

[54] **PROCESS FOR MAKING
ELECTROCHEMICAL ELECTRODES**[75] Inventors: **Perry H. Brown**, Norwell; **Maurice H. Tremblay**, Westboro, both of Mass.[73] Assignee: **Brunswick Corp.**, Chicago, Ill.[22] Filed: **Oct. 12, 1971**[21] Appl. No.: **188,376****Related U.S. Application Data**

[60] Division of Ser. No. 5,882, Jan. 26, 1970, which is a continuation-in-part of Ser. No. 861,024, Sept. 25, 1969, abandoned.

[52] U.S. Cl. **136/120 FC**[51] Int. Cl. **H01m 13/04**

[58] Field of Search 136/120 FC, 86 D; 28/76 P, 28/72 P, 76 T; 139/425

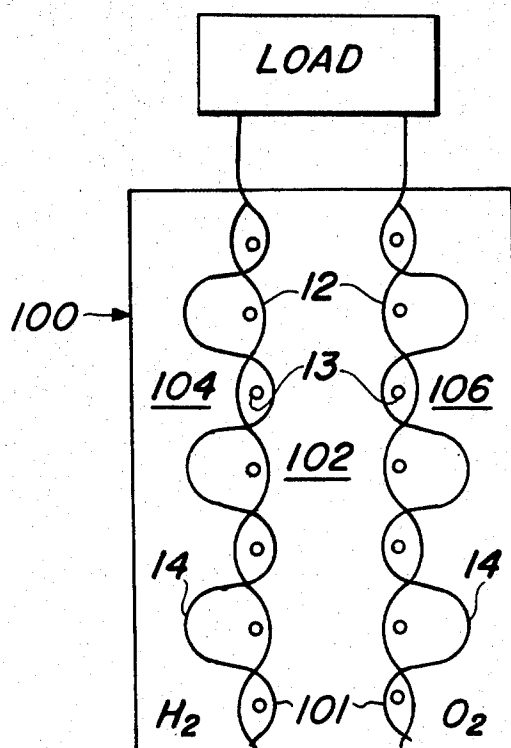
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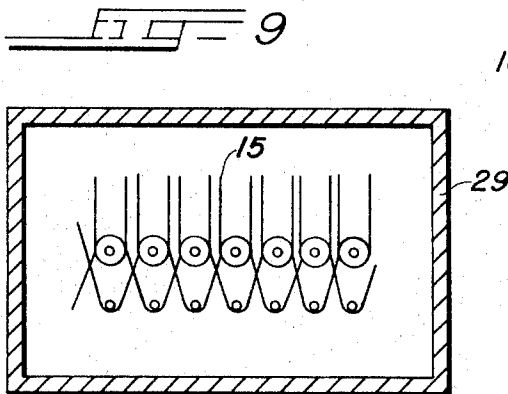
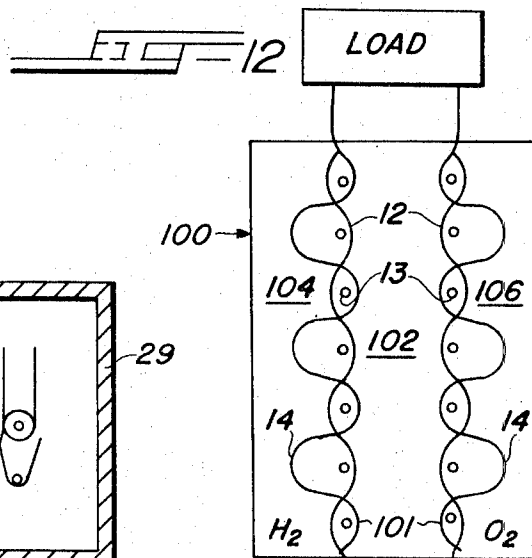
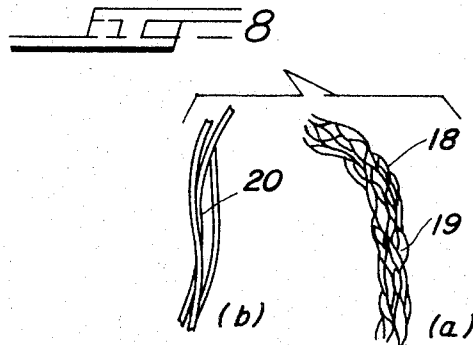
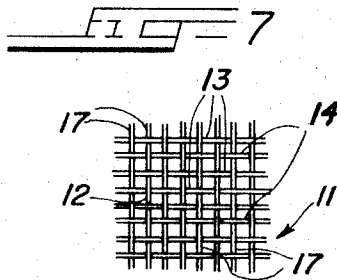
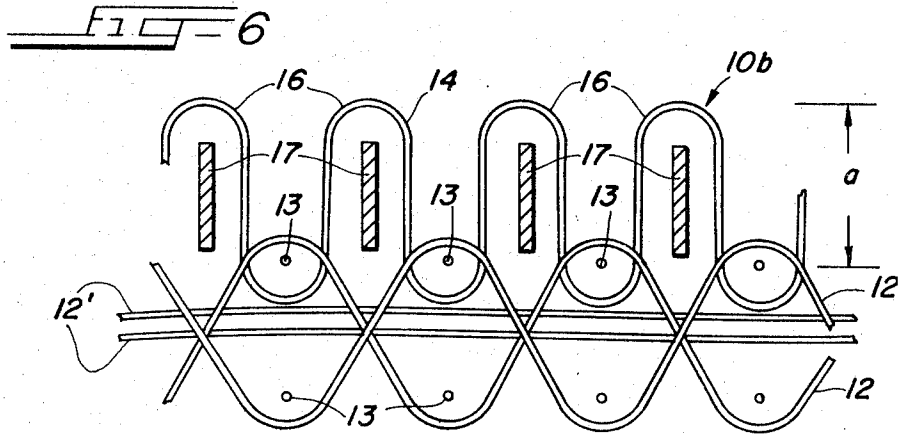
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Primary Examiner—L. Dewayne Rutledge*Assistant Examiner*—M. J. Andrews*Attorney, Agent, or Firm*—John G. Heimovics; Donald S. Olexa; Sheldon L. Epstein[57] **ABSTRACT**

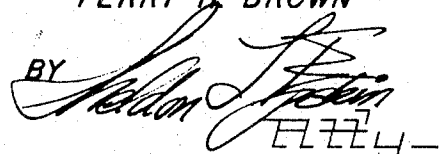
An electrochemical electrode of a metallic velvet-like material comprising a woven textile pile fabric wherein at least a portion of the woven base fabric and/or the velvet surface-forming pile yarns is metallic is described. The metallic yarn may comprise a blended yarn formed of staple metal fibers and conventional nonmetallic textile fibers, or may be formed of continuous metal filament material. The metal fibers, or filaments, are preferably formed with rough, unmachined, unburnished, fracture-free outer surfaces for improved retention in the velvet pile fabric. The electrode has particular application in fuel cells, batteries and other electrochemical systems where high usable surface areas (per unit volume) are needed to promote three-phase reactions.

4 Claims, 12 Drawing Figures



SINTERING

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PROCESS FOR MAKING ELECTROCHEMICAL ELECTRODES

BACKGROUND OF THE INVENTION

CROSS-REFERENCE

This application is a division of Application Ser. No. 5,882 filed on Jan. 26, 1970 which-in-turn is a continuation-in-part of our application Ser. No. 861,024 filed on Sept. 25, 1969, now abandoned.

FIELD OF THE INVENTION

This invention is in the field of electrochemistry and, more particularly, is a new electrochemical electrode for fuel cells, batteries and other electrochemical systems which require high usable surface areas on their electrodes to make the systems economical for commercialization.

DESCRIPTION OF THE PRIOR ART

In a number of electrochemical systems, poor electrode performance prevents commercialization. In the case of a system such as the fuel cell, poor electrode performance is believed to be caused by limited surface areas available to promote the required three-phase electrode reactions in which both the electrolyte and either the fuel or oxidizer gas are brought together at common points on the electrode surface. Detailed descriptions of this problem and suggested solutions appear in many patents on fuel cells found in U.S. Class 136-86 and in references such as Liebhafsky & Cairns, *Fuel Cells and Fuel Cell Batteries*, Wiley, 1968.

In essence, the prior art solutions for improving electrode performance have concentrated on increasing electrode surface area by the use of expensive catalysts and, more recently, by the use of very fine powder metal and fiber metal electrodes. The improved performance noted when finer powders and fibers are used suggests that surface area limitations are of prime importance. The problem that has arisen is that there is little chance to make further increases in surface area now that particle and fiber dimensions of approximately 1 micron have been realized.

A careful analysis of electrode structure and performance in a typical three-phase (gas-electrolyte-metal) reaction reveals that a very small percentage of the available surface area of a conventional electrode is actually used to promote and support a reaction. A typical prior art fuel cell electrode comprises a porous powdered metal compacted structure or a randomly oriented fiber metal web which may be 1-20 mils or more in thickness. The electrode is partially flooded from one side with an electrolyte such as an acid, a base, or a molten carbonate. A gas such as hydrogen (at the anode) or air (at the cathode) enters the electrode from the other side. By one of a number of techniques, a stable gas-electrolyte interface is established within the electrode. Recalling that the combined, simultaneous presence of gas, electrolyte and electrode is necessary to have a reaction, it is interesting to note that while the electrode may be 20 mils or more thick, the gas will only permeate an electrolyte such as a molten carbonate to a depth of about 5-10 microns. Thus, the great portion of the electrode's total surface area is beyond the 5-10 micron deep gas-electrolyte interface and is unusable. It therefore cannot make any contribution to the electrode's performance.

In order to overcome this limitation on the usable surface area of an electrochemical electrode which can promote a reaction for a fuel cell or other system, the electrodes of this invention were developed. Typically, those electrodes comprise a pile or velvet-like or plush-like fabric wherein the pile comprises spun yarns which act as wicks for the electrolyte (in the case of fuel cells) and which may be covered by only a few microns of electrolyte. With such a thin coating, the gas (in the case of a fuel cell) can readily permeate through the electrolyte layer to the metal electrode to initiate and sustain an efficient three-phase reaction. The fine capillary-like wicks preferably containing continuous metallic filaments are oriented in the direction of mass flow (perpendicular rather than parallel to the gas-electrolyte interface) to aid rather than hinder liquid and ionic mass transport. In addition the fabric supporting the pile yarns acts as a current collector. In systems other than fuel cells, fluids other than electrolytes and fuel or oxidizer gases may be used.

DESCRIPTION OF A PREFERRED EMBODIMENT

The electrochemical electrodes of this invention comprise a pile or velvet-like fabric wherein at least a portion of the woven fabric and/or pile yarn is metallic. The electrodes may also include a metallic portion of the textile in the form of small diameter metal filaments or fibers which may be blended with conventional textile materials or comprise the entire yarn. Further, the yarn may be a spun yarn comprising metal fibers. The metal filaments or fibers may have a diameter of down to 1 micron or smaller to provide desirable flexibility and uniformity of blend whereby the pile fabric may be formed by substantially conventional textile forming apparatus. The metal fibers may comprise staple length fibers or may comprise continuous filaments as desired. In the preferred form, the fibers or filaments may have a rough unmachined, unburnished, fracture-free outer surface for improved retention, higher surface area and good electric conductivity between the fibers in the pile fabric. The fibers may be metallic throughout, or may comprise nonmetallic fibers having an electrically conductive metallic coating.

The metal fibers and filaments may have further improved retention and conductivity in the fabric by means of bonding. The bonding may be effected by metallurgical processes such as sintering, brazing, or welding operations and sacrificial materials may be employed for maintaining a desired association of the metal fibers and filaments. Alternatively, when adhesive bonding means are used, they may comprise electrically conductive adhesives. The particular metal material used may be preselected to provide desired catalytic performance, wear, and abrasion, and other physical and chemical characteristics.

BRIEF DESCRIPTION OF THE DRAWING

Other features and advantages of the invention will be apparent from the following description taken in connection with the accompanying drawing wherein:

FIG. 1 is a schematic view illustrating a drawing step in the formation of metallic filaments for use in making a pile or velvet-like textile electrochemical electrode embodying the invention;

FIG. 2 is a schematic view illustrating a further step in the formation of metallic filaments wherein the matrix material is removed;

FIG. 3 is a broken isometric view of a tow of filaments so formed;

FIG. 4 is an enlarged transverse cross-section of a filament illustrating the rough unmachined outer surface thereof;

FIG. 5 is a transverse section of an uncut velvet or pile fabric electrode;

FIG. 6 is a transverse section of a modified form of a pile fabric electrode;

FIG. 7 is a fragmentary face view of the fabric of FIG. 6;

FIG. 8 is a fragmentary enlarged elevation of yarns such as used in the pile fabrics of FIGS. 5 and 6;

FIG. 9 is a schematic elevation of an apparatus for providing sintered bonds between the metallic portions of the fabric;

FIG. 10 is a fragmentary perspective view of a piece of pile electrode embodying the invention;

FIG. 11 is a transverse cross-section of a coated fiber for use in the pile fabric; and

FIG. 12 is a schematic view of a fuel cell incorporating electrodes of this invention.

In the exemplary embodiment of the invention as disclosed in the drawing, an electrochemical electrode, generally designated 10, is shown to comprise a pile, plush or velvet-like textile fabric as may be formed on conventional textile forming apparatus. In a preferred form, the pile electrode comprises metallic filaments or fibers distributed in the yarns of the woven fabric and/or pile. As illustrated in FIG. 7, the electrode's woven fabric, generally designated 11, is formed of a plurality of vertical warp yarns 12 and horizontal filling, or weft, yarns 13. In textile industry terminology, the warp yarns 12 are identified as ends and the filling yarns 13 are identified as picks. In forming the electrode material 10, the pile yarn 14 is introduced which extends outwardly from the surface of the fabric to define the pile, plush or velvet-like surface 15, as shown in FIG. 10. The pile yarn may comprise an extra warp end or an extra filling pick as desired. Alternatively and illustratively, the base fabric 11 may be a warp knitted material or another kind of ordered or geometrically regular material (such as a sliver knit) or it may be a random web material.

Referring to FIGS. 5 and 6, two different methods of forming such a pile electrode are illustrated. Thus, in the pile electrode 10a shown in FIG. 5, the warp ends 12 are interlaced in spaced or ordered relationship to two sets of filling picks, or weft yarns 13. The pile yarn 14 is interlaced with the spaced filling picks 13 to define a plurality of outwardly disposed turned portions or piles 16. The piles 16 may be cut as by shearing or other suitable conventional cutting methods to obtain a velvet surface 15 if open-ended wicks are desired.

In FIG. 6, another form of plush or velvet electrode material 10b is shown to comprise a fabric wherein the warp ends 12 are interlaced about the filling picks 13 with additional warp ends 12 extending generally rectilinearly through the weave. The pile yarn 14 is interlaced only with the upper set of filling picks 13 and may be formed around suitable cutting knives 17 which, in the final step of forming the material, are moved outwardly to sever the piles 16.

Alternatively electrodes similar to those shown in FIGS. 5 and 6 can be made in a single operation in which a yarn system comprises the base fiber and fiber introduced in sliver form extending outward from the base fiber comprise the pile. This process is sometimes referred to as sliver knitting.

As indicated briefly above, the invention includes the blending in of metallic, or metallic coated fibers or filaments. Thus, as shown in FIG. 8a, the yarns may comprise staple length metal fibers 18 blended with conventional staple length textile fibers 19 which may include material such as cotton, wool, glass or plastics or other polymerics which may provide required wicking or structural characteristics. As shown in FIG. 11, yarns may include non-metallic fibers 50 coated with a metallic surface 51.

If desired, the yarns may be formed of continuous metal filaments 20 as illustrated in FIG. 8b. In the preferred embodiment, the fibers 18 and filaments 20 are formed to have a rough, unmachined, unburnished, fracture-free outer surface 21, as shown in FIG. 4, to provide improved retention of the yarns, higher surface area and better conductivity between the pile yarns and the remainder of the electrode 10. Referring to FIGS. 1-3, one highly desirable method of forming such yarns is by providing a plurality of metal rods 22 in a suitable matrix 23 to define a composite 24 which is suitably constricted. As shown in FIG. 1, the composite may be constricted by drawing through a suitable die 25 to produce a reduced composite 26. The composite may be successively reduced as many times as desired until the composite is reduced to a small size wherein the rods 22 are of filamentary diameter. Thus, as shown in FIG. 2, the final composite 27 may be one having filaments 28 therein of an extremely small size, such as down to 50 microns or less. It has been found that such a process produces fine filaments down to one micron, or less, in continuous lengths, such small filaments providing improved flexibility and usefulness in the pile electrode material 10 as such fine wires permit the use of substantially conventional textile apparatus in forming fabrics utilizing such filaments and fibers formed therefrom. An excellent example of a method of forming such filaments and fibers is that disclosed in Roberts et al U.S. Pat. No. 3,394,213 issued July 23, 1968 for a Method of Forming Filaments, and owned by the assignee hereof, to which reference may be had for a detailed disclosure of such a method of forming the desirable rough, unmachined surfaced fibers having high surface areas.

As indicated above, the present invention comprehends providing the electrochemical electrode 10 with at least a portion of the yarns formed of such metallic filaments or fibers as spun yarns. Illustratively, an excellent electrochemical electrode 10 may be formed of such filaments or fibers, where the warp ends 12 and the filling picks 13 of the woven fabrics 11 are formed of nickel. The fibers may have a diameter of approximately 25 microns down to 1 micron or less. The pile yarns may incorporate such metallic filaments or fibers having a diameter similar to the diameter of the woven fabric yarns or smaller. Where the fibers are provided as staple length metal fibers, they may be blended with conventional textile fibers, such as cotton, wool, plastics, or glass, etc. The blend may be one wherein the metal fibers are present in the ratio of from less than 1 to 100 percent by weight in any, some or one of the

yarns, staples or slivers contained in the electrochemical electrode.

In forming such a spun, blended yarn, the yarn may be provided with twist as desired. A manufacturer's twist may be utilized to provide a highly satisfactory blended yarn for this purpose. The rough outer surface of the fibers provides an improved interlocked association of the metal fibers with the organic fibers.

To provide improved retention of the metal fibers in the pile electrode material 10, the metal fibers may be metallurgically bonded by a process such as sintering, brazing, or welding or alternatively they may be adhesively bonded. More specifically, an improved strong woven fabric 11 may be formed by sintering the woven warp and filling yarns to form an effectively bonded joint at the points of contact to serve as current collector. Similarly, other ordered materials as well as random web base fabrics 11 may be bonded to assure a desired distribution of the metal filaments or fibers. Suitable sacrificial materials include synthetic, plastic or organic material which will burn out during the sintering operation. Other methods of removing the sacrificial material, including chemical leaching and organic decomposition may be employed.

The sintering operation may be carried out in a conventional sintering apparatus, such as apparatus 29 shown in FIG. 9. As shown therein, it is preferred that the cutting of the pile yarns to define the plush or velvet surface 15 be performed prior to the sintering operation if cut pile yarns are desired.

As indicated above, the metal filaments may be made extremely small in diameter to provide desired flexibility and to provide blending characteristics in the yarn. Illustratively, the warp ends and filling picks may be formed from filaments 28 provided in tows, such as 8 micron 300 end, 12 micron 90 end, 12 micron 300 end, 25 micron 90 end, 4 micron 1,000 end, 2 micron 1,000 end, 4 micron 5,000 end, 2 micron 5,000 end tows, etc. Such tows preferably are provided with a suitable twist for facilitated weaving. The pile material, illustratively, may be formed of tows such as 2 micron 300, 1,000, 500, etc., end; 4 micron 300, 1,000, 5,000, etc., end; 8 micron 300, etc. end tows, which similarly may be provided with suitable twists, such as 2 to 5 turns per inch twists as desired.

As shown in FIG. 5, and as indicated briefly above, the filling picks 13 may be provided in spaced planar arrangements which are spaced apart at a preselected distance. The spacing as indicated may vary from approximately 0.020 inch to approximately 1/2 inch. The extension of the pile fibers from the base fabric may, illustratively, be approximately 0.010 to 8 inches as desired.

The metal material of the different yarns may be varied as desired. Where the pile yarns are the primary

locus of electrochemical activity, only they need be formed of a precious metal, such as platinum or gold, where the amount of precious material must be minimized. Materials for the remaining yarns may be selected to meet strength and conductivity requirements. Thus, different selections of the metallic materials may be made as desired by the user not only for mechanical properties considerations, but also for corrosion considerations, etc.

For ease in forming of the piles where the smaller diameter filaments or fibers are utilized, such as fibers 4 microns and smaller in diameter, it may be desirable to provide the yarn originally as an unleached composite in which the filaments or fibers are retained in a surrounding matrix body. The composite may be woven into the velvet as a yarn and upon completion of the weaving, the matrix material may be removed as by leaching to free the individual small diameter filaments or fibers in the form of a tow. Obviously, such a composite formation may be utilized in connection with the yarns or fibers of the fabric base as well as with the yarns of the pile portions of the velvet.

In FIG. 12, a schematic view of a fuel cell 100 incorporating electrodes 101 of this invention. The fuel cell 100 comprises an electrolyte 102, which may be an acid or base or a molten carbonate, a pair of gas manifolds 104 and 106 for fuel and oxidizer gases and a pair of electrodes 101 interfaced between the electrolyte 102 and the gas manifolds 104 and 106. As illustrated here, each electrode incorporates a woven fabric including warp ends 12 and filling picks 13 and pile yarn 14 interlocked with the fabric forming a pile surface projecting from one face of the fabric into the adjacent gas manifold. The pile yarn is at least partially metallic and can be either cut or uncut.

The foregoing disclosure of specific embodiments is illustrative of the broad inventive concepts of this invention which apply to other electrochemical systems such as batteries, reformers and the like.

We claim:

1. The process of making an electrochemical electrode comprising the steps of:

- a. forming the pile of a pile fabric with a composite metal wire, said wire comprising a plurality of metal filaments surrounded by a sacrificial metal matrix; and
- (b) removing the sacrificial metal matrix thereby providing the metal filament piles of the electrode.

2. The process of claim 1 wherein the pile is cut.

3. The process of claim 1 wherein the pile is plush.

4. The process of claim 1 wherein the pile is velvet like.

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