CARBON PAPER

Filed July 3, 1972

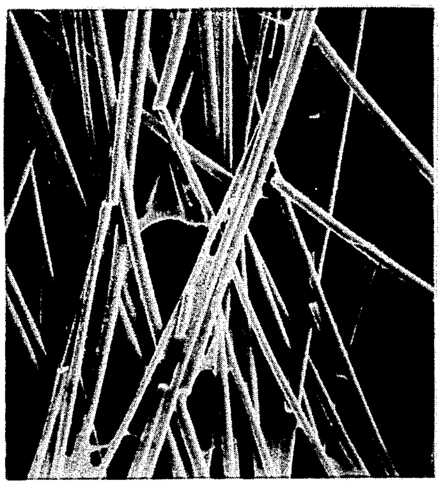

Fig. 1.

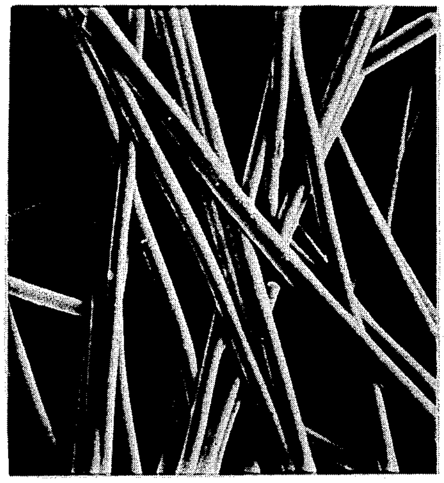

Fig. 2.

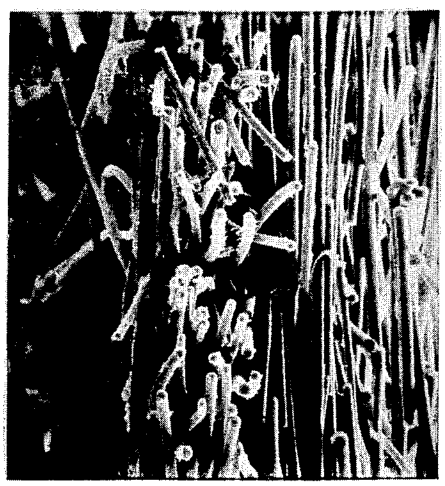

Fig. 3.

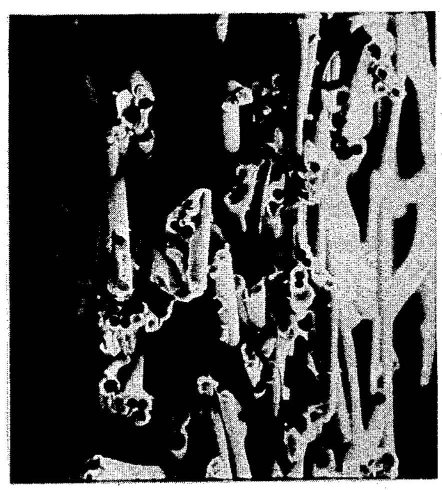

Fig. 4.

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Filed July 3, 1972, Ser. No. 268,600
Int. Cl. C01b *31/04;* H01m *13/02*
U.S. Cl. 117—226 12 Claims

ABSTRACT OF THE DISCLOSURE

An electrically conductive, chemically inert, porous, structurally coherent web of carbon fibres which has a carbon coating thereon. The carbon coatings on the respective carbon fibres are intergrown with one another at those locations where the coated fibres contact one another. At least about fifty percent of the volume in the web is void of coated fibres.

The present invention relates to a pure carbon web that is electrically conductive, chemically inert, porous, and structurally coherent. These webs are particularly suited for use as electrodes in fuel cells and other harsh environments where electrical conductivity is required of a thin porous sheet of material that must be thermally stable and chemically inert even at elevated temperatures of several hundred degrees Fahrenheit. Also, the web is particularly suited for use where it must retain its physical, chemical, and electrical characteristics and dimensions while it is subjected to handling, transportation, and shaping prior to its being assembled into a completed working device.

Previously, porous webs that were intended for use in extreme environments that demanded chemical, thermal, and structural stability were deficient or defective in achieving these characteristics. The materials from which it was proposed to manufacture such porous webs were difficult and expensive to product and manufacture. In general, the proposed structures were unsatisfactory for the intended purposes.

According to the present invention, a web of carbon fibres having a carbon coating is prepared so that the individual carbon fibres are substantially uniformly coated with an annular coating or jacket which is composed of pure carbon. The carbon coatings are intergrown with one another at the intersection between the carbon fibres so that the carbon coatings serve to bind or interlock the carbon fibres into an integral structurally coherent web. The interlocking of the carbon coatings at the locations where the coated fibres contact one another provides good electrical connections throughout the entire mass of the web as well as providing structural integrity for the web. The pure carbon web is chemically inert even in acidic or basic environments at elevated temperatures.

The carbon coating is applied by known chemical vapor deposition methods to a carbon fibre web. The chemical vapor deposition procedure is carried on for a period of time sufficient to substantially uniformly coat the carbon fibres with the pyrolytic carbonaceous material and to provide interlocking between the coated fibres. The chemical vapor deposition procedure is terminated before the deposits grow to the extent that more than 50 percent of the volume in the web is occupied by the coated fibres. Preferably, the chemical vapor deposition procedure is terminated when the carbon deposits have grown to such an extent that between 30 and 50 percent of the volume in the web is occupied by the coated fibres.

According to one method, the carbon fibre web or paper, on which the carbon coating is deposited by chemical vapor deposition procedures, is prepared from carbon fibres using the following procedure. Carbon fibres which may be composed of amorphous carbon, graphite, or admixtures of these forms of carbon are chopped into finite lengths. Conveniently, the basic carbon fibre is chopped into lengths of approximately one-eighth of one inch. The chopped fibres are prepared into a mat or paper on a paper-making machine. The carbon fibres by themselves are generally very hard and smooth so that they do not adhere readily to one another. In order to promote formation of a carbon paper, a binder, such as polyvinyl alcohol, is admixed with the fibre as it is being processed into paper. The polyvinyl alcohol binder serves to bind the carbon fibres together so that the fibres will cling together to form a structurally coherent web. The carbon fibre paper is then impregnated with a dilute solution of a charring synthetic resin, such as, for example, a phenolic resin. The phenolic-impregnated, polyvinyl alcohol bound carbon fibre web is then subjected to a carbonizing step at, for example, approximately 1000 degrees centigrade to volatilize the polyvinyl alcohol binding and to convert the phenolic resin to carbon. The resultant carbon fibre web is bound together by carbon bridges between the carbon fibres. These carbon bridges are the residue that is left from the charring of the dilute phenolic resin. The carbon paper or web is now a pure carbon product, existing almost entirely in the amorphous carbon form. The polyvinyl alcohol binding has been replaced by carbon bridges formed from the residue of the charring synthetic resin. The resultant carbon bound, carbon fibre mat is then subjected to chemical vapor deposition according to known procedures.

According to one known procedure, chemical vapor deposition is accomplished by subjecting the carbon bound, carbon fibre web to temperatures between about 1300 degrees centigrade and 2800 degrees centigrade or more at a reduced pressure in the presence of a dilute hydrocarbon gas. The hydrocarbon gas decomposes to a non-sooting carbon vapor that deposits a carbon coating on the heated, carbon bound, carbon fibre web in a very uniform coating. At the higher temperature the carbon web is almost entirely in the graphite form. As the temperature decreases, the amorphous carbon form increases, and at the lower temperatures the carbon web is almost entirely in the amorphous carbon form. The resultant porous carbon web has a very uniform porosity. The mechanical and electrical characteristics of the web are very uniform when measured along different parallel axis in the web. The mechanical and electrical characteristics vary somewhat with the orientation of the majority of the fibres.

The temperatures employed during the preparation of the carbon fibre web with the carbon coating determine whether the resulting structure will be composed of carbon in the graphite form or the amorphous carbon form. The term "carbon" is used herein to describe the material in the fibres and in the coatings in both the amorphous carbon and graphite forms in which a majority of the coating is graphite and a minority is carbon. As used herein the term "carbon" is intended to include all forms of carbon and all admixtures of these several forms.

The electrical properties of the electrically conductive porous web can be tailored so that they are different when measured in different directions in the plane of the web. In general, the electrical resisitivity decreases in a particular direction as the proportion of fibres oriented in that direction increases. When the distribution of the fibres is substantially uniform in all directions, the electrical resistivity is substantially uniform in all directions. Also, the physical characteristics of the web may be altered by selectively adjusting the orientation of the major portion of the fibres. In general, tensile strength is greatest along an axis that extends generally parallel to the major proportion of the fibres. In general, the electrical resistivity decreases as the percentage of carbon in the graphite form increases. The electrical resistivity, at least in one direction, is less than about 0.020 ohm centimeter.

The carbon coatngs may be activated, if desired, for example, by treating the finished porous web with steam.

The web, if desired, may be manufactured from carbon filaments by a weaving process rather than a paper-making process.

The chemical vapor deposition procedure results in the formation of a carbon coating which substantially uniformly covers each of the individual carbon fibres in the carbon bound, carbon fibre mat. Each of the carbon fibres is encased in its own individual coating, and where the carbon fibres touch one another or are in close proximity to one another, the carbon coatings are grown together so that the fibres are interlocked at their intersections by their respective carbon coatings. The binding formed by the charring synthetic resin is almost entirely replaced by the interlocking of the coatings. The electrical conductivity of the porous web is greatly increased by the presence of the interlocked carbon coatings. The intergrowth of the carbon coatings at the intersections of the respective individual fibres provides a good mechanical connection throughout the entire web so that electricity flows easily across the web without encountering any open connections. Also, the interlocking of the respective carbon coatings greatly improves the structural strength and integrity of the web. The area of the contact between the fibres due to the intergrowth of the coatings is preferably at least approximately as great as the cross-sectional area of the uncoated fibre measured normal to the longitudinal axis of the fibre.

The pure carbon porous webs are prepared with as great a degree of porosity as possible. In general, more than 50 percent of the volume within the web is void, and preferably from about 50 to 70 percent of the volume in the web is empty void. The porosity promotes the flow of fluids through the web when the web is being used. Also, the high degree of porosity permits the fluid transmission properties of the web to be tailored to a particular set of fluid flow requirements by impregnating the web with an inert material, such as polytetrafluorethylene, until a particular degree of desired porosity is achieved. Preferably, the core size of the web is less than approximately 60 microns. The high percentage of void space within the porous web also provides space within which to incorporate a finely divided catalyst. In general, when a catalyst is incorporated into the porous web, it is bound to the web by some inert binder, such as polytetrafluorethylene.

The physical dimensions of the completed pure carbon web may be varied widely, as desired, within the size capacity of the equipment in which it is manufactured. In general, the length and width of the web may range from a few inches to several feet. The thickness of the web is generally not less than 0.2 millimeter nor more than 5 millimeters, although somewhat greater or lesser thicknesses may be utilized if desired. In general, the thickness of the web is less than about one millimeter. The thickness of the web is generally substantially less than about the average length of the coated fibres and preferably less than about one-third of the average length of the coated fibres. Preferably, the bulk density of the carbon web is at least 0.25 gram per cubic centimeter, and the thickness is at most 0.625 millimeter. The weight of the carbon web generally ranges from about 140 to 220 grams per square meter.

When the web is used where electrical current is taken from or applied to the web, the connectiions to the web conveniently take the form of a conductive band of material extending across one edge of the web. The conductive band may be oriented with respect to the orientation of the majority of the fibres to take advantage of any directional characteristics that the web may possess. For example, if the lowest resistivity is desired, the conductive band should be positioned so that it extends generally perpendicular to the direction in which the majority of the fibres are oriented.

In the drawings there is illustrated:

FIG. 1, a plan view photograph taken at a magnification of approximately 200 times of a carbon bound, carbon fibre web prior to chemical vapor deposition;

FIG. 2, a view of the completed pure carbon web similar to FIG. 1 taken at a magnification of approximately 200 times after the carbon web has been subjected to chemical vapor deposition;

FIG. 3, an edge view of a carbon bound, carbon fibre web prior to chemical vapor deposition taken at a magnification of approximately 200 times; and

FIG. 4, a view of the completed pure carbon web similar to FIG. 3 showing the carbon web after the chemical vapor deposition procedure has been completed taken at a magnification of approximately 200 times.

Comparison of the web before and after chemical vapor deposition clearly reveals that the chemical vapor deposition results in the application of a very uniform coating on the individual carbon fibres. Also, the carbon binding illustrated particularly by the thin sheets extending between fibres in FIG. 1 is removed during the chemical vapor deposition procedure and is replaced by the intergrowth and interlocking of the carbon coatings on the respective fibres. The carbon coatings are particularly apparent in FIG. 4.

The web shown in FIGS. 1 and 3 was prepared from carbon fibres that were chopped to ⅛-inch lengths and manufactured into a mat on a paper-making machine, using approximately 10 percent polyvinyl alcohol to bind the mat together. The resultant polyvinyl alcohol-carbon fibre mat had approximately 70 percent of its fibres oriented in one direction. The polyvinyl alcohol bound carbon fibre mat was then impregnated with a dilute solution of charring phenolic resin and was carbonized at a temperature of about 1000 degrees centigrade. The polyvinyl alcohol was completely volatilized at this temperature, leaving the carbon fibres bound together by carbon bridges produced from the charring of the phenolic resin. These carbon bridges are evident in FIG. 1. The electrical resistivity of this carbon bound, carbon fibre web was about 0.17 ohm centimeter measured in the direction in which the majority of the fibres are oriented. The weight per area of this material was about 37 grams per square meter. Its density was about 0.13 gram per cubic centimeter, and its thickness was about 0.26 millimeter. This material was subjected to chemical vapor deposition at about 1300 degrees centigrade for a period of time sufficient to deposit a carbon coating having a thickness such that the diameter of the coated fibres is approximately twice that of the uncoated fibres. The electrical resistivity of the pure carbon porous web measured in the direction of the majority of the fibers is about 0.015 ohm centimeter; the thickness is about 0.5 millimeter; the weight per area is about 180 grams per square meter; and about 65 percent of the volume within the web is void. The carbon in this web is substantially all in the amorphous carbon form.

The chemically inert porous webs according to this invention are generally applicable to all categories of extreme liquid and gaseous fluid environments even at elevated temperatures.

What is claimed is:

1. A porous web electrode comprising:

a plurality of carbon fibres;

a carbon coating substantially uniformly covering each of said carbon fibres, the coated fibres being combined together to define said porous web, a substantial portion of said coated fibres being positioned in approximately the plane of said porous web, the said carbon coatings on said coated fibres generally being intergrown at locations where said coated fibres contact one another, at least about fifty percent of the volume in said porous web being void of coated fibres, said porous web having a weight of from about 140 to 220 grams per square meter and a specific resistivity in at least one direction of less than about 0.020 ohm centimeter; and

means for making electrical connections to said porous web.

2. A porous web of claim 1 wherein the carbon fibres contain a substantial amount of graphite.

3. A porous web of claim 1 wherein the thickness of said web is less than about the average length of the coated fibres.

4. A porous web of claim 1 wherein the thickness of said web is less than about one millimeter.

5. A porous web of claim 1 wherein the carbon coatings are intergrown with one another at the intersections of the carbon fibres to such an extent that the area of the contact between the coated fibres at the said intersections is approximately at least as great as the cross-sectional area of the said carbon fibres.

6. A porous web of claim 1 wherein the carbon coatings on the coated fibres are substantially pure graphite.

7. A porous web electrode of claim 1 wherein at least about sixty percent of the coated fibres are oriented in one general direction and the means for making electrical connections to said porous web includes a conductive band extending generally perpendicular to said one general direction.

8. An electrically conductive porous web comprising:

a plurality of carbon fibres;

a carbon coating substantially uniformly covering each of said carbon fibres, the coated fibres being combined together to define said porous web, a substantial portion of said coated fibres being positioned in approximately the plane of said porous web, the said carbon coatings on said coated fibres generally being intergrown with one another at the intersections of the carbon fibres in said porous web to such an extent that the area of the contact between the coated fibres at said intersections is approximately at least as great as the cross-sectional area of said carbon fibres, from about fifty to seventy percent of the volume in said porous web being void of coated fibres, said porous web having a thickness from about 0.2 to 1 millimeter, said porous web having a weight of from about 140 to 220 grams per square meter and a specific resistivity in at least one direction of less than about 0.020 ohm centimeter.

9. An electrically conductive porous web comprising:

a plurality of carbon fibres;

a carbon coating substantially uniformly covering each of said carbon fibres, the coated fibres being combined together to define said porous web, a substantial portion of said coated fibres being positioned in approximately the plane of said porous web, the thickness of said porous web being from about 0.2 to 5 millimeters, said thickness being less than about one-third the average length of said carbon fibres, the said carbon coatings on said coated fibres being generally intergrown at locations where said coated fibres contact one another, at least about fifty percent of the volume in said porous web being void of coated fibres, the pore size of void space within said porous web being less than approximately 60 microns, said porous web having a weight of from about 140 to 220 grams per square meter and a specific resistivity in at least one direction of less than about 0.020 ohm centimeter.

10. A porous web of claim 9 wherein the carbon coating comprises activated carbon.

11. A process of manufacturing a porous web electrode comprising:

subjecting a web of carbon fibres to chemical vapor deposition of carbon;

continuing said chemical vapor deposition of carbon until a substantially uniform carbon coating is formed on said carbon fibres and the resultant coated fibres are generally intergrown at locations where said coated fibres contact one another;

discontinuing said chemical vapor deposition of carbon before the coated fibres occupy more than about fifty percent of the volume in said web, and after said porous web reaches a weight of from about 140 to 220 grams per square meter and a specific resistivity in at least one direction of less than about 0.020 ohm centimeter; and

recovering the resultant electrically conductive, chemically inert, structurally coherent, porous web electrode.

12. A process of claim 11 including selecting a web of carbon fibres that has a substantial portion of the carbon fibres positioned in approximately the plane of said web, and a majority of said carbon fibres are oriented in one general direction.

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U.S. Cl. X.R.

117—46 CG, 106 R, 228; 136—120 FC, 121, 122; 204—290, 294; 423—447

Disclaimer

3,829,327.—*Thomas T. Omori*, Glendale, and *Hiroshi Imaoka*, Gardena, Calif. CARBON PAPER. Patent dated Aug. 13, 1974. Disclaimer filed Mar. 27, 1978, by the assignee, *Kreha Corporation of America*.

Hereby enters this disclaimer to claims 1 through 12, inclusive, of said patent.

[*Official Gazette July 11, 1978.*]