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### Electrically Conductive Layer Material

The invention relates to an electrically highly conductive sheet or layer material consisting of a carbon composite material. The layer material possesses good mechanical tenacity, a high modulus of elasticity, and a low density, while at the same time being highly flexible. The layer can be made either gas tight or porous, and the surfaces may be textured.

Conductive, non-metallic layer materials designed for use as arresters for electrostatic charges, as shielding against electromagnetic interferences, as resistance material for electric heating mats, and as separators and bipolar plates for electrochemical applications, especially fuel cells, are already known in the art. The key advantages these materials offer over metals are their low weight and high level of resistance to chemically aggressive media. In most cases, low electric resistance and high mechanical tenacity are desired.

Carbon composite materials consisting of thermoplastics or resins compounded with conductive soot (black) or graphite are specified in the prior art. One composite material of this type is presented, for example, in DE 3135430 C2. Such materials exhibit a low level of electric conductivity, because the intense mixing of the binder, which is used in its liquid form, causes it to partially coat the electrically conductive carbon particles. The result is that some degree of electric contact between the conductive parti-

cles is lost.

Conversely, DE 4234688 C2 specifies a very highly conductive composite material, which also is produced by compounding heat-curable resins. However, in this case an intercalation graphite compound that is produced by doping fibrous carbon particles with halogens or alkali metals serves as the conductive material. The carbon particles are separated from the gas phase beforehand by means of a catalyzed cracking process, after which they are graphitized at 2400°C. The entire process is quite extensive, furthermore the stability of the intercalation compound for use in electrochemical applications, for example in polymer-electrolyte-membrane (PEM) fuel cells, is not guaranteed.

In US 4.643.956 a separator plate is described which is first molded from resin and coke particles, and is then finished via a cost-intensive, multi-step graphitizing process up to nearly 3000°C. The plates are very highly conductive and chemically stable. However, due to the absence of a polymer component, they exhibit a substantial degree of brittleness.

With the present invention, all the disadvantages described above are avoided.

The object of the invention is to provide a cost-effective, highly flexible, and electrically very highly conductive layer material made of carbon composite material. The layer material may be gas tight or porous.

Another object of the invention is to provide a simple, cost-effective method for producing this layer material.

A further object of the invention is to specify use of this layer material for bipolar separators in PEM fuel cells and as mechanical reinforcement for gas diffusing electrodes.

These objects are attained by the layer material made of carbon composite material as specified in Claim 1, by the method used to produce this layer material in accordance with Claim 9, and by the use of the layer material for a bipolar separator and/or mechanical reinforcement for gas

diffusing electrodes in PEM fuel cells, in accordance with Claims 21 and 22.

In accordance with the invention, the first object is attained with a layer material comprised of fibers, electrically conductive carbon particles that mutually have highly conductive contact points, and a polymer, which fills the hollow spaces between the carbon particles only, either fully or partially, without adversely affecting the contact points between the carbon particles. In most cases the layer material also contains a supplementary agent, which remains in the layer material as a result of special production processes.

Fibers having a high degree of mechanical tenacity and a high modulus of elasticity are preferably used. It is particularly preferable to use carbon fibers (carbonized), because they exhibit outstanding mechanical properties and at least some electrical conductivity. It is advantageous for the length of the fibers to correspond to at least 30 layer thicknesses.

Conductive black (soot), graphite, or mixtures thereof are preferably used as the electrically conductive carbon particles.

To give the layer material mechanical tenacity, a hardened, thermoplastic resin is preferably used which binds the carbon particles or the agglomerates thereof and the fibers. Especially preferable for use here are phenolic resin or epoxy resin.

For the use of a supplementary agent, one of the production processes according to the invention is the reason. Polytetrafluoroethylene (PTFE) in the form of fine particles (ca. 120-500 nm) is preferably used. The supplementary agent PTFE gives the layer material a typically water repellent character, which is primarily desirable if the layer material is to be used as a mechanical reinforcement of gas diffusing electrodes in fuel cells.

The share of fibers as a percentage of the overall mass of the layer is preferably 0-40%, while that of conductive soot and/or graphite is 10-75%, and that of the hardened polymer is 10-70%. In a layer having a large volume of open pores, the percentage of polymer used will be near the lower end of the given range.

The method used to produce the layer material must ensure that the carbon particles and the fibers have sufficient mutual electric contact between each other, before the curable resin is added. In the method of the invention, the liquid, uncured resin is not incorporated by mixing it with carbon powder and fibers, as is customary in state-of-the-art methods, but is instead incorporated by impregnating a preformed, porous layer material containing carbon particles and fibers.

The pores of the preformed layer material can thus be fully or partially filled, without significantly disrupting the already existing electrical contacts between the electrically conductive particles. The pores of the preformed layer material are preferably filled by the fact that the liquid resin penetrates the carbon material via capillary attraction. One advantage of this process also is that carbon or glass fibers are retained at their original length, rather than being broken by a mixing process.

The resin taken up by the preformed layer material is then cured, preferably under conditions of heat and pressure. The pressure may be applied in a continuous process using a calender machine by heated rollers, or in a discontinuous process using a press. If a texturing of the surfaces, for example a channel structure, is desired, then a pressing tool can be correspondingly designed, which tool can be used to impress the desired texture into the layer during the curing process.

As the preformed layer material, a commercially available carbon fiber paper (Toray, Japan) or, most preferably, a carbon nonwoven fiber mat that is filled with soot and/or graphite powder and tiny PTFE particles, produced in accordance with DE 195 44 323 or EP 0298690, may be used. In the simplest case, the preformed layer material consist of the carbon components pressed together to form a layer, and possibly a small quantity of a binder (such as PTFE). In many cases, however, these preformed layer materials are not inherently stable, in other words they must be held in the pressing mold until they are further processed.

In the carbon fiber paper (Toray, Japan) the fibers are already relatively firmly bonded via graphitization of a polymer. However, this graphitization causes the fibers and the bonding to be brittle, which is then reflected in the mechanical properties of the final product. Furthermore, the graphitization process is cost-intensive and thus is not in keeping with the object of the present invention.

With the use of the carbon nonwoven fiber mat that is filled with soot and/or graphite as the preformed layer material, PTFE serves as the preliminary binder for the carbon particles. There is no risk of coating of the carbon particles by small quantities of PTFE, since the PTFE remains in solid form during the entire production process.

Astonishingly, when the method of the invention has been used, a hard, highly flexible layer material is produced from the soft, sensitive starting material. The conductivity of the final product is nearly identical to the conductivity of the starting material.

#### Example 1:

A nonwoven mat comprised of carbonized carbon fibers having a surface-based mass density of  $30 \text{ g/m}^2$  is impregnated with a suspension of soot and PTFE via a rolling process, in accordance with DE 195 44 323. Water and isopropyl alcohol in a volume ratio of ca. 1:1 is used as the suspension liquid. PTFE is added in the form of tiny particles having a diameter of ca. 180 nm, also in an aqueous suspension. The ratio of PTFE to the overall quantity of soot and PTFE can range from 2% to 40%. In this example, an 8-percent ratio of PTFE is used. Vulkan XC 72 or Black Pearls produced by the Cabot firm, or preferably, Ketjenblack produced by Akzo Nobel may be used as the soot.

The surface-based mass density of the mat, which has been impregnated as homogeneously as possible and then dried, should be  $50\text{-}150 \text{ g/m}^2$ . In this example the mass density is ca.  $90 \text{ g/m}^2$ . In order to thermally decompose the dispersing agents from the PTFE suspension, the impreg-

nated mat is sintered at ca. 350°C for 5 min. The acceptable temperature range for sintering is between 250°C and 400°C.

5 In order to produce the preformed layer material, one or more impregnated nonwoven mats, depending upon the desired layer thickness, are pressed together, possibly at an increased temperature. The electric contact points between the particles of soot are formed partially by this pressing step, and partially by the preceded rolling process. The pressing pressures are between 5 and 500 bar, and the temperature should be below 400°C. In this example, 100 bar and 120°C were used. Although this porous layer material is flexible, it has a low degree of elasticity and a low level of mechanical tenacity.

10 In order now to obtain the layer material of the invention, a solution or suspension of a one- or two-component epoxy resin, in this case particularly a two-component epoxy resin having a viscosity of approximately 1,500 mPas, and an alcohol, in this case ethanol, is prepared. The mass ratio of premixed epoxy resin components to alcohol is approximately 1:1; this will result in a gas tight layer at the end of the process.

20 The preformed layer material is dipped into the suspension, or is sprayed or brushed with the suspension. Based upon the capillary attraction between the preformed layer material and the suspension, the latter penetrates the preformed layer material, in most cases through layer thicknesses of more than 1 mm. After a homogeneous impregnation of the material has been achieved, the alcohol is removed via evaporation at a slightly increased temperature. This impregnation process may be repeated one or more times.

25 The epoxy resin is then cured, preferably under pressure and at an increased temperature. In this particular example, 120°C and 275 bar are used. By using three impregnated nonwoven mat layers having a mass of 90 g/m<sup>2</sup> each in the preformed layer material, a laminate as specified in the invention, approximately 0.4 mm thick, is obtained.

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The layer material is gas tight and water-repellent. The electric resistance measured parallel to the layer using the four-point method is approximately 0.018 Ohm cm. The ratio between the minimum bending diameter D and the layer thickness d can be viewed as a measurement of flexibility. For the material specified here, the ratio of D/d was measured at approximately 50.

Example 2:

The use of the layer material specified in Example 1 of the invention as a bipolar plate of a PEM fuel cell stack, especially for the reaction gases hydrogen and oxygen or air, can be implemented in two different ways:

a) An unstructured, smooth layer material is used for the electrically conductive gas separation layer, and the typically necessary gas flow field structures (for example, a channel structure, e.g. incorporated into a porous carrier) for the cathode and the anode are applied to the opposing surfaces of the layer material of Example 1. By stacking gas separation layers, flow fields, and membrane electrode units in the proper sequence, and by applying a suitable sealing and gas feed set-up, a PEM fuel cell stack is obtained.

b) A press tool having a (negative) structure suitable for a gas flow field (for example, a channel structure) is used in the pressing process, especially during the curing phase of the layer material of Example 1 of the invention. The result after curing is a layer material that has the structure of the tool on one or both sides. By stacking and compressing the gas separation layers produced in this manner which comprise the flow field structure, with membrane-electrode units a PEM fuel cell stack is obtained.

Example 3:

A layer material comprised of soot, PTFE, and a nonwoven carbon fiber mat is produced as described in Example 1. In contrast to Example 1, a 10-percent solution of phenolic resin in isopropyl alcohol is added for solidifying the layer. The preformed layer material is impregnated twice with this

solution, after which it is dried. After being simultaneously pressed and cured at 160°C - 180°C, a layer material is obtained which is porous due to the lower polymer content. It is water repellent and has a high modulus of elasticity. The pore volume can be adjusted within broad limits by varying the polymer content. For this reason this layer material can be advantageously used as a reinforcement layer for gas diffusing electrodes.

Example 4:

The porous, conductive layer material of Example 3 can advantageously be used as mechanical reinforcement for gas diffusing electrodes, especially of PEM fuel cells. Frequently, gas diffusing electrodes are comprised of relatively soft and sensitive flat structures, made most often of graphitized carbon fibers and soot. These electrodes can be deflected as a result of the pressure applied to the channel structure of the bipolar plate, which pressure is necessary to reduce the electric transfer resistance between the electrode and the bipolar plate. Due to such deflection, the synthetic membrane that lies between the electrodes, and in most cases is very thin, can become damaged, or the deflection can cause the electrodes to close the channels.

When laminating or pressing the layer material of Example 3 of the invention (which may also be bound with epoxy resin), in its cured or non-cured state, to the anode and/or the cathode, the disadvantages discussed can be avoided due to the mechanical reinforcement.

Example 5:

A commercially available carbon fiber paper (from the Toray firm) of graphitized fibers may also be used as the preformed layer material. Impregnation may take place with undiluted epoxy resin of low viscosity. The curing process is carried out at low pressures of approximately 1 - 80 bar, and at an increased temperature that is suited to the type of epoxy resin used. This will substantially improve the mechanical stability and flexibility of the carbon fiber paper. However, this layer material cannot

achieve low bending radii described in Example 1 due to the low stretch strength of the graphitized fibers.

The electric conductivity parallel to the surface of the layer is not affected by the impregnation process.

5           Example 6:

10           The conductivity of the layer materials of Examples 1, 3, and 4 can be increased by replacing the soot by a mixture of soot and graphitized carbons in the process of producing the preformed layer material. For the graphitized component, short cut graphitized fibers having a preferred length of 10  $\mu\text{m}$  to 1 mm and a preferred diameter of 2  $\mu\text{m}$  to 20  $\mu\text{m}$  are particularly well suited. A suitable material, for example, is presented by the Donacarbo SG 241 fibers produced by Ashland-Südchemie-Kernfest GmbH, which fibres have a length of 0.13 mm and a diameter of 13  $\mu\text{m}$ .

15           The mass ratio of the graphitized component to overall mass of the conductive material preferably is between 10% to 75%. The share of PTFE can be reduced to 3% - 5% in comparison with Example 1. All steps in the process can be implemented analogously to Example 1.

          Example 7:

20           Particularly when the layer material is to be used in fuel cells for bipolar plates or for a reinforcement of the gas diffusing electrodes, a high level of electric conductivity perpendicular to the layer, and a low level of transfer resistance to other electrically conductive materials, are of advantage. In order to reduce the transfer resistance (at a given pressure), the layer material can be coated on at least one of its surfaces with an electrically  
25           highly conductive material, preferably before the binder is cured, and most preferably before the layer is impregnated with the binder. In the case of a multilayer construction, as described in Example 1, it is also advantageous to coat any surfaces that will later be part of the laminate.

30           Particularly well suited is a coating containing graphitized carbon, especially in the form of graphitized carbon fibers. One example of such a

suitable material is the Donacarbo SG 241 fibers, produced by Ashland-Südchemie-Kernfest GmbH, which have a length of 0.13 mm and a diameter of 13  $\mu\text{m}$ . The carbon fibers are preferably suspended and applied via spraying to a layer material according to the present invention, while in the production phase prior to impregnation with the binder. It is also advantageous to apply a supplementary binder that binds the fibers to one another and to the layer material, in order to ensure that the fibers do not become detached during the subsequent steps of the process.

A special method for producing a suspension for spraying is:

- Mixing of Donacarbo SG 241 fibers and 20 g  $\text{H}_2\text{O}$  by stirring lightly;
- Mixing of 0.42 g of a 60-percent PTFE dispersion (such as TF 5032, available from the firm Dyneon) and 10 g  $\text{H}_2\text{O}$  by stirring lightly;
- Mixing the above two suspensions.

Preferably by spraying, solid substance coatings of 0.2 - 5  $\text{mg}/\text{cm}^2$  are applied. After the suspension liquids have dried, a sintering process analogous to the one of Example 1 is advantageous, due to the use of the PTFE suspension as a supplementary binder. The further steps in the process may now be implemented approximately as in Example 1, beginning with the impregnation with the (primary) binder.



## Patent Claims

1. Electrically conductive, flexible, and mechanically stable layer material containing a preformed, conductive, porous layer material, which contains non-metallic particles as a conductive component, characterized in that the pores of the preformed layer material are completely or partially filled with a cured resin, and the conductive particles are to an essential extent not coated with this resin.

2. Electrically conductive, flexible, and mechanically stable layer material in accordance with Claim 1, characterized in that the conductive components of the preformed layer material consists of graphite and/or soot.

3. Electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 1 through 2, characterized in that the preformed layer material contains fibers.

4. Electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 1 through 3, characterized in that the particles of the preformed layer material are bound together before processing via supplementary agents.

5. Electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 1 through 4, characterized in that the preformed layer material is comprised of a compressed, packed material.

6. Electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 1 through. 4, characterized in that the preformed layer material is comprised of one or more nonwoven fiber mats impregnated with soot and a binder.

7. Electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 1 through. 6, characterized in that the resin contains a phenolic resin or an epoxy resin.

8. Electrically conductive, flexible, and mechanically stable layer



material in accordance with any of Claims 1 through 7, characterized in that it contains structures in the form of projections and indentations on at least one of its surfaces.

5 9. Method for producing an electrically conductive, flexible, and mechanically stable layer material containing a preformed, conductive, porous layer material which contains non-metallic particles as a conductive component, characterized in that the pores of the preformed layer material are completely or partially filled with a curable resin, while the conductive particles are, to an essential extent, not coated with this resin.

10 10. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with Claim 9, characterized in that the conductive component of the preformed layer material consists of graphite and/or soot.

15 11. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 10, characterized in that the preformed layer material contains fibers.

20 12. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with one of Claims 9 through 11, characterized in that the particles of the preformed layer material are preliminarily bound together by means of supplementary agents.

25 13. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 12, characterized in that the preformed layer material is made of a compressed, packed material.

30 14. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 13, characterized in that the preformed layer material is comprised of one or more nonwoven fiber mats which are impregnated with soot and



a binder and prepressed.

15. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 14, characterized in that the resin contains a phenolic resin or an epoxy resin.

16. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 15, characterized in that the still uncured resin penetrates the preformed layer material via capillary action.

17. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 16, characterized in that the still uncured resin is pressed into the pores of the preformed layer material by pressure.

18. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 17, characterized in that the still uncured resin is diluted with a liquid before the preformed layer material is filled.

19. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 18, characterized in that the resin is cured under pressure and/or increased temperature.

20. Method for producing an electrically conductive, flexible, and mechanically stable layer material in accordance with any of Claims 9 through 19, characterized in that structures in the form of projections and indentations are created on at least one of the surfaces via embossing, at least during the curing process.

21. Use of the electrically conductive and mechanically stable layer material as a bipolar plate of PEM fuel cells.

22. Use of the electrically conductive and mechanically stable layer material as mechanical reinforcement for gas diffusing electrodes.