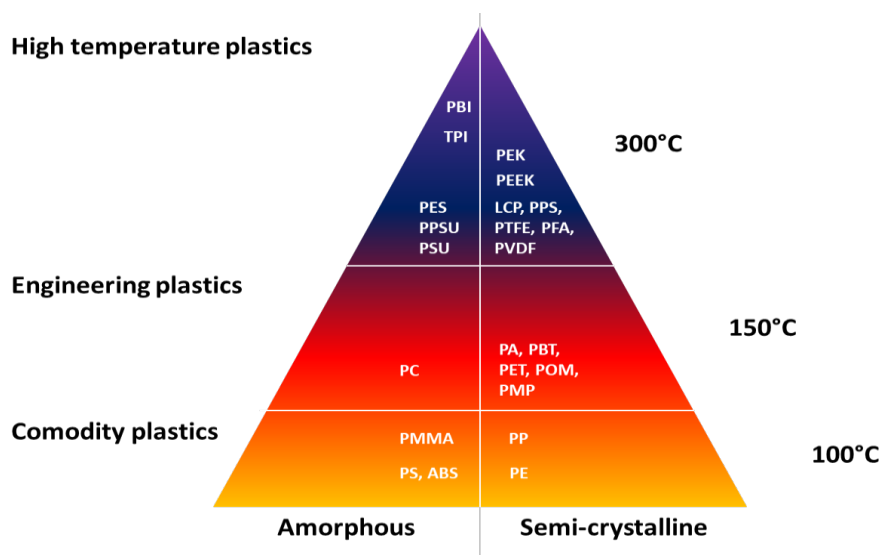


Figure 1. The plastics pyramid: preferred materials for HT-PEM applications are located in the upper right region.

4 Results and discussion

Certainly, the final criteria of success for any bipolar plate is the in-situ performance and stability under real fuel cell conditions. However, fuel cells are highly complex systems with numerous sources of inconsistency. Thus, ex-situ bipolar plate characterization is required for material development and quality control. Several test methods are well established for bipolar plates and shall be presented here with an example for test results. The list of test methods below is not considered to be complete.

3.1 Thermogravimetric analysis (TGA)

During fuel cell operation PEM bipolar plates are exposed to high temperatures, such as 80°C. Not only the

binder polymer, but also the carbon fillers have to be characterized with respect to their thermal stability.

In the next TGA example, several PPS bonded bipolar plate samples with different contents of highly conductive carbon nano tubes (0% to 4% CNT) are investigated by TGA. As shown in the graph above, the peak of thermal decomposition at approximately 550°C is equal for all samples. However, in the region between 200 and 300°C a small weight drop has been detected, which can be related to the CNT concentration. Despite this reaction takes place at temperatures higher than the HT-PEM fuel cell, it has to be considered as a potentially significant degradation mode for long term operation, e.g. in CHP applications. Further experiments with conductivity boosters will be performed by Eisenhuth in the near future in order to evaluate the critical limits for these additives.

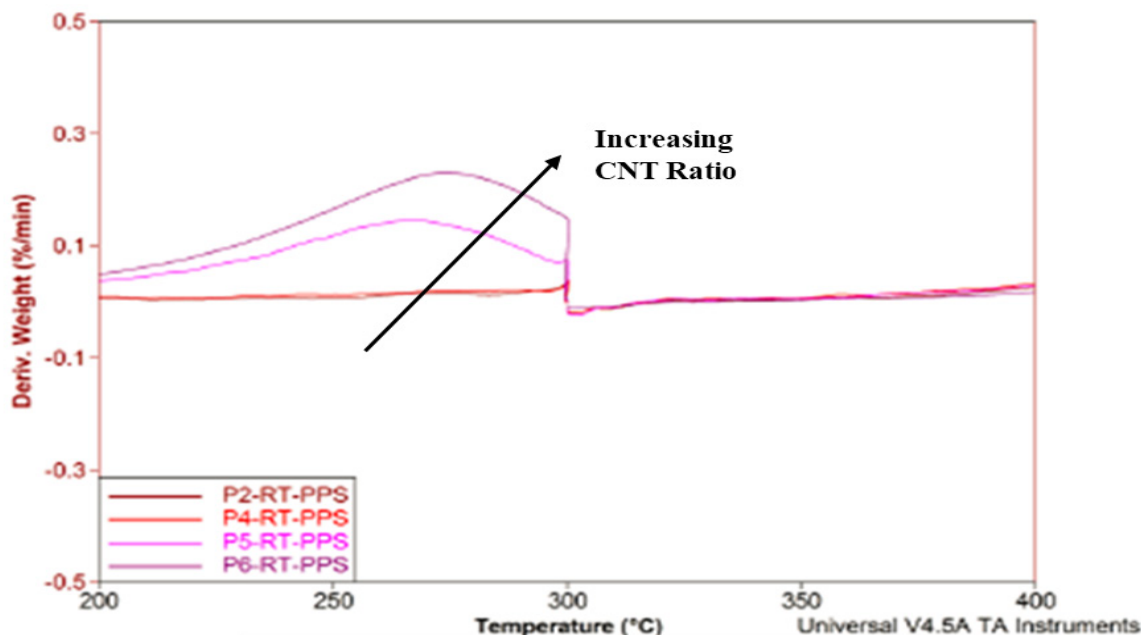


Figure 2. Thermogravimetric analysis of PPS based HT-PEM plates doped with 0 to 4% CNT. Thermal degradation of CNT was observed at 200-300°C.

3.2 Electrical conductivity measurements (in-plane)

Clearly, electrical conductivity both in-plane and through-plane is one of the most important properties of the bipolar plate. Despite most fuel cell (component) laboratories have access to electrical conductivity testing equipment, by now there is no standardized test method for bipolar plates, and comparing results from different sources can show significant differences even if the same samples are tested. One of the main reasons may be surface effects and pre-treatment of the sample. As shown in the figure below, Eisenhuth has implemented an own testing system for this application, which is suited for in-plane conductivity testing.



Figure 3. Testing device for electrical conductivity (in-plane) at Eisenhuth.

The in-plane conductivity device allows for a conductivity mapping over the whole sample area of 200x300 mm. Therefore, it can characterize the material with respect to the degree of homogeneity. Conductivity mapping is an important tool both for quality control and for material and process development. For graphite composite plates it is well known that compounding and molding are highly sensitive to process details and may generate inhomogeneous structures of surface and bulk of the material. Certainly, the development target is a homogeneous distribution of conductivity with only minimal deviations between different points on the sample. In BPP4 plates the compounding and manufacturing process are mature and well controlled, and the conductivity mapping shows an even distribution with values of approximately 100 S/cm (0.10 Ω·cm respectively). In the case of in the newly developed PPS materials the manufacturing process is under development and some material samples still show a significant relief structure in the conductivity mapping.

In the case of the shown example, the data propose the molding process as a source of inconsistency, because the same pattern – higher resistivity on the lower and right edge – was found in several samples. One explanation for these results is that graphite platelets are oriented parallel to the surface when filling the mold and therefore contribute to conductivity less than in the case of a fully isotropic material.

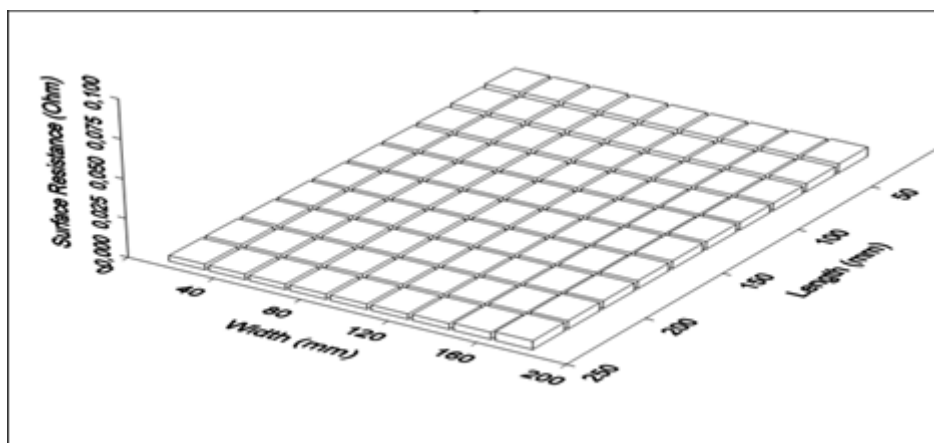


Figure 4. In-plane conductivity mapping of PPS based bipolar plates. Material meets the specifications with a lower resistivity and improved homogeneity, all data points $< 0.10 \Omega\cdot\text{cm}$.

5 Conclusion

As shown, the usage of PPS-Compounds is a good selection in order to achieve a good performance in a PEM high temperature Fuel cell systems. In addition, it has a good performance as far as in-plane conductivity is concerned. Test in systems has shown that the material as well has a very good long-life performance. Due to the above mentioned characteristics, the plates can be used also in high temperature PEM systems with an operating temperature of up to 180°C .

The next steps are to improve the processability of the materials. This can be done easily by new compound-material recipes which are actually und evaluation now.

The authors thank the German Federal Ministry of Transport and Infrastructure (BMVI) for financial support (project No. 03B11008A).

References

1. Apelt S Hickmann T Marek A Widdecke H 2006 Wie leitfähige Compounds wirken Kunststoffe Nr. 12 pp 86-90
2. Larminie J Dicks A 2000 Fuel Cell systems explained Wiley New York.
3. Sievers G W Anklam K Henkel R Hickmann T Brueser V 2019 Corrosion-protection of moulded graphite conductive plastic bipolar plates in PEM electrolysis by plasma processing International journal of hydrogen energy 4
4. Kakati B Kr Verma A 2011 Carbon polymer composite bipolar plate for PEM fuel cell Saarbrücken
5. B Krause P Pötschke T Hickmann Improvement of highly filled graphite/PP composite-based bipolar plates for fuel cells by addition of carbon black Polymer Processing Society 33 AIP Conference Proceedings

6. Hickmann T 2008 Kunststoffe in der PEM Brennstoffzelle – plastic applications in PEM fuel cells VDI Berichte Nr. 2035 pp 81-83
7. Bonnet M 2013 Kunststofftechnik Springer Verlag Hamburg