Short communication

Electrically conductive LCP–carbon composite with low carbon content for bipolar plate application in polymer electrolyte membrane fuel cell

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Abstract

Lightweight polymer–carbon composites with high specific electrical conductivity at a carbon content below 40 vol.% were developed. The electrical and mechanical properties and the hydrogen permeability of carbon fiber and particle reinforced liquid crystalline polymers were examined. Vectra® A 950, SIGRAFIL® carbon fibers and Vulcan® XC 72 R carbon black were employed. The composites are found to have sufficient mechanical properties and a hydrogen permeability low enough to be utilised as bipolar plate material in fuel cell applications. The density of the new composite is 20% lower than the density of commercial bipolar plates made from carbon reinforced polymeric composite materials, due to the lower carbon content. The current density at 0.5 V in an operating fuel cell is only 20% lower compared to commercial materials with more than 80 vol.% carbon content and meets the requirements for bipolar plate application.
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Keywords: LCP; Composite; Carbon; Bipolar plate; Fuel cell

1. Introduction

Due to expected shortage of fuel resources within the next decades and environmental pollution by the use of fossil fuels, it is necessary to develop alternative forms of energy generation. Many possibilities exist to produce energy for stationary applications, but in the automotive industry the options are limited.

Propulsion systems of all kind of vehicles have to be lightweight compared to the total weight of the vehicle, and they must provide energy immediately at the customers demand. This excludes wind, water and solar energy as possible energy sources. Nuclear power is accessorily a safety threat and cost-efficient only for power levels of $>10^6$ W [1]. The only viable energy source for automotive applications are fossil fuels which can be converted into kinetic energy by means of combustion engines, hybrid systems, like, e.g. fuel cells combined with electric motors, or purely electrically powered vehicles.

Electrical energy can be stored either in batteries or directly produced from environmentally friendly generated hydrogen or methanol in a fuel cell. For example, hydrogen can be generated by electrolysis of water with energy from solar cells [2] or wind turbines [3].

Whereas batteries always have a limited capacity and would therefore restrict operation of vehicles to small distance [4], a fuel cell can be supplied with fuel continuously, theoretically for an unlimited period of time. At present, fuel cells have quite a high weight, which is up to 70% due to the bipolar and end plates [5]. Especially, for an application in the automotive industry, weight reduction is a very important factor.

To reduce the weight of a fuel cell, new materials for bipolar and end plates are necessary. These materials must have high electrical conductivity and a lower density compared to the available materials, like, e.g. steel, aluminium and graphite. Processability, however is an important issue in

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mass production. Therefore, thermoplastic polymer–carbon composites are an interesting alternative to metals or carbon.

Several requirements have to be fulfilled by such a composite [5]:

- specific electrical conductivity higher than gas diffusion electrode (2.5 S cm^{-1} [6]);
- hydrogen permeability equal or below the range of the permeability of the ionic conducting membrane;
- thermal and mechanical stability at working conditions;
- low density;
- corrosion resistance;
- low thermal expansion coefficient;
- reproducibility;
- easy finishing;
- recyclability.

As hydrogen fuel cells are operated in a temperature range between 80 and 130 °C [5,7], mechanical stability of the bipolar plates is necessary at these temperatures. Unfortunately, most thermoplastic polymers show a low Young modulus in the range of 0.2 GPa (LDPE) to 3.9 GPa (PEK) [8]. Thermoplastic polymers have a high thermal expansion coefficient in the range of $(50–340) \times 10^{-6}$ K^{-1} [9] and often glass transition temperatures below 100 °C [8,9]. High hydrogen permeability [10] is also a disadvantage. Liquid crystal polymers (LCP) have a high glass transition temperature and good mechanical properties due to their molecular structure [11]. Thermotropic LC co-polyesters sold under the trade name Vectra® (Ticona, Germany) show very low hydrogen permeability of only 78 cm^3 m^{-2} d^{-1} bar^{-1} (Vectra® A 950) at room temperature [10].

2. Experimental

2.1. Preparation of the composites

Commercially available Vectra® A 950, SIGRAFIL® C30 T060 EPY carbon fibers (SGL Carbon Group, Germany), SIGRAFIL® C25 M250 UNS carbon fibers (SGL Carbon Group) and Vulcan® XC 72 R carbon black (Cabot, USA) were employed. A twin screw microcompounder (DSM, Netherlands) was used for the preparation of fiber reinforced polymer granules. Both the carbon fibers and Vectra® A 950 were dried for 24 h at 60 °C before mixing. The polymer was blended with carbon fibers in the microcompounder at 310 °C and 60 rpm for 10 min. The extrudate was cut into granules of about 2 mm length and diameter. Granules with fiber concentrations varying from 3.5 to 44 vol.% were prepared. Fiber length of C30 T060 EPY fibers was about 360 μm after extrusion, whereas C25 M250 UNS fibers showed an average fiber length of 180 μm. For several concentrations, the granules were coated additionally with carbon black in a T2F mixer (Willy A. Bachofen, Switzerland) for 15 min.

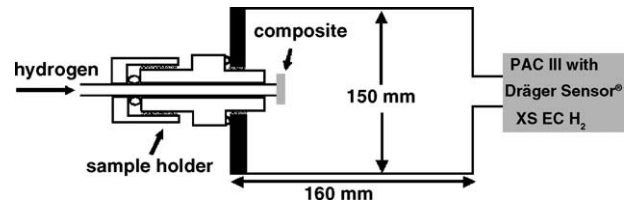The granules were transferred to a mold (25 mm × 25 mm × 2 mm) and heated in a hot press (Perkin-Elmer

Fig. 1. Cross-section of the chamber for hydrogen permeability measurements.

Hydraulic Press, heating elements from Specac). Heating was turned off at 296 °C and a load of 50 kN was applied. The pressure was applied until the temperature dropped below 160 °C. At 75 °C, the composite plate was demolded. A thin layer of about 100–200 μm at the bottom and top side of the plates was removed with a MF 70 milling cutter (Proxxon, Germany), since a thin insulating polymer layer formed during hot pressing. Formation of such insulating layer was more profound at low carbon fiber content. Bottom and top sides of the samples were sputtered with gold to provide good electrical contacts. Samples of 5 mm × 5 mm were cut with the MF 70 milling cutter for electrical conductivity tests.

2.2. Measurement of electrical conductivity

Samples were cleaned with acetone and placed in a in-house-built four-point-probe measuring cell. The polymer–carbon composite was fixed between two gold-plated copper plates (8 mm diameter). Unevenness of the samples was compensated with SIGRAFLEX® graphite foils (SGL Carbon Group) sandwiched between each copper plate and the sample. Through-plane measurements were carried out using a Potentiostat 1285 (Solartron Analytical, Great Britain) and the software CorrWare. Voltage was applied from 0 to 1 V and the resulting electrical current was measured. For composites with high electrical conductivity, the maximum voltage applied was 100 mV, to avoid heating due to high electrical energy dissipation.

2.3. Measurement of hydrogen permeability

Hydrogen permeability measurements were carried out in a self-made test chamber. In Fig. 1, a cross-section of the chamber is shown. Samples of 15 mm × 15 mm were cut out of the hot pressed plates with the MF 70 milling cutter. A steel tube (external diameter 8 mm, wall thickness 1 mm) was heated in a flame for a few seconds and then the hot face was inserted into the sample up to 1 mm deep. The assembly was cooled rapidly by placing the steel tube in cold water, the sample was kept dry during this process. Then all sides of the sample (except the surface inside the tube and an equivalent area on the lower surface) were sealed with a two-component adhesive. After mounting the sample holder, a pressure of several millibar argon–hydrogen gas (hydrogen content 5%) was applied. The concentration of hydrogen in the chamber

was measured using a DrägerSensor® XS EC H$_2$ on a PAC III (Drägerwerk AG, Germany).

2.4. Mechanical tests

Samples of 20 mm × 10 mm × 2 mm were cut out of the hot pressed composite plates with the MF 70 milling cutter. Three-point bending tests were carried out on those samples using a 2980 Dynamic Mechanical Analyzer (TA Instruments, USA) at 1 Hz and temperatures from 30 to 150 °C with an amplitude of 40 μm.

2.5. Fuel cell performance

A bipolar plate made of the composite material (31.8 vol.% C30 T060 carbon fibers, 7.7 vol.% carbon black) was tested as an anode in a hydrogen fuel cell. A meander structured flow field (1 mm wide, 1 mm deep) was milled out in a 40 mm × 40 mm × 2 mm composite plate. A Nafion® 117 membrane, coated with platinum on charcoal on both sides was used as membrane electrode assembly (MEA). Humidified hydrogen (85 °C, 31 h^{-1}, 2 bar) and oxygen (55 °C, 11 h^{-1}, 2 bar) were fed to the anode and cathode compartment, respectively. The platinum content of the MEA was 0.17 mg cm^{-2} on anode and cathode side. Two 375 μm thick carbon fiber felts (type GDL 10 BB, SGL Carbon Group) were used as gas diffusion electrodes. At the cathode side, a SIGRACET® BBP4 bipolar plate (SGL Carbon Group) was installed. After reaching the cell operation temperature of 80 °C, a pre-treatment of 30 min at a current density of 0.5 A cm^{-2} was performed, before starting the measurement.

3. Results

3.1. Electrical conductivity

The specific electrical conductivity σ was calculated according to Ohm's law. All composite samples obey the ohmic law and were found to be purely ohmic resistances. In Fig. 2, the specific electrical conductivity is plotted versus the
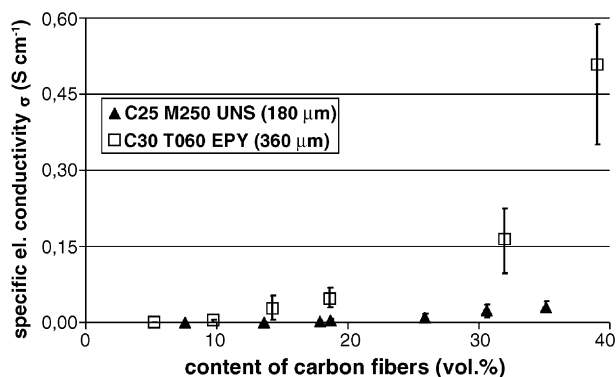

Fig. 2. Influence of fiber length and fiber concentration on specific electrical conductivity of a composite.
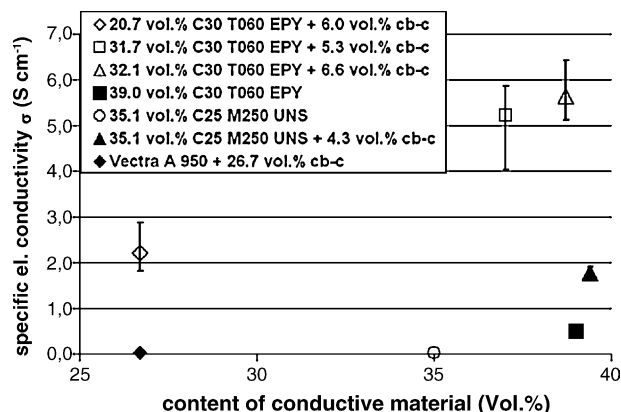

Fig. 3. Specific electrical conductivity of composites made from carbon fiber reinforced granules with carbon black coating (cb-c), compared to composites without cb-c and pure Vectra® A 950 with cb-c.

content of carbon fibers for some composites without carbon black. Conductivity increases with increasing concentration of conductive fibers and fiber length, as reported in the literature [12]. The average length of C25 M250 UNS carbon fibers is 180 μm. For C30 T060 EPY, a length of about 360 μm was measured on a thin film of composite material using a calibrated stereo optical microscope. However, the maximum specific electrical conductivity of about 0.6 S cm^{-1} is far below the minimum requirement of 2.5 S cm^{-1} [6] for an application as bipolar plate. In Fig. 3, the effect of the carbon coating is shown. A significant increase of the specific electrical conductivity has been observed for the composites made from carbon black coated granules, compared to composites without carbon black. Pure Vectra® A 950 coated with carbon black shows poor electrical conductivity. A composite with 32.1 vol.% C30 T060 EPY fibers and 6.6 vol.% carbon black coating (cb-c) reaches an average specific electrical conductivity of 5.6 S cm^{-1}, which is significantly higher than the specific electrical conductivity of a gas diffusion electrode (2.5 S cm^{-1} [6]).

3.2. Hydrogen permeability

The gas permeability K of a material is described by Darcy's law. Substituting the flow velocity with the molar flow rate n/t per area A and $K^* = K/\eta$, Darcy's law can be written as:

$$K^*[\mathrm{mol\,cm^{-1}\,s^{-1}\,bar^{-1}}] = \frac{d \cdot n}{\Delta p \cdot A \cdot t}$$

For the application as bipolar plate in a fuel cell, the hydrogen permeability of a material must be equal or below the range of the hydrogen permeability of the ionic conducting membrane [5]. Li et al. [13] have reported values of about 10^{-10} mol cm^{-1} s^{-1} bar^{-1} for the hydrogen permeability of Nafion® 117.

Only composites with C30 T060 EPY fibers were examined, as they show a higher specific electrical conductivity.

Table 1

Hydrogen permeability and permeated amount of hydrogen per day for several composites (2 mm thickness) compared to Nafion® 117 (175 μm thickness)

Composite material	Hydrogen permeability, K^* (10^{-11} mol cm^{-1} s^{-1} bar^{-1})	Permeated hydrogen (10^{-5} mol cm^{-2} d^{-1})
25.5 vol.% C30 T060 EPY	0.574	0.248
34.6 vol.% C30 T060 EPY	5.37	2.32
32.1 vol.% C30 T060 EPY + 3.2 vol.% cb-c	23.0	9.94
32.0 vol.% C30 T060 EPY + 4.5 vol.% cb-c	27.3	11.8
35.9 vol.% C30 T060 EPY + 4.9 vol.% cb-c	74.7	32.3
32.1 vol.% C30 T060 EPY + 6.6 vol.% cb-c	195	84.4
Nafion® 117	10.0	49.4

Hydrogen permeability of Nafion® 117 has been taken from literature [13]. Amounts of permeated hydrogen are calculated from measured permeabilities.

Hydrogen permeabilities for several composites are given in Table 1. Permeability increases with increasing fiber concentration. The coating procedure with carbon black leads to higher permeability compared to composites with fibers as only conductive component. For the technical application as a bipolar plate, the total amount of permeated hydrogen is important. Table 1 gives calculated values for composites with 2 mm thickness, compared to Nafion® 117 of 175 μm thickness (49.4×10^{-5} mol cm^{-2} d^{-1}). In case of the composite with 32.1 vol.% fibers and 6.6 vol.% cb-c, the calculated amount of permeated hydrogen is slightly higher (89.4×10^{-5} mol cm^{-2} d^{-1}), for 35.9 vol.% fibers and 4.9 cb-c it is lower (32.3×10^{-5} mol cm^{-2} d^{-1}). Hydrogen permeability values of these composites is in the range of the hydrogen permeability of the ionic conducting membrane, and their electrical conductivity fulfils the requirements of [5].

3.3. Mechanical properties

The relative storage modulus of some composites compared to storage modulus of pure Vectra® A 950 at room temperature is shown in Fig. 4. For all samples, the modulus decreases with increasing temperature. As reported in the literature [14], fiber reinforced composites are found to have significantly better mechanical properties than that of pure polymer. At a temperature of 80 °C, the remaining storage modulus of the composite with 25 vol.% fibers is 175% of the modulus of Vectra® A 950 at room temperature. The carbon black coating acts as inhomogeneity and reduces the storage modulus compared to the fiber reinforced composite. The storage modulus of a composites with 31.7 vol.% fibers and 5.3 vol.% cb-c at the operating temperature of the fuel cell (80 °C) is about 10% higher than the modulus of Vectra®
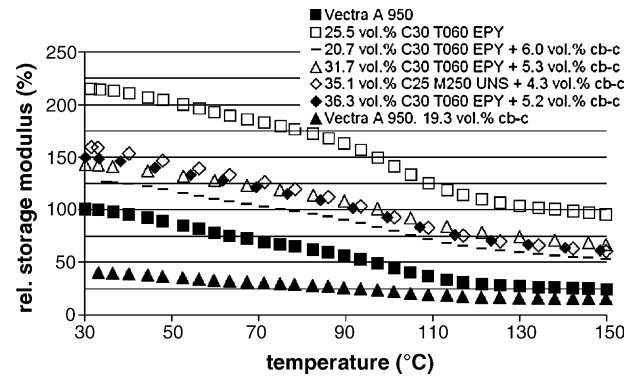

Fig. 4. Storage modulus of several composites compared to storage modulus of Vectra® A 950 (100% is the storage modulus of Vectra® A 950 at room temperature).

A 950 at room temperature. Pure Vectra® A 950 coated with carbon black has very poor mechanical properties, because of the missing stabilizing effect of the fibers.

Due to the low carbon content, the density of the composite with 32.1 vol.% C30 T060 EPY carbon fibers and 6.6 vol.% cb-c is 1.56 g cm^{-3}. The commercially available composite material bipolar plate SIGRACET® BBP4 has a density of 1.97 g cm^{-3} [15].

3.4. Bipolar plate of composite material tested in a fuel cell

The current-voltage characteristic curve of a composite with 31.8 vol.% C30 T060 EPY carbon fibers and 7.4 vol.% cb-c is shown in Fig. 5, and compared with a commercial composite material (SIGRACET® BBP4). The commercial product contains more than 80 vol.% of electrically conductive carbon in a matrix of phenolic resin. The maximum current density of the assembly containing the new composite is just 20% below the maximum current density of the assembly containing the commercial product, which consists of more than twice the amount of carbon.
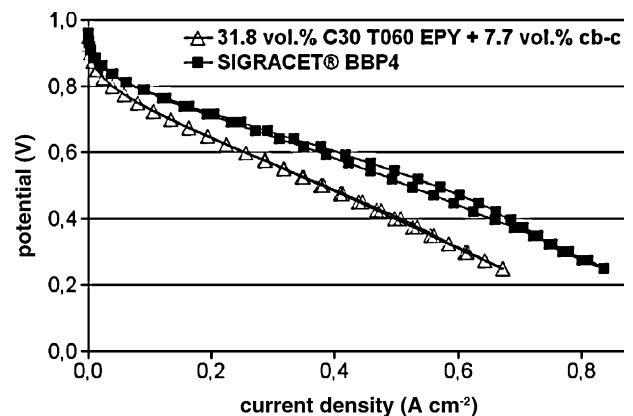

Fig. 5. Current–voltage characteristic curves of a bipolar plate of composite material (31.8 vol.% C30 T060 EPY fibers and 7.7 vol.% cb-c) and commercial SIGRACET® BBP4 bipolar plate.
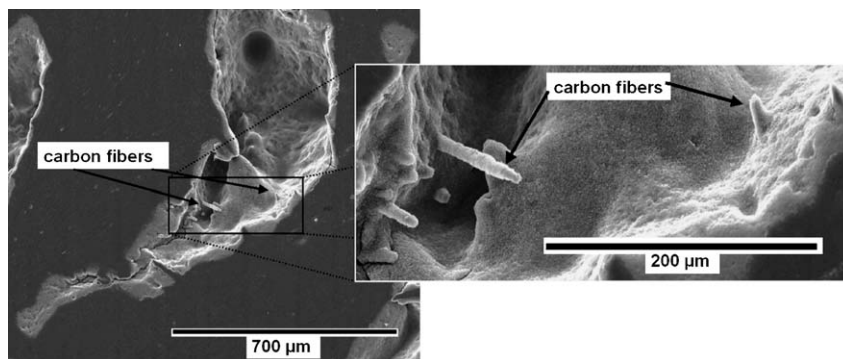
Fig. 6. SEM picture of hot pressed composite with 32.1 vol.% C30 T060 EPY carbon fibers and 6.6 vol.% carbon black coating. The carbon black mostly fell out during preparation of the SEM sample, so that the fibers can be seen.

4. Discussion

To achieve electrical conductivity, a percolating conducting path is necessary. A thin layer of insulating material with high electrical resistance within a conducting path increases the total resistance of the path. At low concentrations of homogeneously distributed carbon fibers, almost all fibers will be fully covered with the insulating matrix. Because of this, these fibers cannot contribute to the electrical conductivity of the composite. A distortion of a conducting path may also appear at the boundary of two granules in the hot pressed composite. The high specific electrical conductivity of the composites made of carbon black coated carbon fiber reinforced granules results from contacting fibers of two different granules in the plate via the coating, as shown in Fig. 6, whereas carbon black coating without fibers results in poor electrical conductivity and also a deterioration of the mechanical properties.

Fig. 6 shows a scanning electron microscope image of a composite with 32.1 vol.% C30 T060 EPY carbon fibers and 6.6 vol.% carbon black. Several carbon fibers extend into a pore. After hot pressing, this pore was filled with carbon black. As the sample was cut for SEM observation, most of the carbon black in the pore fell out.

Fig. 7 shows a model of the conductivity paths in a composite made of carbon black coated carbon fiber reinforced granules. The model was developed based on the presented experimental results. Insulating polymer granules (white) are filled with electrically conductive carbon fibers (black). At the boundaries of the granules, there are zones of conductive carbon black (grey). If a voltage is applied between A and B, there are six continuous paths available for electrical current (marked with grey dots and roman numbers). Without the carbon black zones, there would be only two conductive paths (I + VI).

The increased hydrogen permeability of the composites with carbon black can be elucidated based on the microstructure. The carbon black particles are inhomogeneously distributed at the boundaries of the fiber reinforced granules and they are not strongly bonded to the polymer matrix. The small particles are not totally compacted during hot press-

ing of the polymer melt. So, there are a lot of microscaled pores and voids, which assist in the permeation of the small hydrogen atoms.

The mechanical properties of the composites consisting of carbon fiber reinforced granules with carbon black coating do not accomplish the values of composites without carbon black, as the local concentrations of carbon black act as inhomogeneities. But a strengthening effect of the fiber reinforcement is still preserved, in comparison with pure polymer. The fuel cell test demonstrated, that a bipolar plate of composite material has thermal and mechanical stability at an operating temperature of 80 °C. The density of $1.56\,\mathrm{g\,cm^{-3}}$ lies about 20% below the density of commercially available composite bipolar plates. Density reduction and functional properties comparable to recently used commercial materials is an important step forward towards automotive applications.

As no metal is used, the corrosion resistance of the composite is excellent. The thermal expansion coefficient of the composite was not examined, but is expected to be low, due to the low thermal expansion coefficient of the carbon fibers, the carbon black and the LCP. Reproducibility of mechanical,
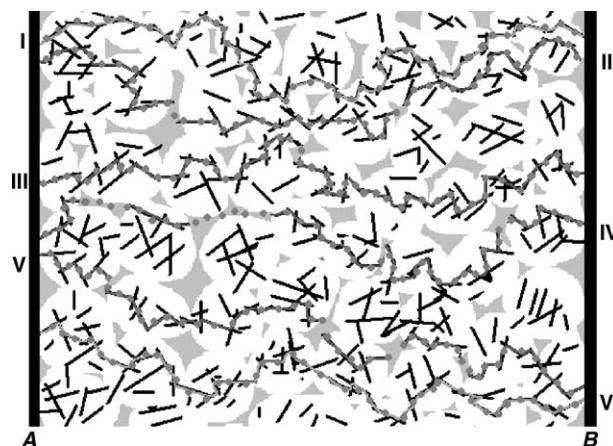

Fig. 7. Model of conductive paths in a composite hot pressed from carbon fiber reinforced granules coated with carbon black. Carbon fibers (black) and carbon black (grey) form six continuous paths (grey dots) from (A) to (B). Without the carbon black, four of the paths are cut, only paths I and VI remain for conductivity.

thermal and electrical properties of the composites with same amount of fibers and carbon black is very high ($\pm10\%$). Machining of the pressed plates (milling of the meander structured flow field) is easy, as the material is not so hard and brittle as steel or graphite. Recycling is expected to be less difficult than recycling of bipolar plates made of commercially available composite material, as the LCP-carbon-composite contains neither fluorinated polymers nor phenolic resins.

5. Conclusions

A new LCP–carbon composite with electrical conductivity matching the needs for bipolar plate applications has been developed. With half of the carbon content compared to a commercially available material, the new composite has a lower density and is less brittle. Future work will concentrate on increasing the adhesion of the carbon black to the polymer-matrix.

Acknowledgements

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