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(54) **CONDUCTIVE NONWOVEN**

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(57) **ABSTRACT**

The invention relates to a conductive nonwoven fabric that is carbonized and/or graphitized and possesses a bending rigidity <8 taber, a density of 0.1 g/m^3 to 0.5 g/m^3, a thickness of 80 μm to 500 μm, and an electrical conductivity of 10 to 300 S/cm in the nonwoven fabric strip and 30 to 220 S/cm^2 perpendicular to the nonwoven fabric strip.

CONDUCTIVE NONWOVEN

[0001] The invention relates to a conductive nonwoven fabric.

[0002] Conductive nonwoven fabrics are used as gas diffusion layers in membrane electrode assemblies (MEAs) for PEM (proton exchange membrane) fuel cells and must be conductive for electrons and gas-permeable. They must furthermore demonstrate channel structures for transporting away the water of reaction that is formed during operation of the fuel cells, and must possess an inherent rigidity at a limited thickness. Furthermore, they should have a good surface smoothness at least on one side.

[0003] At present, two-dimensional textile materials such as conductive woven fabrics or wet-laid nonwoven fabrics are usually used as the starting materials for gas diffusion layers. Nonwoven fabrics with a thickness of 0.3 to 0.5 mm are known from JP 06/123050, which are made up of carbonizable polymer fiber materials such as polyacrylic nitrile (PAN) or oxidized polyacrylic nitrites, with a mass per unit area of 100 to 200 g/m^2. To achieve the required electrical conductivity, these textile fabrics are carbonized at temperatures between 1000 and 2100° C., whereby a carbon content of approximately 90 to 96% is achieved. A reduction in mass per unit area by 30 to 60 weight-percent is connected with the carbonization, i.e. graphitization process. Usually, these fabrics, which are now conductive, are very rigid and demonstrate a relatively open structure. It is known to impregnate or coat the woven fabrics or nonwoven fabrics with dispersions of conductive particles such as graphite or carbon black, in order to achieve the required rigidity and in order to improve the conductivity in the X, Y, and Z direction, and subsequently to press them in order to achieve a high degree of surface smoothness.

[0004] Furthermore, it is known from the documents JP 10/777624 or JP 10/777625 to produce gas diffusion layers directly from carbon fibers, in a wet-laying process, in order to make subsequent carbonization of the precursor fibers unnecessary. In this connection, polyvinyl alcohol (PVA) solutions or polyethylene terephthalate (PET) substrates are used as a binder for the carbon fibers. Subsequently, the hydrophobic properties of the gas diffusion layer can still be adjusted by finishing them with a hydrophobization agent such as polytetrafluoroethylene (PTFE) dispersions and subsequent sintering.

[0005] The known methods for the production of gas diffusion layers for PEM fuel cells possess the disadvantage that they cannot be rolled up for transport and processing and that they must be filled with conductive fillers in order to achieve the required conductivity values.

[0006] The invention has set itself the task of indicating a conductive nonwoven fabric that overcomes the disadvantages of the state of the art.

[0007] According to the invention, this task is accomplished by a conductive nonwoven fabric that is carbonized and/or graphitized and possesses a bending rigidity <8 taber, a density of 0.1 g/m3 to 0.5 g/m^3, a thickness of 80 μm to 500 μm, and an electrical conductivity of 10 to 300 S/cm^2 in the nonwoven fabric strip and 30 to 220 S/cm^2 perpendicular to the nonwoven fabric strip.

[0008] The conductive nonwoven fabric according to the invention is obtained from preoxidized fibers as a precursor stage for carbon fibers that are mixed, if necessary, with up to 30 wt.-% of a percursor fiber that serves as a binder fiber, as well as up to 30 wt.-% of a water-soluble fiber with a fiber titer of 0.5 to 6.7 dtex, to form a fiber fleece with a mass per unit area of 60 to 300 g/m^2, by bonding of the fiber fleece with high-pressure fluid jets at pressures of 100 to 300 bar, compression of the bonded fiber fleece by 50 to 90% of its starting thickness by calandering, and carbonization and/or graphitization under an inert gas atmosphere, at 800° C. to 2500° C. The conductive nonwoven fabric obtained in this way demonstrates a channel structure in the direction of the layer thickness of the nonwoven fabric. The preoxidized fibers and, if applicable, the binder fibers and water-soluble fibers, are mixed homogeneously and deposited to form a fiber sheet. The fiber sheet, with a mass per unit area of 30 to 300 g/m^2, is passed to a bonding unit, in which the fibers are swirled and intertangled by high-energy water jets, at pressures of 100 to 300 bar. After this treatment, part of the fibers demonstrates an orientation in the direction of the Z direction (thickness) of the nonwoven fabric.

[0009] Preferably, the conductive nonwoven fabric is one in which 80 to 90 wt.-% of a mixture of binder fibers and preoxidized fibers in a weight ratio of 0:1 to 1:3 and 10 to 20 wt.-% of a water-soluble fiber with a fiber titer of 0.8 to 3.3 dtex are used. This composition of the fibers and their fineness result in conductive nonwoven fabrics with a porosity of 70 to 95. Preferably, the conductive nonwoven fabric is furthermore one in which two different water-soluble fibers were used, one of which is water-soluble at temperatures of 10 to 40° C. and the other of which is water-soluble at temperatures of 80 to 120° C. By using fibers with a different solubility in water, the fibers in the temperature range of 10 to 40° C. are already dissolved out of the fiber fleece during the water-jet bonding process, and defined channels are formed in the nonwoven fabric layer, allowing improved gas permeability and improved removal transport of the water of reaction in the gas diffusion layer produced from them. The fibers that are not soluble in water until a temperature range of 80 to 120° C. remain in the bonded nonwoven fabric and become binder fibers in the wet state, because of their stickiness. For this purpose, the nonwoven fabric is passed through a calander while it is still wet, and compressed there.

[0010] Preferably, the conductive nonwoven fabric is one in which the ratio of the water-soluble fibers relative to one another is 3:1 to 1:3. The rigidity of the gas diffusion layer and its porosity can be adjusted with this ratio.

[0011] A conductive nonwoven fabric that is made up of several fiber layers with different pore sizes is particularly preferred, where the fibers of the individual layers possess different titers. The progressive build-up of the conductive nonwoven fabric from several fiber layers promotes the transport reaction to the proton exchange membrane and the removal transport of the water of reaction that is formed.

[0012] Conductive nonwoven fabrics in which partially crosslinked phenolic resin fibers, polyester and/or polypropylene fibers are used as the precursor fibers, homopolymers, copolymers, and/or terpolymers of PAN (polyacrylic nitrile) fibers, cellulose fibers and/or phenolic resin fibers are used as the preoxidized fibers, and PVA (polyvinyl alcohol) fibers are used as the water-soluble fibers are particularly preferred. The gas diffusion layer that is obtained from a nonwoven fabric made of these fibers can be carbonized well, for one thing, and for another, it can be easily adjusted with regard to its pore distribution and its rigidity.

[0013] A conductive nonwoven fabric that is hydrophobized by application of a hydrophobization agent such as PTFE (polytetrafluoroethylene) is particularly preferred. The transport processes at the phase border surfaces can be further improved by hydrophobization.

[0014] According to the invention, the conductive nonwoven fabric is produced in such a manner that

[0015] a) preoxidized fibers, if necessary in a mixture with up to 30 wt.-% carbonizable precursor fibers that serve as binder fibers, and up to 30 wt.-% water-soluble fibers, are mixed,

[0016] b) laid to form a fiber fleece with a mass per unit area of 60 to 300 g/m^2, using the dry method, and using stripper and/or carding machines,

[0017] c) bonded with high-pressure fluid jets, at pressures of 100 to 300 bar,

[0018] d) predried to a residual moisture of 10 to 50%,

[0019] e) calandered at contact pressures of 20 to 1000 N/cm^2 and temperatures of 100 to 400° C., and

[0020] f) carbonized and/or graphitized at temperatures between 800 and 2500° C.

[0021] Preferably, production takes place in that in step

[0022] a) fibers with a fiber titer of 0.8 to 3.3. dtex and a fiber length of 30 to 70 mm are used,

[0023] b) fiber fleeces with a mass per unit area of 30 to 180 g/m^2 are laid,

[0024] e) calandering takes place at a contact pressure of 40 to 700 N/cm^2 and a temperature of 180 to 300° C., and

[0025] f) carbonization as well as graphitization takes place at a temperature between 1000 and 1800° C.

[0026] It is particularly preferred that in step

[0027] e) at least two nonwoven fabric layers are calandered together.

[0028] The invention will be explained in greater detail below, using examples.

EXAMPLE 1

[0029] A preoxidized PAN fiber (oxidized PAN fiber—OPF) with a fiber titer of 0.8 dtex and a fiber length of 60 mm is laid on a carding system to form a fiber fleece with a mass per unit area of 100 g/m^2. The fiber fleece is passed to a bonding unit in which the fibers are tanglelaced and intertangled with one another by high-energy water jets on both sides, at pressures of approximately 100 bar in the first step and approximately 170 bar in the second step, in each instance. The nonwoven fabric is predried to a residual moisture of 15 to 20%. While still in the wet state, the nonwoven fabric is passed to a felt band calander and compressed at a temperature of approximately 220° C. and at 20 bar. As a result of the calandering process, the thickness of the water-jet-bonded nonwoven fabric is reduced from 0.8 mm to a thickness of 0.4 to 0.5 mm. Subsequently, the nonwoven fabric is passed to a carbonization unit in which carbonization takes place under a nitrogen atmosphere, at approximately 1000 to 1400° C. The resulting conductive nonwoven fabric demonstrates a crosswise conductivity, i.e. in the layer plane, of 12 S/cm in the machine direction, 18 S/cm crosswise to the machine direction, at a bending rigidity of <1 taber and an air permeability of 6.0 l/m^{2}sPa, and its through conductivity, i.e. perpendicular to the layer plane, is 90 S/cm^2, where this value was determined at a surface pressure of 4.07 bar. Its density is 0.16 g/cm^3, the porosity is 91%, and the average pore diameter is 25 μm.

EXAMPLE 2

[0030] A two-layer fiber fleece made up of a first fleece layer with a mass per unit area of 50 g/m^2, made up of 80 wt.-% OPF with a fiber titer of 1.2 dtex and a fiber length of 60 mm, as well as 20 wt.-% of a TTP fiber (textile tow precursor) with a fiber titer of 1.7 dtex and a fiber length of 40 mm, and a second fleece layer with a mass per unit area of 50 g/m^2, made up of 80 wt.-% OPF with a fiber titer of 0.8 dtex and a fiber length of 60 mm, as well as 20 wt.-% of a TTP fiber with a fiber titer of 0.8 dtex and a fiber length of 40 mm, which were cross-laid on a carding system, is passed to a bonding unit in which the fibers are tanglelaced and intertangled with one another by high-energy water jets on both sides, at pressures of approximately 120 bar in the first step and approximately 190 bar in the second step, in each instance. The nonwoven fabric is predried to a residual moisture of approximately 10%. While still in the wet state, the nonwoven fabric is passed to a roller calander with a steel roller and a roller coated with cotton, where the temperature of the steel roller was approximately 210° C. and that of the roller coated with cotton was approximately 150° C., and compressed at a line pressure of 80 kp/cm^2. As a result of the calandering process, the thickness of the water-jet-bonded nonwoven fabric is reduced from 0.8 mm to a thickness of 0.16 mm. Subsequently, the nonwoven fabric is passed to a carbonization unit in which carbonization takes place under a nitrogen atmosphere, at approximately 1000 to 1400° C. The resulting conductive nonwoven fabric demonstrates a crosswise conductivity, i.e. in the layer plane, of 54 S/cm in the machine direction, 54 S/cm crosswise to the machine direction, at a bending rigidity of 1 taber and an air permeability of 2 l/m^{2}sPa, and its through conductivity, i.e. perpendicular to the layer plane, is 120 S/cm^2, where this value was determined at a surface pressure of 4.07 bar. Its density is 0.32 g/cm^3, the porosity is 82%, and the average pore diameter is 15 μm.

EXAMPLE 3

[0031] A preoxidized PAN fiber (oxidized PAN fiber—OPF) with a fiber titer of 0.8 dtex and fiber lengths of 60 mm is laid on a carding system to form a fiber fleece with a mass per unit area of 100 g/m^2. The fiber fleece is passed to a bonding unit in which the fibers are tanglelaced and intertangled with one another by high-energy water jets on both sides, at pressures of approximately 100 bar in the first step and approximately 170 bar in the second step, in each instance. The nonwoven fabric is predried to a residual moisture of 15 to 20%. While still in the wet state, the nonwoven fabric is passed to a calander made up of a steel roller and a plastic roller and compressed at a temperature of approximately 350° C. and at 250 kp/cm^2. As a result of the calandering process, the thickness of the water-jet-bonded nonwoven fabric is reduced from 0.9 mm to a thickness of 0.14 mm. Subsequently, the nonwoven fabric is passed to a carbonization unit in which carbonization takes place under a nitrogen atmosphere, at approximately 1000 to 1400° C. The resulting conductive nonwoven fabric demonstrates a crosswise conductivity, i.e. in the layer plane, of 93.7 S/cm in the machine direction, 73 S/cm crosswise to the machine direction, at a bending rigidity of <1 taber and an air permeability of 1.0 l/m^{2}sPa, and its through conductivity, i.e. perpendicular to the layer plane, is 195 S/cm^2, where this value was determined at a surface pressure of 4.07 bar. Its density is 0.43 g/cm^2, the porosity is 78%, and the average pore diameter is 7 μm.

What is claimed is:

1. A conductive nonwoven fabric, wherein it is carbonized and/or graphitized and possesses a bending rigidity <8 taber, a density of 0.1 g/m^3 to 0.5 g/m^3, a thickness of 80 μm to 500 μm, and an electrical conductivity of 10 to 300 S/cm^2 in the nonwoven fabric strip and 30 to 220 S/cm^2 perpendicular to the nonwoven fabric strip.

2. The conductive nonwoven fabric according to claim 1, obtained from preoxidized fibers for carbon fibers that are mixed, if necessary, with up to 30 wt.-% of a percursor fiber that serves as a binding fiber, as well as up to 30 wt.-% of a water-soluble fiber having fiber titers of 0.5 to 6.7 dtex, by being laid up to form a fiber sheet having a mass per unit area of 30 to 300 g/m^2, bonding of the fiber sheet using high-pressure fluid jets at pressures of 100 to 300 bar, compression of the bonded fiber fabric by 50 to 90% of its starting thickness by calandering, and carbonization and/or graphitization under an inert gas atmosphere, at 800° C. to 2500° C.

3. The conductive nonwoven fabric according to claim 1 or **2**, wherein 80 to 90 wt.-% of a mixture of precursor fibers and preoxidized fibers in a weight ratio of 0:1 to 1:3 and 10 to 20 wt.-% of a water-soluble fiber having fiber titers of 0.8 to 3.3 dtex are used.

4. The conductive nonwoven fabric according to one of claims 1 to 3, wherein two different water-soluble fibers were used, one of which is water-soluble at temperatures of 10 to 40° C. and the other of which is water-soluble at temperatures of 80 to 120° C.

5. The conductive nonwoven fabric according to claim 4, wherein the ratio of the water-soluble fibers relative to one another is 3:1 to 1:3.

6. The conductive nonwoven fabric according to one of claims 1 to 5, wherein it is made up of several fiber layers having different pore sizes, the fibers of the individual layers possessing different titers.

7. The conductive nonwoven fabric according to one of claims 1 to 6, wherein at least two nonwoven fabric layers that have been bonded by high-pressure fluid jets are combined by calandering.

8. The conductive nonwoven fabric according to one of claims 1 to 7, wherein partially crosslinked phenolic resin fibers, polyester and/or polypropylene fibers are used as the precursor fibers, homopolymers, copolymers, and/or terpolymers of PAN (polyacrylic nitrile) fibers, cellulose fibers and/or phenoloresin fibers are used as the preoxidized fibers, and PVA (polyvinyl alcohol) fibers are used as the water-soluble fibers.

9. The conductive nonwoven fabric according to one of claims 1 to 8, wherein it is hydrophobized by application of a hydrophobization agent such as PTFE (polytetrafluoroethylene).

10. A method for the production of the conductive nonwoven fabric according to one of claims 1 to 9, wherein

a) preoxidized fibers, if necessary in a mixture with up to 30 wt.-% carbonizable precursor fibers that serve as binding fibers, and up to 30 wt.-% water-soluble fibers, are mixed,

b) laid up to form a fiber sheet having a mass per unit area of 30 to 300 g/m^2, using the dry method, and using stripper and/or carding machines,

c) bonded with high-pressure fluid jets, at pressures of 100 to 300 bar,

d) predried to a residual moisture of 10 to 50%,

e) calandered at contact pressures of 20 to 1000 N/cm^2 and temperatures of 100 to 400° C., and

f) carbonized as well as graphitized at temperatures between 800 and 2500° C.

11. The method according to claim 10, wherein in step

a) fibers having a fiber titer of 0.8 to 3.3. dtex and a fiber length of 30 to 70 mm are used,

b) fiber sheets having a mass per unit area of 30 to 180 g/m^2 are laid,

e) calandering takes place at a contact pressure of 40 to 700 N/cm^2 and a temperature of 180 to 300° C., and

f) carbonization as well as graphitization takes place at a temperature between 1000 and 1800° C.

12. The method according to claim 10 or **11**, wherein in step e) at least two nonwoven fabric layers are calandered together.

13. The conductive nonwoven fabric according to one of claims 1 to 12, wherein they are used as the base material for electrodes and gas diffusion layers, at a density of 0.1 g/cm^3 to 0.25 g/cm^3.

14. The conductive nonwoven fabric according to one of claims 1 to 12, wherein they are used as gas diffusion layers in polymer electrolyte fuel cells, at a density of 0.25 g/cm^3 to 0.40 g/cm^3.

15. The conductive nonwoven fabric according to one of claims 1 to 12, wherein they are used as electrodes in supercapacitors, at a density of 0.40 g/cm^3 to 0.50 g/cm^3.

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