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(71)(72) Applicant and Inventor: DODGE, Cleveland, E. [US/US]; Quarry Hill Road, Pownal, VT 05261 (US).

(74) Agent: HANDAL, Anthony, H.; Handal & Morofsky, 80 Washington Street, Norwalk, CT 06854 (US).

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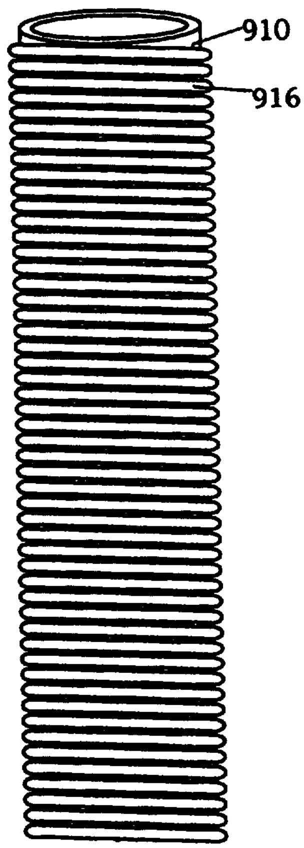
(57) Abstract

A lightweight hydrogen fuel cell assembly employing a wet perfluorosulfonic acid electrolytic membrane (918), prone to swelling, has a tubular shape (910) and inner (916) and outer (920) helically wound electrodes which assist compression of the electrolytic membrane (918) and provide novel and efficient current collection means. Disclosed embodiments include a self-contained portable fuel cell in which the cell is shaped to accommodate a canister of hydrogen fuel and an array of cells arranged around a common hydrogen fuel tank or canister.



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TUBULAR FUEL CELLS AND THEIR MANUFACTURE

TECHNICAL FIELD

The present invention relates to hydrogen power cells of the type which receive hydrogen or other gaseous combustible fuel and produce electricity electrochemically. More particularly, it relates to a wet-electrolyte type of fuel cell which can be rapidly initiated even at room temperature and is lightweight and portable.

BACKGROUND

Hydrogen fuel cells having a layered electrode structure in which a solid-phase proton-transporting electrolyte is sandwiched between a porous anodic electrode and a porous cathodic electrode, are known for example from Adlhart U. S. Patent No. 4,175,165. Such cells employ catalytic zones at the electrodes to disocciate hydrogen and oxygen molecules into the reactive atomic form. Cell efficiency is dependent upon continuous extensive surface contact at both electrode- electrolyte interfaces. Additionally, all-important safety considerations require that the cell be tightly sealed against leakage of potentially explosive gaseous fuels such as hydrogen. A problem with wet-electrolyte fuel cells is that swelling of the electrolyte caused by accumulating water can readily cause fuel leakage or impede generation efficiency, or both.

Adlhart discloses a fuel cell comprising a stack of grooved bipolar cell plates bolted together and secured with tension straps. Although quickly operational at room temperature, Adlhart's construction employs sturdy steel or alloy structural members resulting in a heavy and bulky construction designed to prevent fuel leakage. Adlhart's construction is cumbersome, expensive, hard to manufacture and does not provide an easily portable electricity source of substantial capacity.

In my U.S. Patent No. 5,336,570 dated August 9,1994, the disclosure of which is hereby incorporated herein by reference thereto, I disclosed a lightweight and portable hydrogen fuel cell of the proton-exchange membrane type which resists swelling of the membrane by clamping the membrane between two catalytic electrodes in a tubular or frusto-conical configuration, obtaining improved hydrogen sealing and breathability. Although this construction is significantly effective in achieving its design objectives, better engagement between the electrodes and the electrolytic membrane would be desirable. Also, there are difficulties in collecting generated currents without undue losses. With the need for high current output, and an operating voltage of only about 0.7 volts per cell, contact resistances and resistance encountered in the plane of the electrode by currents flowing in the electrode to a collection terminal or terminals at its periphery can generate significant losses. A solution to these problems of electrode-membrane engagement and current collection would be desirable. Further drawbacks of the constructions set forth in my U.S. Patent '570 relate to ease and cost of manufacture. It would furthermore be desirable to have a fuel cell of the type disclosed in my Patent '570 which was easier and less expensive to manufacture.

Described in more detail below in connection with Figures 1-2 of the drawings are two embodiments of fuel cell employing an externally wound filament of plastic-coated glass fiber to exert an evenly distributed clamping pressure on the electrodes. These embodiments were disclosed in my International PCT application No. WO 94/05051 published on 3 March 1994 as Figures 19 and 20 thereof, which International application was based on my U.S. patent application S.N. 08/015,411 which matured into the aforementioned U.S. Patent No. 5,336,570. They do not overcome the above-described current collection problems.

Wilson et al. in "High Performance Catalyzed Membranes of Ultra-Low Pt Loadings for Polymer Electrolyte Fuel Cells" J. Electrochem. Soc. vol. 139 No. 2 February 1992 disclose catalyst film and electrolytic membrane structures useful in the practice of this invention.

Vanderborgh et al. in a paper prepared for Belvoir Research, Development and Engineering Center, Fort Belvoir, VA entitled "ANALYSIS OF FUEL CELLS, REACTANT DELIVERY SYSTEMS, AND SYSTEM INTEGRATION FOR INDIVIDUAL POWER SOURCES", numbered "LA-UR-93-345" discuss and disclose ancillary systems and engineering, relating in particular to management of fluids such as coolant air, source gases and moisture, which teaching can also be useful when practicing certain embodiments of this invention.

SUMMARY OF THE INVENTION

In accordance with the invention, an easy to manufacture, light-weight fuel cell with structural current collectors that contact the cells electrodes over an extended area and promote engagement of the electrodes with the cell's electrolytic membrane, is provided. A method of manufacturing the fuel cell is also provided.

In one aspect the invention provides a wet-operating electrolyte, curved shape, oxygen-reduction fuel cell comprising gas-pervious, curved current-collecting electrodes shaped to mate one with another, gas-dissociating catalyst zones at each electrode and a proton transport electrolytic member constrained between the current collecting electrodes, the current-collecting electrodes are load-bearing structures acting to compress the electrolytic member characterized in that at least one of the electrodes includes a coiled winding acting to assist compress the electrolytic member.

Preferably, the fuel cell has a generally tubular shape with tubular components, each the electrode comprising concentric tubular coils, the electrolytic member being compressed between the tubular coil electrodes.

Preferably also, the fuel cell comprises a porous gas diffusion layer, one for each current collector, to spread gas permeating the current collectors for uniform delivery to catalyst layers adjacent the electrolytic member. The gas diffusion layers can comprise carbon black in a porous conductive binder.

In another aspect the invention provides a hydrogen fuel cell which is shaped to receive and embrace a hydrogen supply canister to provide a self-contained portable electricity generating unit. The fuel cell can include the hydrogen supply canister, the hydrogen supply canister having a volume and being received into the fuel cell to an extent of at least one half of that volume.

In another aspect, the invention provides a method of manufacturing a hydrogen fuel cell comprising a self-supporting shaped, layered electrode structure in which a solid-phase proton-transporting electrolyte is sandwiched between a porous anodic electrode and a porous cathodic electrode, the method comprising the steps of

a) coating a first, shaped self-supporting electrode with a curable, liquid-phase, proton-transporting electrolytic material to provide an electrolytic coating;

b) curing the electrolytic coating to the solid phase;

c) assembling the coated electrode with a second, mating, shaped electrode to provide the layered structure;

d) and assembling the electrode structure with a support base.

Preferably, the method comprises a further step of coating the first electrode with a catalyst-containing curable, liquid-phase proton-transporting material. In a preferred embodiment, the curing step has two stages: a first, solvent-evaporation stage at a moderately elevated temperature, and a second purification or decontamination stage at a higher temperature.

The invention also provides a method of manufacturing a such a fuel cell comprising the steps of:

a) forming a first gas-pervious, load bearing, current collecting electrode to a first shape;

b) forming a second gas-pervious, load bearing, current collecting electrode to a second shape mateable with the first shape; and

c) assembling the first and second current-collecting electrodes with the electrolytic member into a self-supporting structure;

wherein each electrode comprises an open-work load-bearing metal structure, formed for example of titanium. Preferabaly, the metal structure is selected from the group consisting of a coiled winding, expanded metal and metal braiding.

Preferably, one or more of the fuel cell components is shaped around a former and the method can comprise inserting plugs at the ends of the fuel cell to seal the fuel cell against loss of combustible gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a cross-sectional view of an embodiment of hollow tubular fuel cell according to the prior art, which fuel cell employs an external filament winding and internal support member;

Figure 2 is a side elevation of another embodiemtn of fuel cell according to the prior art, in which a stacked flat plate fuel cell assembly is wound with an external filament;

Figure 3(a) is a perspective view of a first hollow member in accordance with another embodiment of the inventive hydrogen fuel cell;

Figure 3(b) is a cross-sectional view of the first hollow member shown in Figure 3(a);

Figure 4(a) is a perspective view showing a first conductive winding wound around the first hollow member shown in Figure 3(a);

Figure 4(b) is a cross-sectional view of the first hollow member and the first conductive winding shown in Figure 4(a);

Figure 5(a) is a perspective view showing an electrolyte member disposed around the first conductive winding;

Figure 5(b) is a cross-sectional view of the electrolyte member, the first conductive winding and the first hollow member shown in Figure 5(a);

Figure 6(a) is a perspective view showing a second conductive winding wrapped around the electrolyte member;

Figure 6(b) is a cross-sectional view of the second conductive winding, the electrolyte member, the first conductive winding and the first hollow member shown in Figure 6(a);

Figure 7(a) is a perspective view showing a second hollow member disposed around the second conductive winding;

Figure 7(b) is a cross-sectional view showing the second hollow member, the second conductive winding, the electrolyte member, the first conductive winding and the first hollow member shown in Figure 7(a);

Figure 8(a) is a cross-sectional view showing male and female end caps prior to installation on the inventive hydrogen fuel cell;

Figure 8(b) is a cross-sectional view of a male end cap modified for series connection;

Figure 9 is a cross-sectional view showing two joined adjacent hydrogen fuel cells;

Figure 10 is an isolated enlarged view schematically showing the first conductive winding, the electrolyte member and the second conductive winding;

Figure 10(a) is a perspective view of a modified conductive winding;

Figure 11 is a cross-sectional view showing male and female end caps prior to installation in accordance with an alternate construction;

Figure 12(a) is a top plan view of a multiple fuel cell assembly in accordance with another aspect of the present invention;

Figure 12(b) is a bottom plan view of the multiple fuel cell assembly shown in Figure 12(a);

Figure 12(c) is a view similar to Figure 12(a) of another embodiment of fuel cell assembly;

Figure 12(d) is a view similar to Figure 12(c) of the fuel cell assembly of Figure 12(c);

Figure 13(a) is an isolated side plan view showing the fuel cells of the multiple fuel cell assembly shown in Figure 12(a);

Figure 13(b) is an isolated side plan view showing a hydrogen gas supply tank of the multiple fuel cell assembly shown in Figure 12(a);

Figure 13(c) is a schematic view similar to Figure 13(a) of a multiple fuel cell assembly equipped with fluid flow management means;

Figure 14 is a vertical cross-sectional view of a portable hydrogen fuel cell designed to accommodate its own hydrogen supply in the form of a quick release hydrogen bottle;

Figure 15(a) is a schematic sectional views of a further embodiment of tapered tubular fuel cell;

Figure 15(b) is a schematic view of an inner housing component of the fuel cell shown in Figure 15(a);

Figure 15(c) is a schematic view of an outer housing component of the fuel cell shown in Figure 15(a);

Figure 15(d) is a similar view of the fuel cell of Figure 15(a) after application of seals to the ends of the cell;

Figure 15(e) is an alternative embodiment of electrode diffusion tube for use in the fuel cell assembly of Figure 15(a); and

Figure 15(f) is an enlarged partial sectional view of the layered wall structure of the fuel cell of Figure 15(a).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the invention comprise a hydrogen powered electricity generating cell incorporating a plurality of layers shaped laminar members each having relatively small thickness and an extensive active area of, for example, approximately 75 square centimeters, in the case of a tubular cell about 10 cm. long and averaging about 7.5 cm. diameter. Such a cell can generate approximately three watts of electricity at approximately 0.7 volts.

Referring to the prior art embodiment of Figure 1, an inner anode 814 and an outer cathode 818 have sandwiched between them an electrolytic member 816, these members being formed of materials such as those having the characteristics described elsewhere herein. This composite tubular fuel cell assembly is supported in end caps 822 and 824 each of which is internally threaded at 832 for connection of a hydrogen supply which can be passed from one cell to the next.

Within tubular anode 814 is a tubular, porous support tube 840 which is rigid and has sufficient strength to bear the clamping pressure provided by external tightly wound filament 842. The presence of porous tube 840 is optional depending upon the structural strength of the anode 814 and of cathode 818. Porous tube 840 can be constructed of any suitable material, for example, it can be formed of rigid paper or ceramic, or may constitute a self-supporting screen of a rigid plastic material. Although, a metallic screen could be used, from a mechanical point of view it is preferred to avoid the use of metals in contact with hydrogen, where possible. Other structures, such as cross-members or bracing can also provide the support functions of porous tube 840. Porous tube 840 is also accommodated within end caps 822 and 824 and the whole tubular assembly is tightly sealed into end caps 822, 824 against hydrogen leakage by an insulating plastic sealant 844. Electrical connections are shown schematically at 846.

The purpose of the external wound filament 842 is to exert an evenly distributed clamping pressure on cathode member 818 to hold anode 814 and cathode 818 in tight, intimate engagement with electrolytic member 816 and to withstand swelling of electrolytic member 816 caused by generation of water therein. Accordingly, the material employed for filament 842 should be of relative high tensile strength and it should also be resistant to the corrosion that can occur in a damp, warm or even hot oxidizing atmosphere. Accordingly, metal wires are not ideal and, if used should be plastic coated. A preferred material is a plastic-coated, glass fiber filament, for example a TEFLON (DuPont's trademark for polytetrafluoroethylene)-coated, glass-fiber sewing thread. This filament has good tensile strength, is highly resistant to corrosion or other chemical attack, even at elevated temperatures, and the use of TEFLON gives it a hydrophobic, water-shedding character, facilitating the discharge of water from the fuel cell.

Filament 842 is wound with a pitch providing spacing between individual windings for the access of oxygen to the cathode, and for egress of water, or water vapor, therefrom. Preferably, this pitch is such that the spacing is between half and twice the thickness of an individual winding, with cross-layering of multiple windings being possible, so long as adequate gas-access and water release is provided.

Fuel cells such as that depicted in Figure 1 can be assembled by winding flexible woven carbon cloth sheets around a rigid porous plastic tube with a film of NAFION (trademark) electrolyte inserted between the carbon cloth layer which will provide the fuel cell's cathode 818 and, if necessary, the composite tubular assembly is then cut to length, and sealed into end caps 822, 824.

In a modified prior art embodiment, a wound casing material, such as the TEFLON-coated, glass fiber filament referred to hereinabove, to hold electrode members in intimate contact with an electrolyte can be extended to a stacked plate, fuel cell assembly in which multiple flat layered cells lie one on top of another as disclosed, for example in Aldhart and as shown in Figure 2 In the embodiment of Figure 2, flat laminar fuel cell assemblies 860, each comprising a proton exchange membrane sandwiched between cathodic and anodic electrodes are interspersed between gas-distribution plates 862. External filament windings 864 (shown with exaggerated spacing for clarity) can be tightened around the assembly, optionally in multiple layers, which may be wound with opposing pitch angles to traverse one another, provided that sufficient openings remain for adequate air or oxygen access to the distribution plates 862.

Though providing useful advances in the art, these filament wound embodiments of fuel cell suffer still have a number of drawbacks. Both embodiments are unduly complex to manufacture. The tubular embodiment of Figure 1 can be lightwieght and portable but is subject to current collection difficulties owing to the necessity of passing current through end connectors, while the Figure 2 embodiment suffers all the drawbacks of weight and expense inherent in stacked plate fuel cell assemblies. These problems are solved by the present invention, some embodiments of which are illustrated in Figures 3-15.

One embodiment of the inventive hydrogen fuel cell is shown in Figures 3(a) through 11. Referring to Figure 3(a), in accordance with this embodiment of the hydrogen fuel cell, a first hollow member 910 is provided defining an interior space and having a peripheral surface. The first hollow member 910 receives a hydrogen containing gas and has a construction effective for passing the hydrogen containing gas from the interior space to the peripheral surface. The first hollow member 910 may comprise a porous tube, in which case the hydrogen containing gas passes through the pores in the porous tube from the interior space to the peripheral surface.

Alternatively, as shown in Figures 3(a), 3(b), the first hollow member 910 may comprise a hollow tube having through-holes 912 for passing the hydrogen containing gas from the interior space to the peripheral surface. Grooves 914 can be disposed on the peripheral surface in communication with the through-holes 912 for facilitating dispersal of the hydrogen containing gas.

As shown in Figures 4(a) and 4(b), a first conductive winding 916 is wound around the peripheral surface of the first hollow member 910 to form an anode. The first conductive winding 916 includes a catalyst effective for decomposing hydrogen molecules in the hydrogen containing gas into active atomic hydrogen. The first conductive winding 916 may be made from titanium wire having a platinum coating or a platinum plating. The first conductive winding 916 forms an anode of the hydrogen fuel cell.

As shown in Figures 5(a) and 5(b), a proton-exchange electrolyte member 918 is disposed around the first conductive winding 916 to transport protons. The electrolyte member 918 preferably comprises a NAFION (trademark) perfluorosulforic acid polymer (also called an ionomer) film tube which is shrunk around the first conductive winding 916 so that the anode of the hydrogen fuel cell is in intimate contact with the electrolyte member 918. Such shrink-fitting can be effected by using the marked ability of NAFION (trademark) polymer membrane to swell when wetted. A wet polymer sleeve electrolyte member 918 is fitted over a first conductive winding 918 sized to be a close fit when the electrolyte member is wet. Thus enveloping first conductive winding 916, electrolyte member 918 is dried to shrink it tightly on to first conductive winding 916, in a state of considerable tension.

As shown in Figures 6(a) and 6(b), a cathode is formed by winding a second conductive winding 920 around the electrolyte member 918. The second conductive winding 920 also has catalytic properties effective for decomposing oxygen molecules in an oxygen containing gas into active oxygen atoms. The second conductive winding 920 may comprise a titanium wire having a platinum coating or a platinum plating. As is well known in the catalyst arts, rare metal catalyst such as platinum, palladium or their equivalents are more effective in a finely divided state. The present invention also contemplates provision of such finely divided catalyst, preferably more or less evenly distributed, across the gas-permeating outer surfaces of electrolyte member 918. While such catalytic means may be integral with the windings 916 and 920, for example as the above-described coating, it may alternatively be separately introduced into the interstices of the windings 916 and 920. After the cathode is formed by winding a second conductive winding 920 around the electrolyte member 918, the electrolyte member 918 is expanded (such as by swelling due to the addition of water to the electrolyte member 918).

Referring to Figures 7(a) and 7(b), a second hollow member 922 is provided for containing the first hollow member 910, the anode (first conductive winding 916), the electrolyte member 918 and the cathode (second conductive winding 920). The second hollow member 922 receives the oxygen containing gas, which may be ambient air, air enriched with O_2, or pure O_2, or the like.

As shown in Figure 8, a male end cap 924 and a female end cap 926 are provided for sealing the inventive hydrogen fuel cell. The ends of the anode and the cathode (first conductive winding 916 and second conductive winding 920) terminate in wire ends 928 which are received into connection ports 930 of the male end cap 924 and the female end cap 926. The connection ports 930 of the male end cap 924 provide electrical connection between the wire ends 928 of the anode and cathode and respective electrical connection terminals 932. The connection ports 930 of the female end cap 926 provide electrical connection between the wire ends 928 of the anode and the cathode, and include respective electrical connection sockets 934. The electrical connection sockets 934 can receive the electrical connection terminals 932 of the male end cap 924 of another hydrogen fuel cell when connected (as shown in Figure 9), if end-to-end fuel cell connection is desired. Alternatively sockets 934 and terminals 932 may be capped or may be plugged to a connector block or strip, or the like, designed to accommodate multiple such cells.

Hydrogen gas is introduced through a hydrogen gas port 936 of the male end cap 924 and enters into the interior space of the first hollow member 910. The hydrogen port 936 of the male end cap 924 terminates at a male fitting 938 which is received by a female receptacle 940 of the hydrogen port 936 of the female end cap 926. Oxygen containing gas is introduced into the inventive hydrogen fuel cell through an oxygen port 942 on the male and female end caps 924, 926. The oxygen port 942 on the male end cap 924 terminates in an oxygen port fitting 944 which is received by a female receptacle 946 of the female end cap 926.

The modified male end cap 924 shown in Figure 8(b) provides for series connection between fuel cells by reversing the polarity of connection terminals 932 versus connection ports 930 with a crossover 933. Crossover 933 connects a radially inner connection port 930, mating with a negative polarity wire 928 on one cell, to a radially outer connection terminal 932, mating with a positive polarity connection socket 934 on an adjacent cell. Series connection will usually be desirable for higher voltage output, since fuel cells according to the invention can generate very substantial currents but yield only modest individual voltages, perhaps 0.6 or 0.7 volts.

As shown in Figure 9, the interfittability of the end caps, coupled with the fact that all joints to be sealed against hydrogen leakage are at the opposed ends of each cell enables the cells to be assembled end-to-end in modular fashion. When two hydrogen fuel cells are thus joined together, the male end cap 924 of the first hydrogen fuel cell mates with the female end cap 926 of the second hydrogen fuel cell so that the anode and cathode connection terminals 932 plug into the respective connection sockets 934 of the female end cap 926 for electrical connection between the anode and cathode of the respective hydrogen fuel cells.

The male fitting 938 of the male end cap 924 is received by the female receptacle 940 of the female end cap 926, and the oxygen port fitting 944 of the male end cap 924 is received by the female receptacle 946 of the female end cap 926 thus joining the first hydrogen fuel cell to the second hydrogen fuel cell. Multiple hydrogen fuel cells may be connected in a similar manner. The hydrogen fuel cells may then be clamped together or otherwise secured (not shown). Joints between adjacent cells can readily sealed with a suitable polymeric sealant. Because of the configuration of the inventive fuel cell, expansion of electrolytic member 918, as it absorbs by-product water, does not subject the cell's seals to separating forces.

As shown in Figure 10, the first conductive winding 916 (anode) is in close intimate contact with the NAFION (trademark) electrolyte member 918. Also, the second conductive winding 920 (cathode) is in close intimate contact with the NAFION (trademark) electrolyte member 918. During operation of the inventive hydrogen fuel cell, hydrogen gas is supplied to the interior space of the first hollow member 910 and passes through the first hollow member 910 to the peripheral surface thereof. Hydrogen molecules here come in contact with the platinum catalyst 949 coated on the first conductive winding 916 and decompose into hydrogen atoms which then have their electrons stripped, resulting in the formation of protons which are transported through the NAFION (trademark) electrolyte member 918 to the cathode constituted by the second conductive winding 920. Oxygen containing gas introduced into the second hollow member 922 comes into contact with the platinum catalyst 949 coated on the second conductive winding 920. The oxygen molecules are broken down into oxygen atoms that accept electrons while reacting with protons reaching the cathode side of the electrolyte member, and thus form water. During the operation of the inventive hydrogen fuel cell, electrons are driven to flow in the opposite direction to proton travel providing an electrical current, thereby enabling productive use of the energy released through the operation of the inventive hydrogen fuel cell.

Figure 10 further shows, in a schematic way, how electrolytic member 918 expands as it becomes wet in use to fill the spaces between windings 916 and 920 and to become tightly packed therebetween. This arrangement, as will be apparent from considering Figure 10, provides some means for taking up the expansion of electrolytic member 918 as it absorbs moisture without imposing disruptive forces on the cell structure that might, in other constructions, separate cell elements causing gas leakage.

Arrow 962 in Figure 10, shows a direction of hydrogen access to the electrolytic member 918 between two windings 916 which, if necessary for gas access, can be spaced apart, with a maximum spacing between windings 916 or 920 of about one quarter the diameter of an individual winding. However, for a gas with the migratory powers of hydrogen, the combination of a normal tight-packing of windings 916 and a modest gas pressure of a few pounds per square inch can be adequate to permit hydrogen to access the electrolytic member 918.

Similarly, oxygen can be supplied in the form of compressed air in the direction of arrow 960, using somewhat higher pressures of about 10 to 20 psig. With the structure shown, in order to gain access to the electrolytic member 918 the gases must pass through a closely confining channel between individual windings 916 and 920 where they are exposed to the catalyzing action of surface coating 949 on windings 916 and 920, over an extended area, thus enhancing dissociation into atomic hydrogen or oxygen.

Figure 10(a) shows an alternative construction of fuel cell having windings 916 or 920 designed further to enhance catalytic activity. Here, windings 916 or 920 have a square or rectangular cross-section further to increase the extent of the channel through which the migrating gases travel to access electrolytic member 918. In addition the windings are subjected to surface treatment to increase the surface area of catalyst. The surface treatment can be any one of various forms of mechanical actions effected for example with a diamond die, such as roughening, scoring or grooving. In Figure 10(a) transverse angled grooves are shown which serve to maintain a gas access passage between a gas windings while extending the distance traveled by gases passing over the catalyst surface to improve the catalytic action. Surface roughening or other surface configurations can be employed in place of the grooving.

Because fuel cells of the type disclosed herein develop rather modest voltages of about 0.6 or 0.7 volts, it is important that withdrawal of current from the cell be effected with a very low impedance current collection system. The novel winding structures disclosed herein facilitate very low resistance current collection and contact between adjacent roughened windings 916 as shown in Figure 10(a), is a further safeguard, helping keep resistances low. By employing catalyst-coated windings, as disclosed herein, the invention ensures that there is a catalytical active zone physically outside the boundaries of the electrolytic member 918, the wet environment of which may tend to clog or smother the activity of conventional deposits or surface coatings of finely divided catalyst particles on the membrane itself. Clearly some catalytic activity may occur on the outer surfaces of winding 916 and 920 remote from electrolytic member 918 in a pre-reactivation process, or effecting dissociation of at least a small percentage of molecules before the membrane 918 is encountered.

Figure 11 shows an alternative construction of the inventive hydrogen fuel cell. In this case, the male end cap has a threaded male fitting 938 that screws into a threaded female receptacle 940 of the female end cap 426 of another similarly constructed hydrogen fuel cell. The wire ends 928 of the anode and cathode exit through the second hollow member 922. The oxygen port fitting 944 is threaded for connection with an oxygen gas supply hose (not shown). The oxygen port fitting 944 is disposed on the second hollow member 922, so that the threaded male fitting 938 of a first hydrogen fuel cell can be screwed into the threaded female receptacle 940 of a second hydrogen fuel cell. Multiple hydrogen fuel cells can be easily connected together in this manner.

Figures 12(a) through 13(b) show a multiple fuel cell assembly in accordance with another aspect of the present invention. The multiple fuel cell assembly allows a number of individual fuel cells (such as those having a construction as described herein) to share a single replaceable hydrogen gas supply tank. Figures 12(a) and 12(b) are a top plan view and a bottom plan view, respectively, of the multiple fuel cell assembly. Figure 13(a) is a side plan view of an individual fuel cell 950, and Figure 13(b) is a side plan view of the replaceable hydrogen gas supply tank. A plurality of individual fuel cells 948 is disposed around a central hydrogen gas supply tank 950. Hydrogen gas is received by each individual fuel cell 948 through a corresponding gas supply line 952. The hydrogen gas supply tank 950 has a screw fitting 958 (shown in Figure 13(b)) that is screwed into a distribution cap 956. During operation, hydrogen gas from the hydrogen gas supply tank 950 is distributed to each individual fuel cell 948. The individual fuel cells 948 are contained within common containing walls 954, between which oxygen containing gas flows for use by the fuel cells 948 in the generation of electricity. Alternatively, each individual fuel cell 948 may be contained within a corresponding containing structure, or open to the ambient air. The individual fuel cells 948 can be dimensioned to accommodate a standard gas cylinder, thus obviating the need for a specially manufactured hydrogen supply tank. The structure shown in which fuel cells 948 surround or enclose a hydrogen canister 950 permit transfer of heat from cells 948 to canister 950. This heat can be utilized to cause hydrogen to flow, or to increase the hydrogen flow from supply tank 950 and is particularly beneficial in maintaining hydrogen flow from a hydride hydrogen source, especially under low temperature ambient conditions.

As an example, a configuration of the multiple fuel cell assembly may include 16 individual fuel cells 948 each having a diameter of four inches and a length of 24 inches for an electricity producing active area of about two square feet per cell. The total electricity producing active area in this example configuration is thus 32 square feet. The hydrogen gas supply tank 950 may have a volume of 2.5 cubic feet. The containing walls 954 define a space having an inner diameter of about 22 inches and an outer diameter of about 32 inches so that the overall size of this example of a multiple fuel cell assembly has a 32-inch diameter and a 24-inch length. It is estimated that such an assembly may, when operated at high or optimal efficiency, provide in excess of 10,000 watts of power.

Figures 12(c) and 12(d) show an alternative hydrogen delivery distribution system in which fuel cells 948 are connected in series so that hydrogen can be supplied from one to another down a pressure gradient. Here two radial hydrogen supply lines 970 extend from supply tank 950 to adjacent cells 948. Cells 948 are series interconnected top and bottom, in staggered manner, by links 972, alternately at the tops and bottoms of adjacent pairs of cells so that hydrogen passes up one cell and down the next. As shown here, hydrogen is fed from both ends of the series of cells 948, in two pressure gradients. If a single gradient is preferred, hydrogen may be fed to one end only through a single radial supply line 970.

Fluid Management

If desired, supplemental water, heat and gas circulation systems can be provided to service individual ones of the cells described herein, or preferably to service an array of such cells when assembled into a high power, light weight battery. A preferred such system, used to withdraw by-product moisture or water from the cell which can comprise a fan and recirculating means to withdraw air or oxygen from the cathode side of the cell. Preferred embodiments recirculate, or simply circulate, either air under fan pressure or compressed air in an enclosed system. Where feasible, subject to the intended operating environment of the fuel cell, a few atmospheres of compressed air may be desirable to improve cell efficiency.

A desirable or required operating condition of the type of fuel cell described herein, when employing a wet-operating membrane, is that the anode, hydrogen-receiving side of the cell be kept moist. Often moisture is entrained in the hydrogen flow at the hydrogen source, especially if a hydride source is used. However, supplemental moisturizing of the hydrogen flow may be desirable and water for this purpose can be recovered from the cathode ventilating means described above.

Such fluid handling systems can be incorporated in a cell bank in the manner shown schematically in Figure 13(c). A cathode-side air or water pump 980 moves air over the cathodes of a bank of cells 948 withdrawing moisture or water therefrom, and cooling them. Output of pump 980 passes to a water extractor 982 where water is separated and passes to anode humidifier 984. Dried air from water extractor 982 can be recirculated. Hydrogen pump 986 moves hydrogen through anode humidifier 984 to moisten it and delivers hydrogen to the anodes. With adequate air circulation, cooling is not necessary, but if desired, a heat extractor can be included in the air-water circuit.

<u>Self-contained, renewable power source</u>

Referring to Figure 14, a fuel cell such as that shown in Fig. 13 can be adapted to become a self-contained, renewable power source by receiving a screw-in hydrogen cylinder 990 into the cell, to be substantially contained therewithin. As shown, end plug 522 is modified to receive a cylinder 990 as a close fit, while end cap 520 is supplied with a screw fitting 992 to receive the hydrogen cylinder 990's nozzle 994. An interior liner 996 defines an annular hydrogen chamber 998 which admits nozzle 994 through a snap valve 999.

<u>Manufacture of Figures 3(a) through 11 embodiments</u>

The hydrogen fuel cell shown in Figures 3(a) through 11 can be easily manufactured utilizing methods such, for example, as the inventive manufacturing methods described herein which are adaptable to high volume mass manufacturing techniques. A first hollow member 910 is provided defining an interior space and having a peripheral surface. The first hollow member 910 is for receiving a hydrogen containing gas and is effective for passing the hydrogen containing gas from the interior space to the peripheral surface (Figure 3(a)). A first conductive winding 916 is wound around the first hollow member 910 to form an anode (Figure 4(a)). The first conductive winding 910 has a catalyst effective for decomposing hydrogen molecules from the hydrogen containing gas into H^+ ions (Figure 10). An electrolyte member 918 is disposed around the anode. Preferably, the electrolyte member 918 comprises a tube of NAFION (trademark) film which is shrunk around the first conductive winding 916 (Figure 5(a)). A second conductive winding 920 is wound around the electrolyte member 918 to form a cathode. The second conductive winding 920 has a catalyst effective for decomposing oxygen molecules in an oxygen containing gas into oxygen atoms. After the second conductive winding 920 is wound around the electrolyte member 918, the NAFION (trademark) film electrolyte member 918 is expanded by introducing water to swell the NAFION (trademark) film [Figure 6(a)]. A second hollow member 922 is disposed loosely around the second conductive winding 920 for containing the first hollow member 910, the anode (first conductive winding 916), the electrolyte member 918 and the cathode (second conductive winding 920). The second hollow member 922 receives the oxygen containing gas which is then decomposed by the catalyst formed on the second conductive winding 920 [Figure 7(a)]. Finally, a male end cap 924 and a female end cap 926 are installed to complete the hydrogen fuel cell (Figure 26). A plurality of thus formed hydrogen fuel cells are joined together by mating the male end cap 924 of a first hydrogen fuel cell with the female end cap 926 of a second hydrogen fuel cell (Figure 9 and Figure 11).

<u>Some uses and advantages</u>

Their self-contained, free-standing structure affords the tubular fuel cells of the invention many options for packing or assembling into batteries or arrays that are not possible with a fuel cell stack. In one example of a simple, practical array, useful for a field soldier, or other field operative, three tubular cells, each 2 inches (about 5 cm.) in diameter and 7 inches (about 18 cm.) in length can be mounted vertically onto a 9 inch (about 23 cm.) wide belt wrapped around a solider's waist. These three light-weight cells, preferably each weighing less than one pound (453 gm.), each contain about 30 square inches (193 sq. cm.) of active surface. Referencing the data reported in Figure 1 of Wilson et al., supra, page 16, a theoretical output of 1.5 amps/cm^2 at 0.6 volts is obtainable. Accordingly, if constructed as taught by Wilson et al., such a package of three cells will produce 520 watts, a margin of power of almost two over a current U.S. Army specification for portable electric power sources for soldiers of the future.

The tubular cells of this invention overcome problems caused by the high coefficient of dry-to-wet expansion of NAFION polymer, primarily through the radial strength of extremely light weight carbon fiber sleeves having, in the fibers, tensile strength greater than steel. Moisture-absorbing electrolyte expansion exerts very little pressure on the seals of tubular cells, which as taught herein, are located at the joints at the ends of the cells. Importantly, in contrast to the multiple laminations that must be sealed and gasketed in stacked flat cells, there are only two seals to be made in each tubular cell, at the cell ends around the substantially circular ends of its multiple concentric tubular members. Structural stability is enhanced by using wound electrode members the windings of which can advantageously be heavy gauge conductor wire rated to remove the large currents generated with a minimum of impedance losses. The heavier the gauge, the greater the structural strength. Suitable end seals can be made through the use of cast resin in relatively large cross-sections or even by pressure molding plastic polymer to the ends of each cell.

Unlike compressed flat cell stacks, tubular fuel cells can also be spatially separated, reducing heat build up and thermal management requirements. Water management requirements are also reduced because air can be circulated over substantially the entire cathode area to move water continuously away from it, using natural or forced convection.

Referring now to the embodiment of Figs. 15(a)-(f) there is shown a composite structure of fuel cell having a tapered tubular configuration with a taper along the tube which is here selected to be of the order of 1%. This cell incorporates many of the features of the foregoing embodiments, in combination.

The interfitting, nested, tapered shape of each tubular, sleeve-like cell members facilitates tight assembly of the various cell layers into intimate contact, each with its neighbor, so each electrolyte surfaces is pressed into intimate contact with a respective electrode throughout the electrode area, with a minimum of zones of poor, or unconstrained contact. The taper translates lengthwise stresses, imposed during manufacturing into lateral or radial compressive forces packing the nested layers together and permits lengthwise assembly of closely dimensioned interfitting layers.

The embodiment shown in Figs. 15(a)-(f) preferably employs inner and outer tapered-helix wound current collectors of sufficiently robust construction to constitute load-bearing formers. Also of note is the use of separately fabricated catalyst layers pressed onto either side of an electrolytic proton exchange membrane, sandwiching it, and the use of separately fabricated gas diffusion layers or members to manage distribution of oxygen and hydrogen to the catalyst and membrane layers.

The multi-layer construction of the cell is most readily apparent from the enlarged sectional view of Figure 15(f).

A polymer exchange membrane electrolytic member 1110 is disposed as a central layer. Reading down Figure 15(f), from electrolytic member 1110, in a direction inwardly toward the center of the fuel cell, the layers comprise anodic catalyst layer 1112, anode gas diffusion layer 1114, an anode collection layer 1116 and an optional inner housing member 1118.

Reading upwardly from electrolytic member 1110, in a direction outwardly, of the fuel cell, there is a cathodic catalytic layer 1120, a cathode diffusion layer 1122, a cathode collector 1124 and an oxygen supply passage 1126, the latter being defined in an outer housing member 1128.

Catalyst layers 1112 and 1120 are porous so as to be freely gas-pervious and support a finely divided catalyst, such as platinum in a conductive medium, for example carbon black. Cathode catalyst layer 1120 also exhibits substantial water vapor porosity for the removal of water vapor from the cathode side of the cell. The porous conductive catalyst layers 1112 and 1120 are preferably thin coatings and provide a distinct gas-dissociation stage in intimate contact with electrochemically active electrolytic member 1110 to ionize the dissociated atoms promptly before they recombine into molecules. Catalyst layers 1112 and 1120 are fine-pored and have a very high effective surface area to divide the gas flow into fine microscopic or sub-microscopic streams, and to ensure that a high proportion of gas molecules contacts the catalyst surfaces to be dissociated into atoms. The surfaces of catalyst layers 1112 and 1120 may be thought of as intermeshing with that of electrolytic member 1110 to increase the apparent surface area.

Currently preferred embodiments of the invention, employing the preferred materials recited herein, have a thickness in the range of about 0.002 to 0.007 inch, with an ultra-thin catalyst layer coating of the order of one millionth of an inch.

Gas diffusion layers 1114 and 1122 serve laterally to spread the flow of gases migrating to the interior electrolytic layers of the cell from between the windings of current collector layers 1126 and 1124, permitting a better distribution of gas over the whole surface area of the cells or of the boundaries between the active layers. Each current collector 1116 and 1124 and its associated diffusion layer 1114 or 1122, can be regarded as constituting a corresponding cell electrode, collector 1116 and diffusion layer 1114 constituting the anode, while collector 1124 and diffusion layer 1122 constitute the cathode.

Desirably, electrolytic member 1110 extends beyond the hydrogen-distributing anodic layers 1112 and 1114, for hydrogen leak prevention. As shown in Fig. 15(d), end plugs 1132-1134, which may be prefabricated, but are preferably cast in situ from a non-conductive, hydrogen sealing resin or polymer, close the ends of the cell and provide hydrogen seals. Preferably the ends at least of electrolytic member 1110, anode catalyst layer 1112 and anode gas diffusion layer 1114 are embedded in the end plugs 1132 and 1134.

Current collectors 1116 and 1124 comprise open-form, or foraminated, structural conductive members, here shown as wire windings 1117 and 1125 respectively, each embedded in a conductive, gas-porous, structural matrix 1119 and 1127, respectively.

Windings 1117 and 1125 can be of any conductive material that has adequate tensile strength, load-bearing rigidity and can withstand the corrosive environment within the fuel cell. Metals such as titanium are preferred. A still more preferred winding 1117 and 1125 has a more complex structure and comprises titanium-clad copper wire which can be formed by drawing coaxial tubes of the two metals. Such a coated winding can have its titanium ends bared externally of the electrolyte environment to form copper connectors which are preferable for outputting large currents at low voltages. Depending upon the cell's rating, windings 1117 and 1125 may be quite heavy gauge, up to perhaps one-sixteenth or one-eighth of an inch diameter. Besides windings, other forms of open-work, conductive former can be provided in tubular form, for example, braided or mesh or perforate structures or expanded metal such as expanded titanium available under the trademark DELKER.

With a view to reducing cell impedance, windings 1117 and 1125 may be in the form of coiled-coil filaments employing a fine gauge wire filament coiled to provide the winding, which coiled filament winding is coiled again around the fuel cell. Such a structure is intended to bring more current-collecting wire surface into closer contact with the surface of the electrolytic member 1110.

Matrices 1119 and 1127 are preferably carbon black or other finely divided conductive material dispersed in a structural binder such as a substantially rigid porous resin or ionomer which is preferably hydrophilic to be conductive. Desirably, also a finely divided hydrophobic material such as polytetrafluoroethylene, for example, TEFLON (trademark, DuPont) is included in the matrix to shed water, especially on the cathode side of the cell. The matrix-embedded winding structure of current collectors 1116 and 1124 is lightweight yet has exceptional strength to contain expansion of electrolytic member 1110 and press the cell's electrodes into intimate engagement with it.

While described and shown as separate structural elements, modified embodiments of the invention are contemplated in which current collectors 1116 or 1124 are integral with diffusion layers 1114 or 1122, for example as shown schematically in Figure 15(e).

Optional inner housing member 1118 can provide structural support, if desired, for example, for a smaller embodiment of cell with a lower current rating having a smaller gauge, less robust winding 1116. Inner housing member 1118 can also optionally be adapted to provide other functions, such as hydrogen delivery enhancement.

One form of hydrogen delivery enhancement structure is embodied in grooves 1136 which constitute one or more continuous (tapered) helices delivering hydrogen to anode current collector 1116. Preferably, hydrogen is delivered to the electrolytic member 1118 so far as possible, along a substantial pressure gradient, with the hydrogen moving in one direction through confined passageways so as to keep it moving and avoid stills or stagnancies that may impede cell performance.

Manufacture of tubular cells with wound electrodes

A tubular cell having wound electrodes such as the tapered tubular cell shown in Figs. 33 (a)-(f), can be manufactured by the following method which is readily adaptable to mass production. A tapered steel mandrel is coated on its outer surface with a release agent such as a polytetrafluoroethylene or a silicone. Over this surface is coated a slurry of finely divided platinum particles mixed with carbon black in an organic solvent dispersant. The slurry coating is dried and baked to form a sleeve on the release surface of the conical mandrel, anode diffusion layer 1114.

A tube of NAFION polymer is immersed in water to cause it to swell. It is then placed over the coated mandrel and dried so that it shrinks tightly over the mandrel, forming electrolytic member 1110.

Two half-tube metal molds, dimensioned to fit electrolytic member 1110, are coated with release agent then with a platinum-carbon dispersion, as described above, and baked into place to form cathode diffusion layer 1122. The hot tubes and coating are pressed lengthwise onto the mandrel using its taper to compress the diffusion layers 1114, 1122 on to the polymer-film electrolytic member 1110 so that the catalyst layers transfer to it. The half tubes and mandrel are then removed lengthwise. If desired, or necessary, radial pressure can be exerted by known mechanical means.

Two titanium wire tapered tubes, carefully sized for nesting, one inside and one outside the assembled layers, are placed in tubular molds which are then filled with carbon black which has been treated according to the directions of the Los Alamos Laboratory. The carbon black is molded under heat and pressure so as completely to envelop the titanium wire matrix, except for the ends which extend beyond the molded portion to provide current connectors at each end of the tube. The products are suitable for use as anode and cathode current collectors 1116 and 1124.

Final assembly of the composite tube is effected by placing the electrolyte tube 1110 with catalytic layers 1112 and 1120 over the smaller diffusion tube 1114 and then placing the larger diffusion tube 1122 over the catalyst-covered electrolyte tube 1110. The nested tubes are pressed firmly together, lengthwise, with heat applied, if desired.

Plastic end plates fitted with small gas tube fittings such, for example, as shown in Figures 26(a), 26(b) and 11, are pressed into the inside of the center wire tube at one end and over the outside of the outside wire tube at the other end. A plastic air cover with entrance and exit tube fittings is placed over the end pieces.

Plastic sealant is then poured into the seal area adjoining each end piece to form sealed end plugs 1132 and 1134 and complete the assembly.

The above-described manufacturing steps can be included in a production assembly line which also includes test equipment for final testing of each fuel cell. Many of the operations can be carried out by robots as none of the individual operations requires difficult manipulation.

The fuel cell embodiments of the invention described herein permit simplified fuel cell manufacture through elimination of the complicated sealing and gasketing required to build stacks of flat cells. The innovations described and disclosed herein provide novel fuel cells designed to achieve commercial reliability, that are commercially adaptable to mass production manufacturing techniques at a commercially acceptable price, and are ultra light weight.

In summary, the several embodiments of the invention disclosed herein provide great freedom of choice to an engineer in developing improved wet-membrane, room temperature-operative fuel cells, especially hydrogen fuel cells, by avoiding the constraints imposed in stacked fuel cell assemblies, where swelling of the electrolytic membranes induced by water synthesis in the cells acts in directions that tend to open gas seals designed to contain the gaseous fuel. Fuel leakage, and especially leakage of highly volatile, flammable gaseous hydrogen, with its attendant risks of fire and explosion, is an important problem to avoid. To maintain the seals in stacked, wet-membrane fuel cells, heavy weight cumbersome, expensive and restrictive mechanical structures have been used, prior to the present invention, such as the steel cover plates 24, manifold covers 26 and screws 28, that are used by Adlhart to bolt the fuel cell together and compress the stack (column 7, line 64 to column 8, line 3). Since each cell may have 10 or more laminations and stacks of only about seven cells may have hundreds of apertures to seal, reliability is also poor.

In contrast, the invention permits multiple fuel cells to be disposed freely in a variety of configurations, including in a side-by-side manner, enabling the peripheries of individual cells to be separately sealed by members or sealants that are not subjected to swelling forces generated in the ion-exchange electrolytic membrane.

This separation of functions enables the problem of maintaining intimate contact between the electrode members and the swollen electrolytic membrane to be addressed by separately acting structural means such as the self-clamping tapered electrode members, and the wound filament described herein.

Gas ducting is also facilitated because, in the inventive embodiments, fuel and oxidizing gases do not have to be supplied through load-bearing distribution members, and can access the electrode surfaces through porous members which may also serve structural support functions, or through simple pipe-like ducts, or can be channeled by the electrodes themselves or, in the case of the cathodes may simply be exposed to an ambient atmosphere. Thus, much more open configurations are possible, yielding flexibility in the detailed design of means for supplying hydrogen and oxygen to the inventive fuel cell and for removing water therefrom.

Tubular and tapered tubular embodiments of fuel cell, such as those shown in Figs. 13 on, are particularly well adapted to function at relatively low, albeit elevated temperatures (circa 80-100°C), with wet-operating electrolytic membranes which are prone to substantial swelling in operation, by absorbing the swelling forces between concentric tubular members. Where the concentric tubular members comprise carbon fibers, derived for example from woven carbon cloth, exceptional tensile strength and conductivity is provided in a light weight structure. NAFION (trademark, DuPont), in the present state of the electrolytic membrane arts is a preferred material for the electrolytic member but will swell as much as 16% when wetted. As a fuel cell is repeatedly powered up and shut down during use, its electrolytic member undergoes repeated swelling and shrinkage. Moisture is generated in use. The cell dries out when shut down, and repeatedly heats up and cools down as it is used. Such continued cyclical expansion and contraction imposes enormous stresses on structural confining members of the cell, which are effectively accommodated by the tubular and tapered structures described and shown herein.

If and when available, electrolyte members that do not swell will be desirable for incorporation in fuel cell embodiments such as those shown in Figs. 1-12 to be conveniently available in extended, preferably flexible strips and rolls.

In turn, these innovations permit a wide variety of different structures and geometrical configurations to suit different operating requirements and design parameters, giving skilled workers great freedom of design choices, in adapting the invention to particular circumstances, as witnessed by the strip, tubular and conical cell embodiments described herein which can all be fabricated from lightweight, economical and adaptable carbon-fiber and polymeric materials, and which can also be configured in to flexible structures, giving manufacturers and users an additional range of possibilities.

While an illustrative embodiment of the invention has been described above, it is, of course, understood that various modifications will be apparent to those of ordinary skill in the art. Such modifications are within the spirit and scope of the invention, which is limited and defined only by the appended claims.

Claims

Claim 1. A wet-operating electrolyte, curved shape, oxygen-reduction fuel cell comprising gas-pervious, curved current-collecting electrodes shaped to mate one with another, gas-dissociating catalyst zones at each electrode and a proton transport electrolytic member constrained between the current collecting electrodes, the current-collecting electrodes are load-bearing structures acting to compress the electrolytic member **characterized in that** at least one of the electrodes includes a coiled winding acting to assist compress the electrolytic member.

Claim 2. A fuel cell according to claim 1 **characterized by** having a generally tubular shape with tubular components, each the electrode comprising concentric tubular coils, the electrolytic member being compressed between the tubular coil electrodes.

Claim 3. A fuel cell according to claim 2 **characterized by** comprising a porous gas diffusion layer, one for each current collector, to spread gas permeating the current collectors for uniform delivery to catalyst layers adjacent the electrolytic member.

Claim 4. A fuel cell according to claim 3 **characterized in that** the gas diffusion layers comprise carbon black in a porous conductive binder.

Claim 5. A fuel cell according to claim 1 **characterized in that** the catalyst zones comprise thin films of catalyst particles deposited one on each surface of the electrolytic member.

Claim 6. A fuel cell according to claim 1, 2 or 3 **characterized in that** each winding compises a conductive winding having a platinum coating.

Claim 7. A hydrogen fuel cell **characterized by** being shaped to receive and embrace a hydrogen supply canister to provide a self-contained portable electricity generating unit.

Claim 8. A fuel cell according to claim 7 **characterized by** including the hydrogen supply canister, the hydrogen supply canister having a volume and being received into the fuel cell to an extent of at least one half of the volume.

Claim 9. A method of manufacturing a hydrogen fuel cell comprising a self-supporting shaped, layered electrode structure in which a solid-phase proton-transporting electrolyte is sandwiched between a porous anodic electrode and a porous cathodic electrode, **characterized by** comprising the steps of

a) coating a first, shaped self-supporting electrode with a curable, liquid-phase, proton-transporting electrolytic material to provide an electrolytic coating;

b) curing the electrolytic coating to the solid phase;

c) assembling the coated electrode with a second, mating, shaped electrode to provide the layered structure;

d) and assembling the electrode structure with a support base.

Claim 10. A method according to claim 9, comprising a further step of coating the first electrode with a catalyst-containing curable, liquid-phase proton-transporting material.

Claim 11. A method according to claim 10, **characterized in that** the curing step has two stages: a first, solvent-evaporation stage at a moderately elevated temperature, and a second purification or decontamination stage at a higher temperature.

Claim 12. A method of manufacturing a shaped, non-flat, layered fuel cell of the wet-electrolyte type, having fuel cell components comprising current collecting electrodes and a wet-operating electrolytic member compressed between the electrodes, wherein oxygen is reduced by a combustible gas, the method comprising the steps of:

a) forming a first gas-pervious, load bearing, current collecting electrode to a first shape;
b) forming a second gas-pervious, load bearing, current collecting electrode to a second shape mateable with the first shape; and
c) assembling the first and second current-collecting electrodes with the electrolytic member into a self-supporting structure;

characterized in that each electrode comprises an open-work load-bearing metal structure.

Claim 13. A method according to claim 12 **characterized in that** the fuel cell components include gas diffusion members to spread reaction gases for uniform distribution to opposed surfaces of the electrolyte.

Claim 14. A method according to claim 12 or 13 **characterized in that** the metal is titanium.

Claim 15. A method according to claim 12 or 13 **characterized in that** the metal structure is selected from the group consisting of a coiled winding, expanded metal and metal braiding.

Claim 16. A method according to claim 12 or 13 **characterized in that** one or more of the fuel cell components is shaped around a former.

Claim 17. A method according to claim 12 or 13 **characterized by** comprising inserting plugs at the ends of the fuel cell to seal the fuel cell against loss of combustible gas.

Claim 18. A method of manufacturing a shaped, non-flat, layered fuel cell of the wet-electrolyte type, having fuel cell components comprising current collecting electrodes and a wet-operating electrolytic member compressed between the electrodes, the method **characterized by** comprising the steps of:

a) forming a first gas-pervious, load bearing, current collecting wound titanium wire electrode to a coiled, tapered open-ended tube;

b) forming a second gas-pervious, load bearing, current collecting titanium wire electrode to a coiled tapered tube sized to receive the first electrode and to mateably clamp the electrolytic member between the electrodes; and

c) assembling the first and second current-collecting electrodes with the electrolytic member by inserting one component into another lengthwise;

d) pressing the components together lengthwise to compress the electrolytic member radially; and

e) plugging the tube endwise to seal the cell against loss of combustible gas.

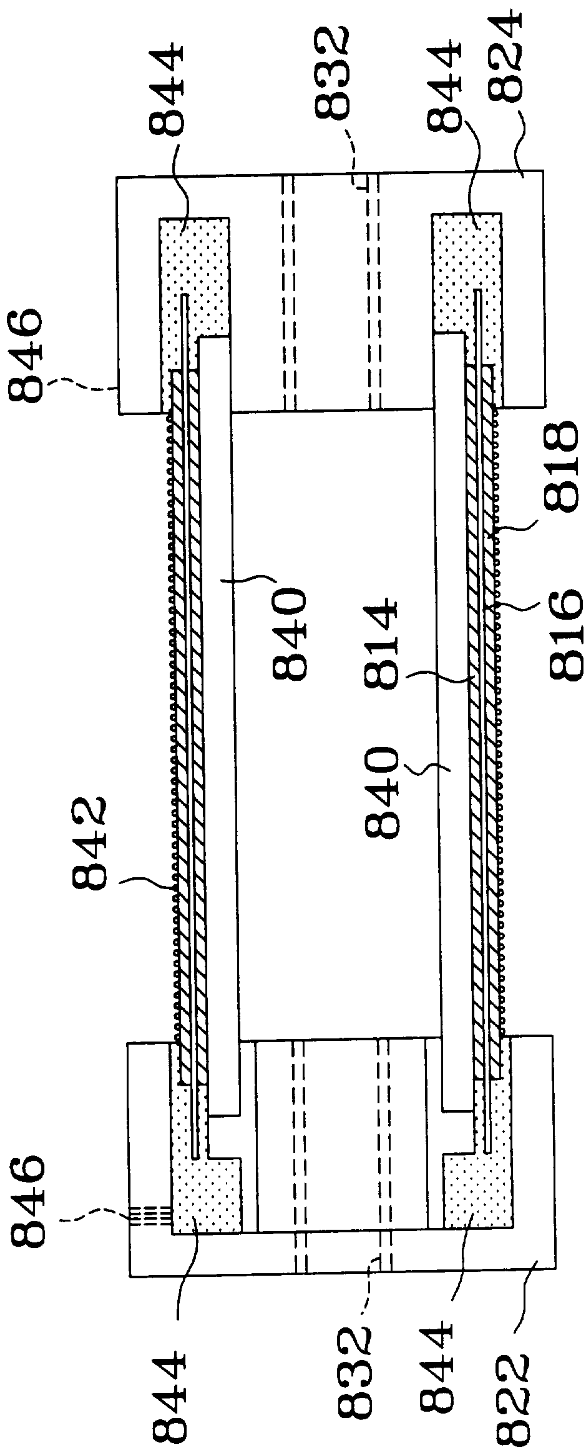

Figure 1

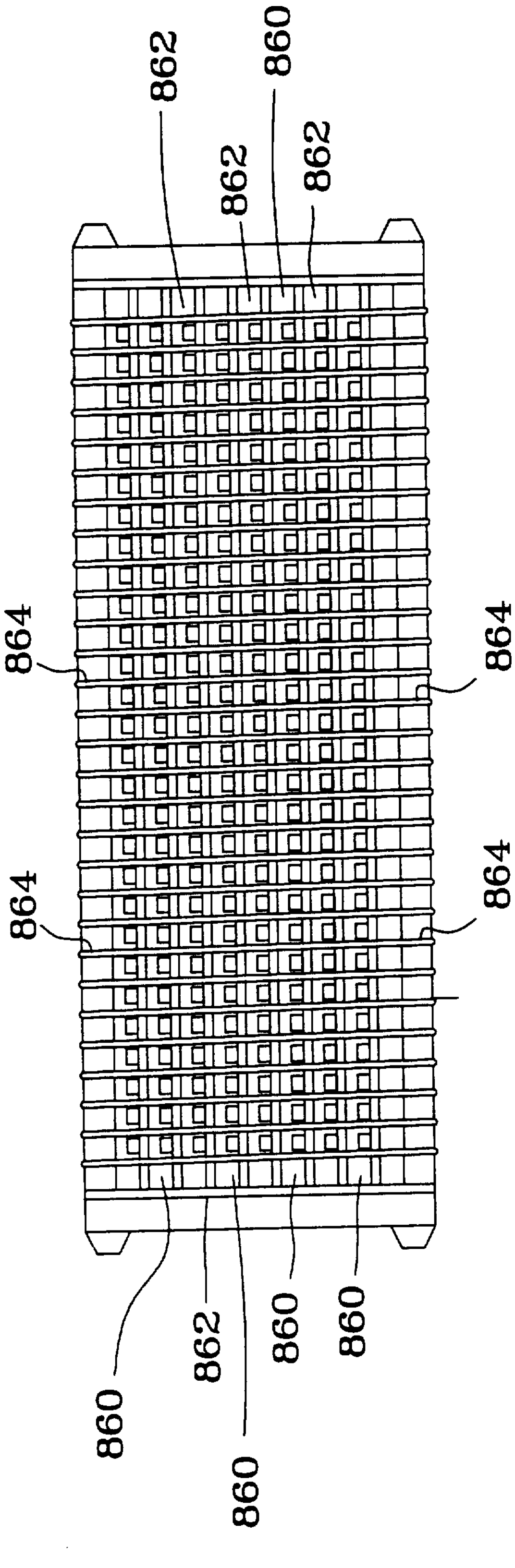

Figure 2

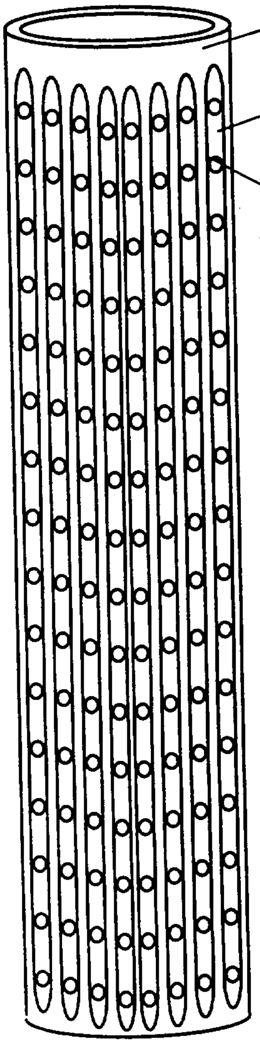

Figure3(a)

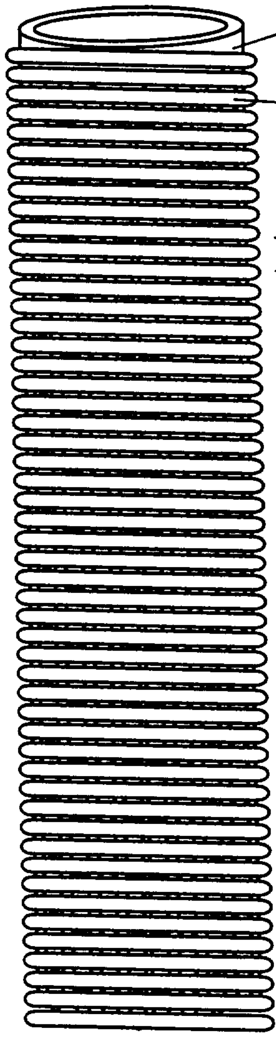

Figure 4(a)

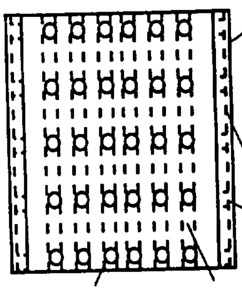

Figure 3(b)

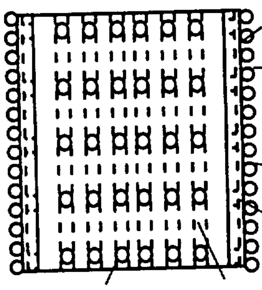

Figure 4(b)

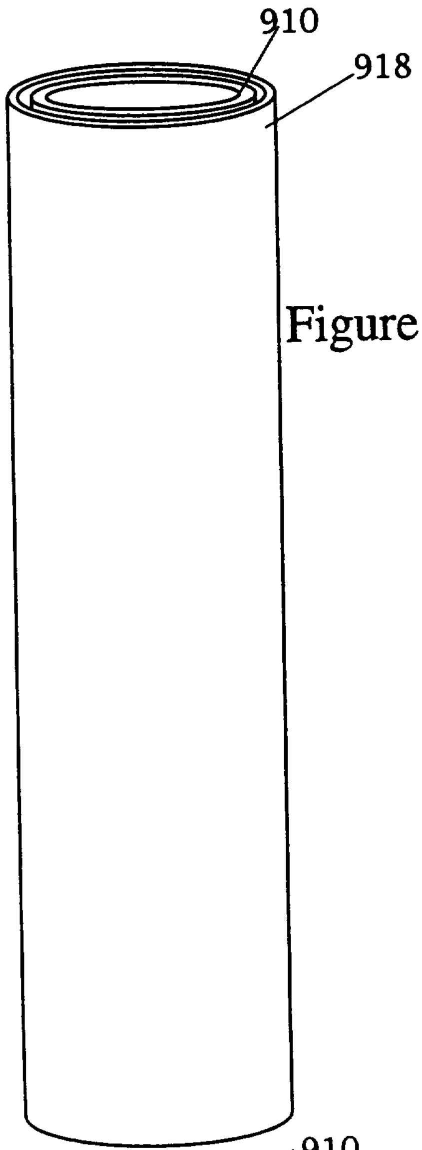

Figure 5(a)

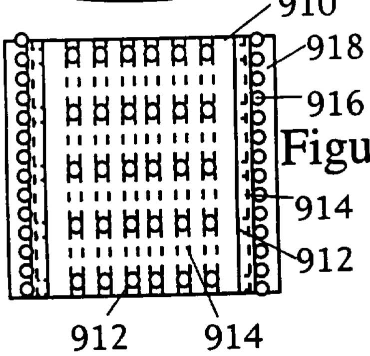

Figure 5(b)

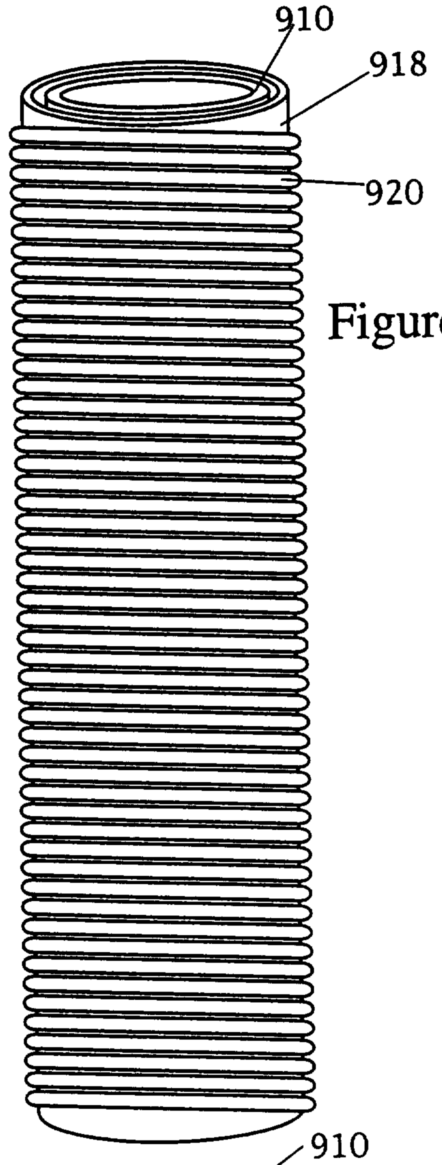

Figure 6(a)

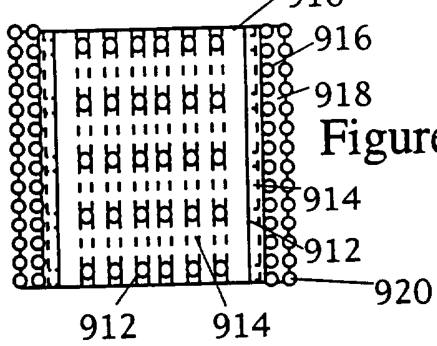

Figure 6(b)

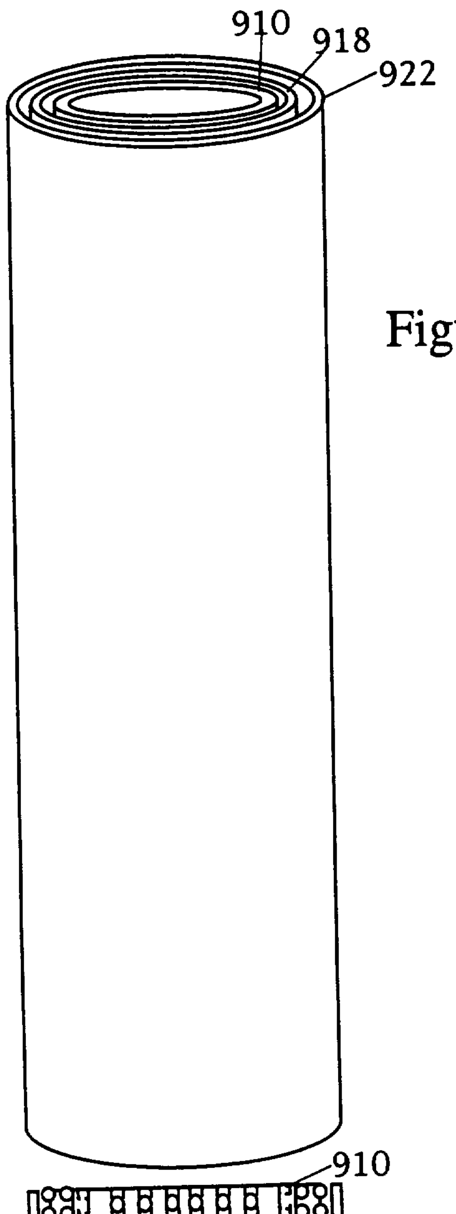

Figure 7(a)

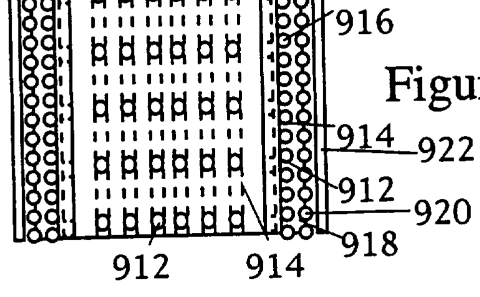

Figure7(b)

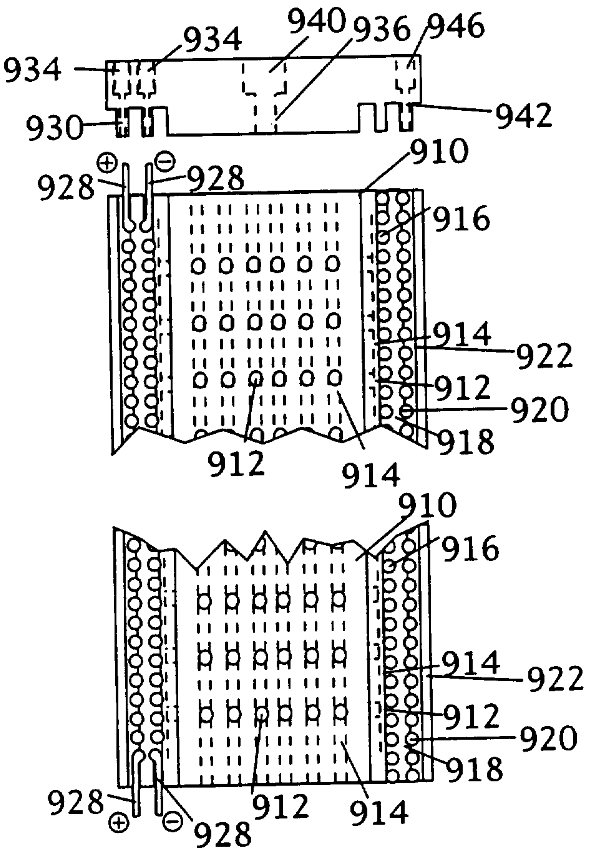

Figure 8(a)

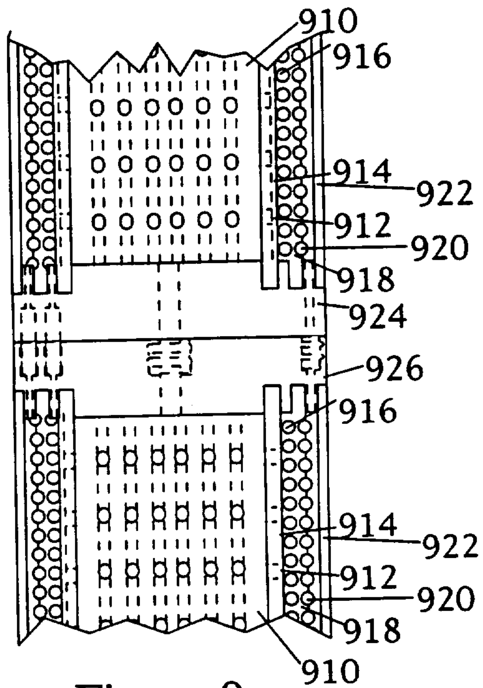

Figure 9

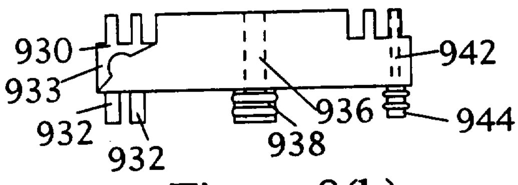

Figure 8(b)

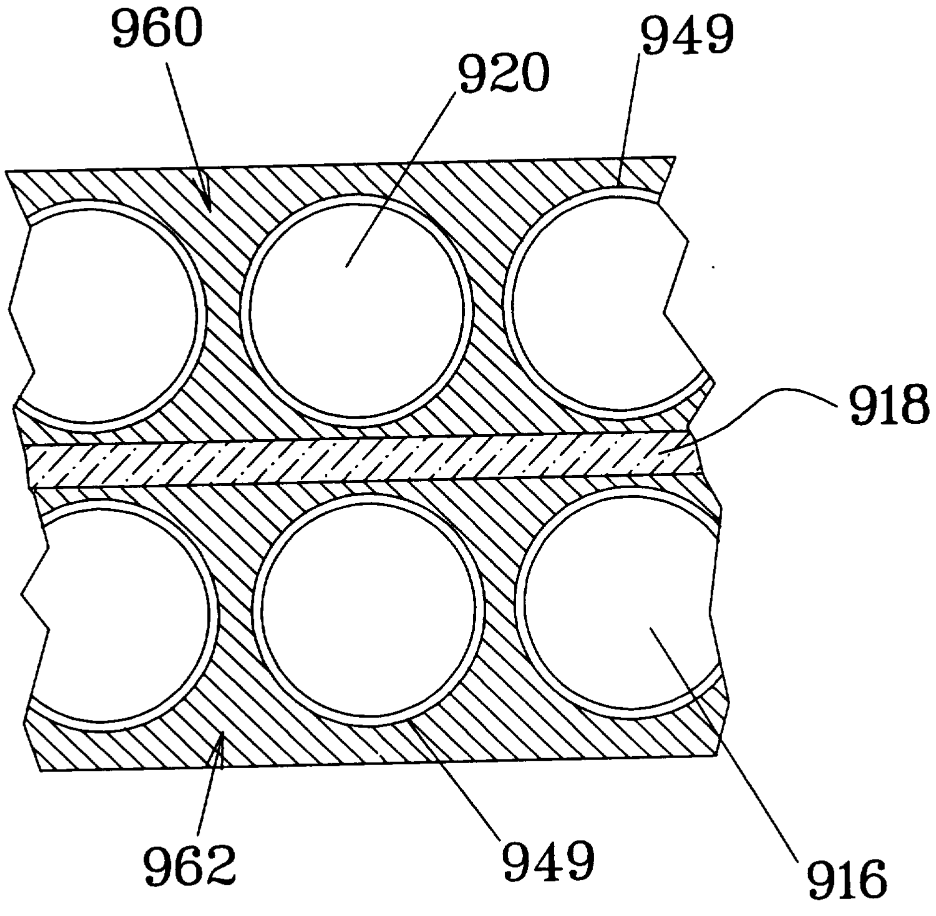

Figure 10

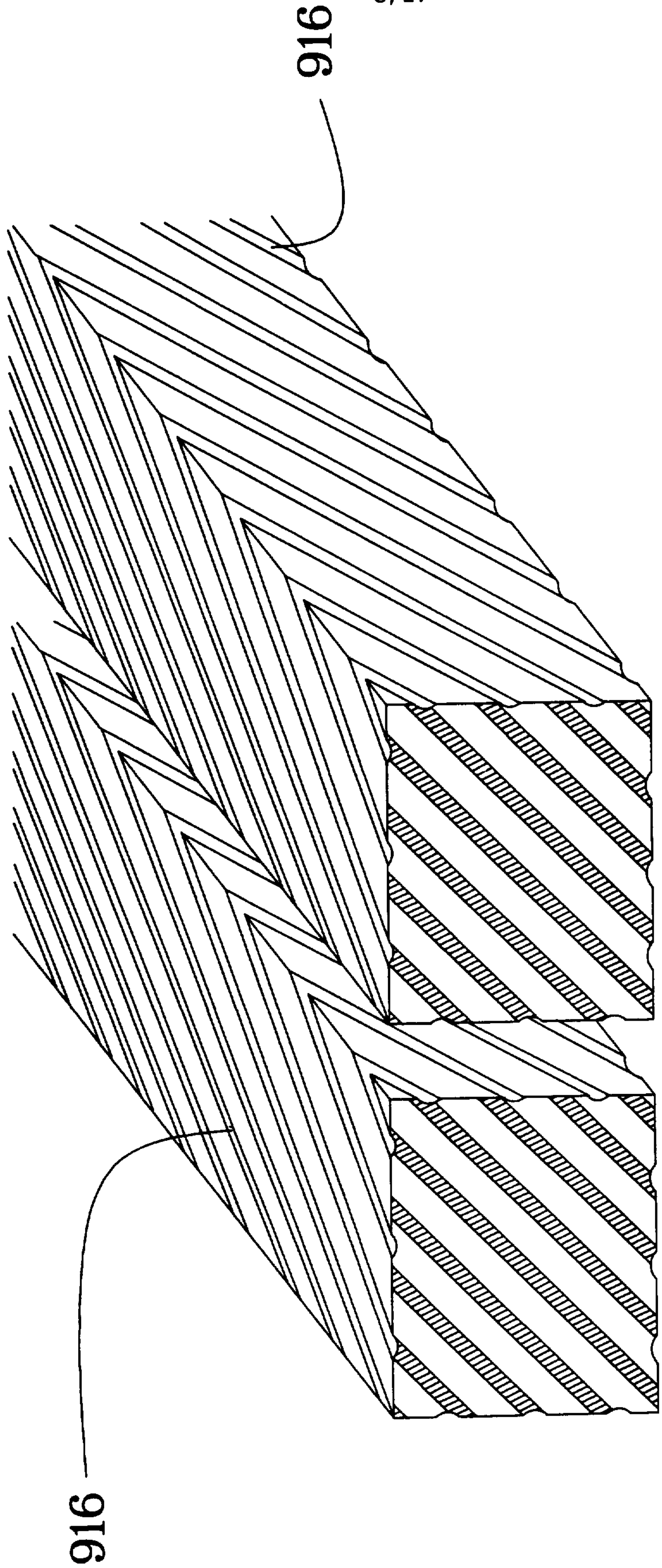

Figure 10(a)

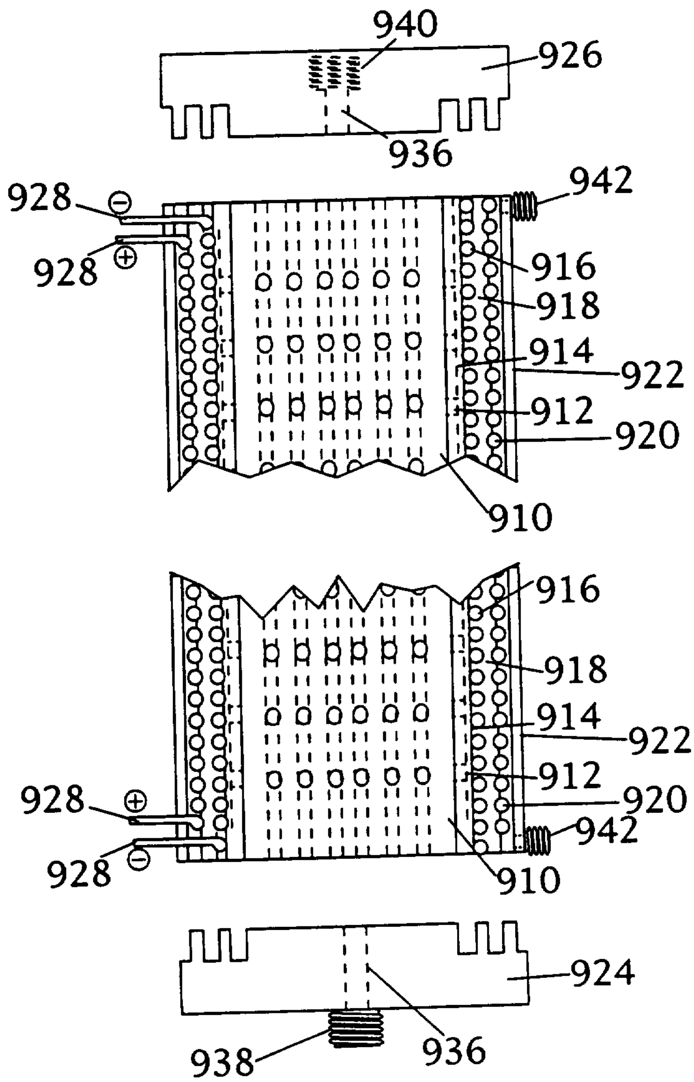
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Figure 11

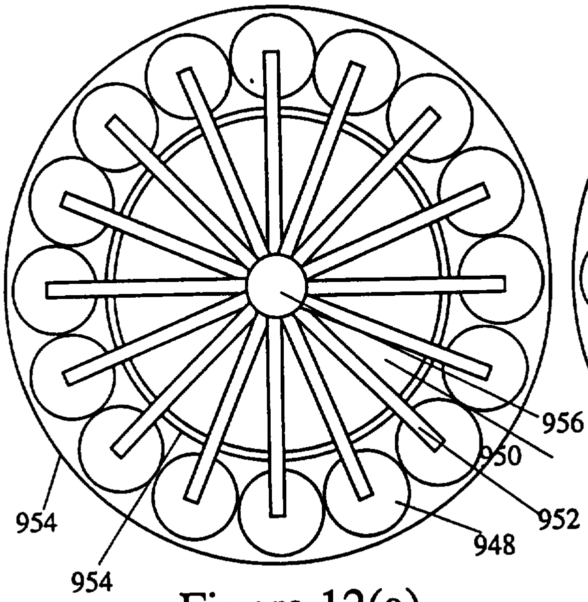


Figure 12(a)

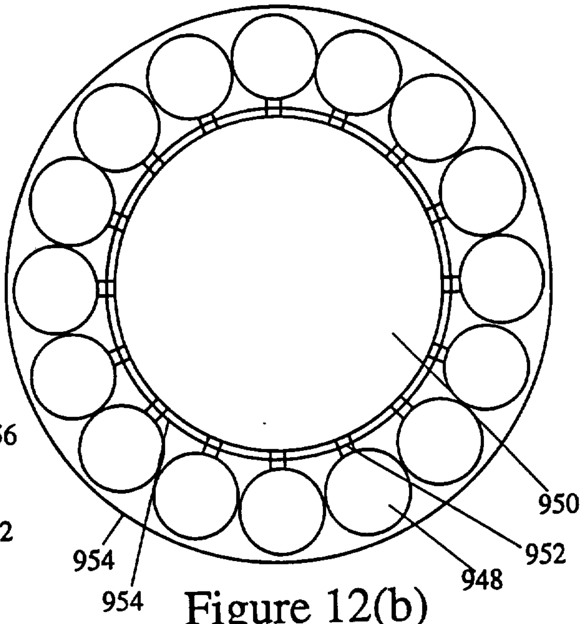


Figure 12(b)

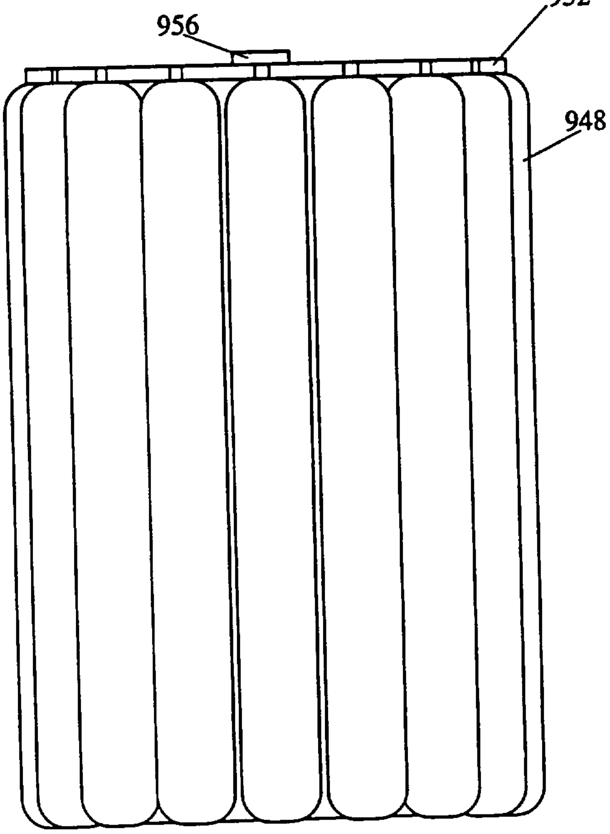


Figure 13(a)

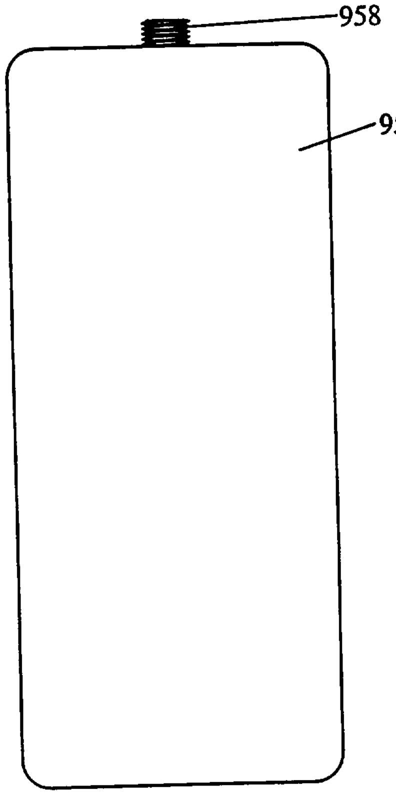


Figure 13(b)

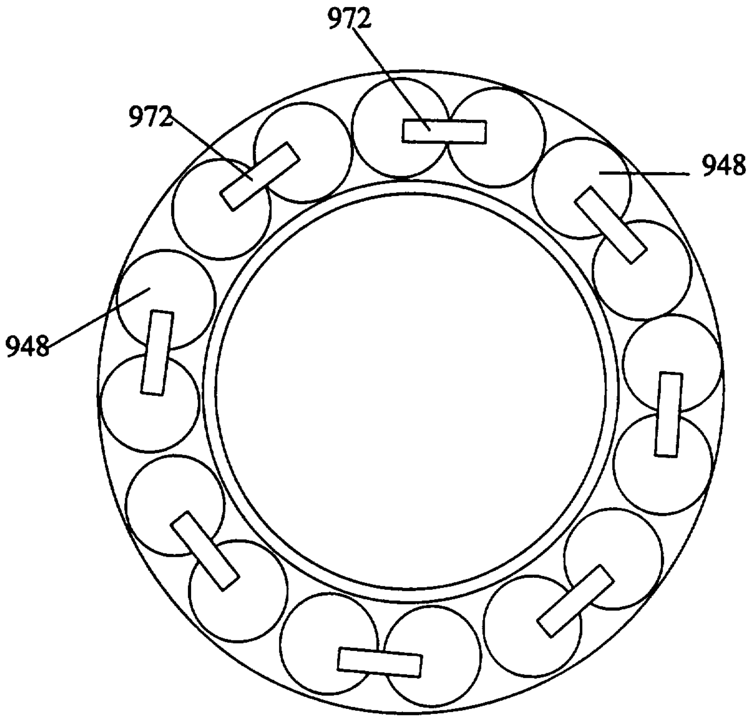


Figure 12(d)

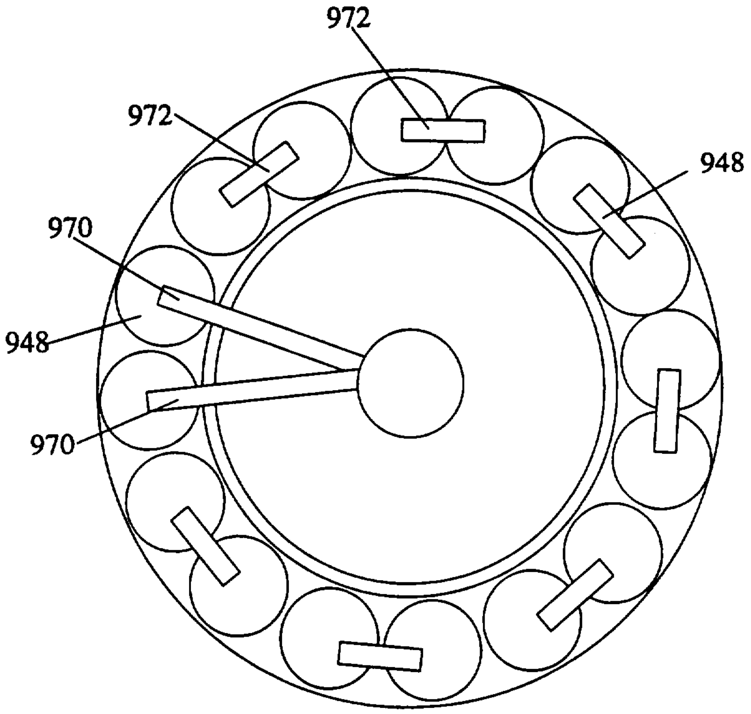


Figure 12(c)

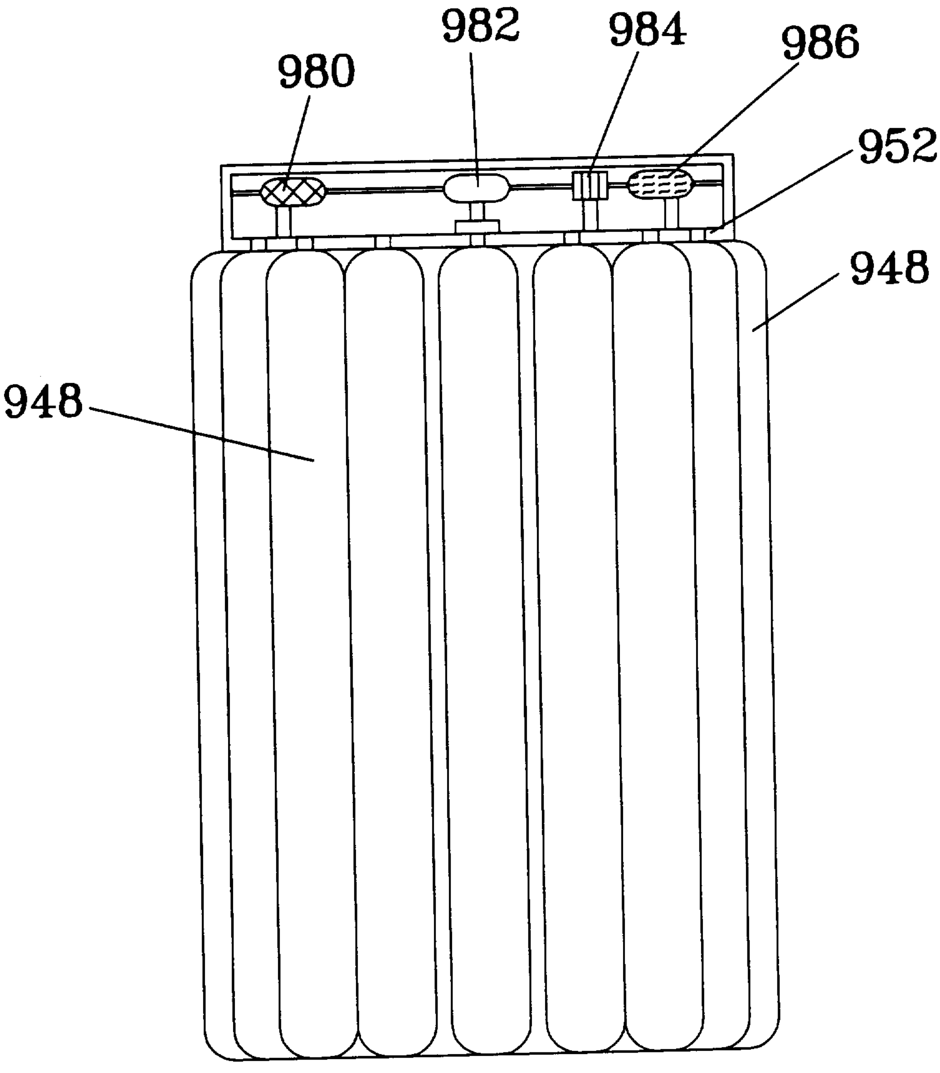


Figure 13(C)

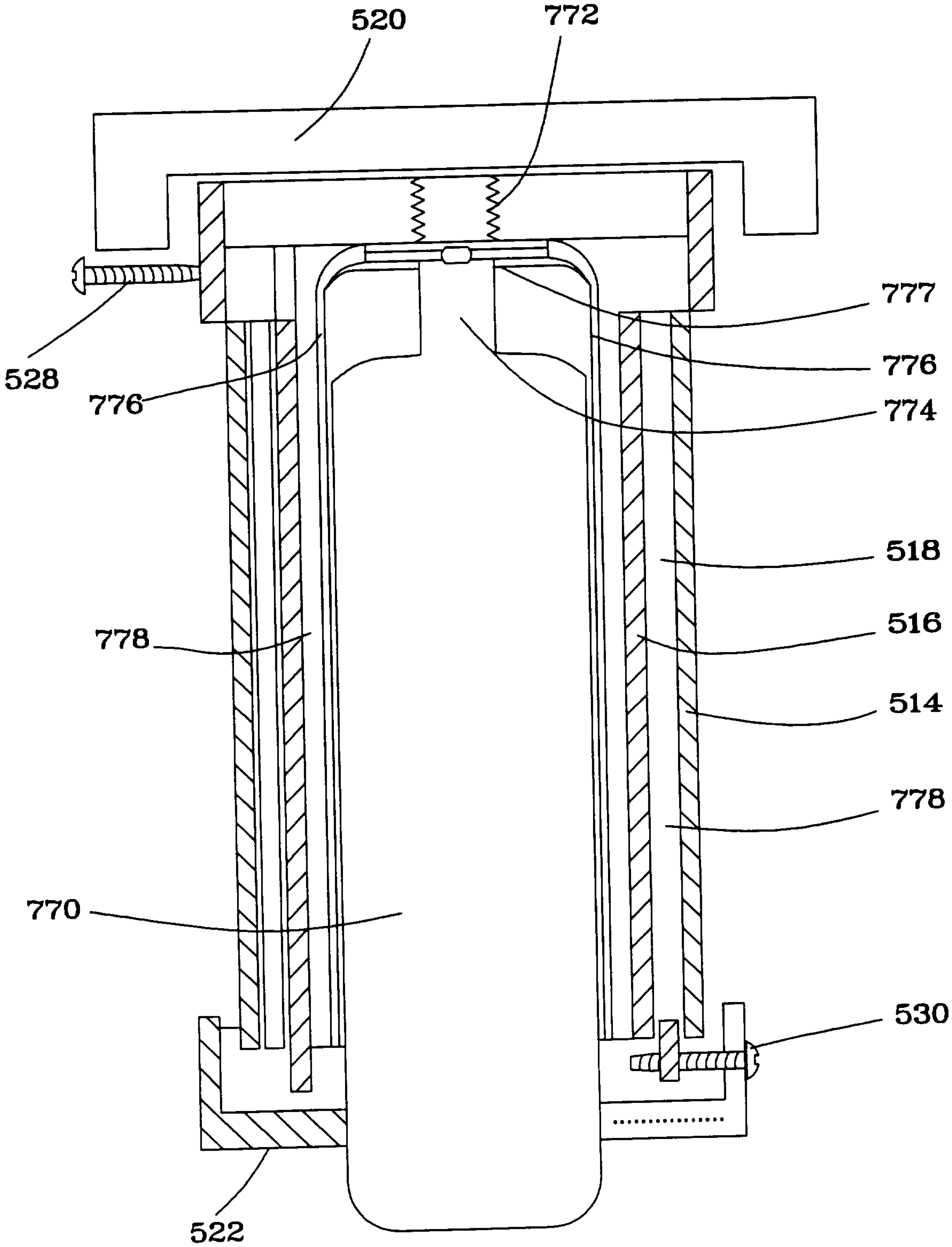
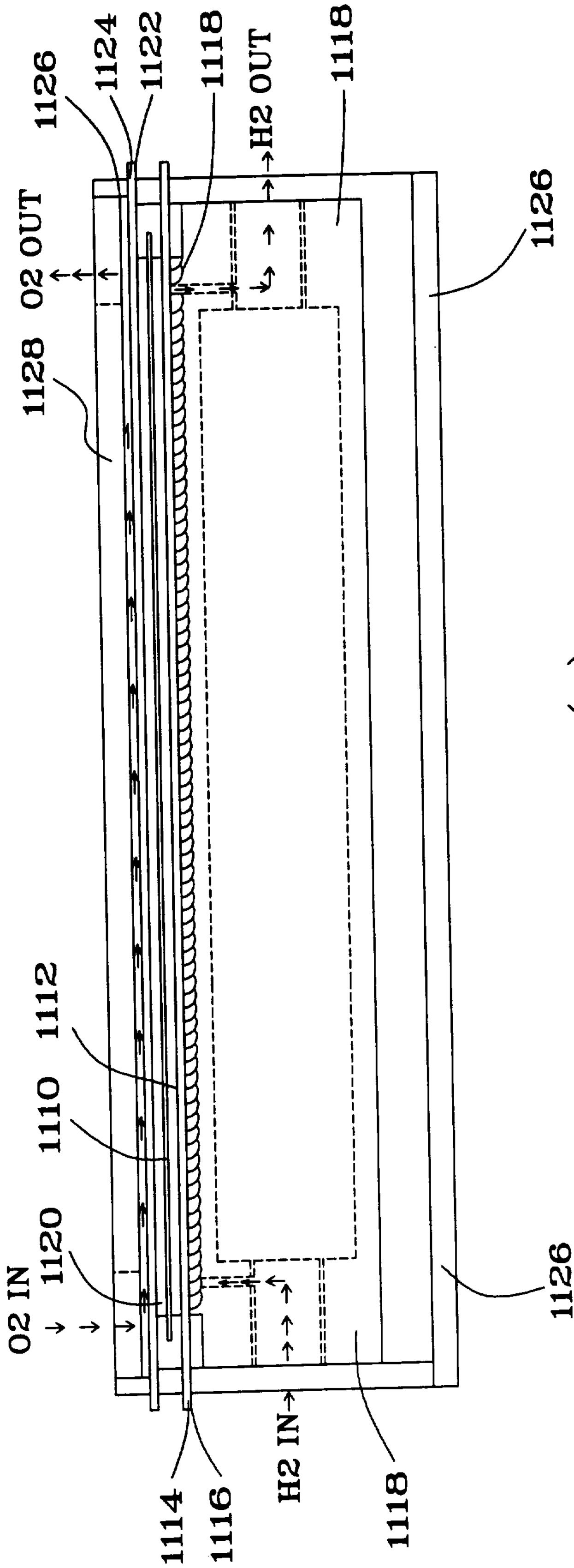


Figure 14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1116
H2 IN
1118

Figure 15(a)

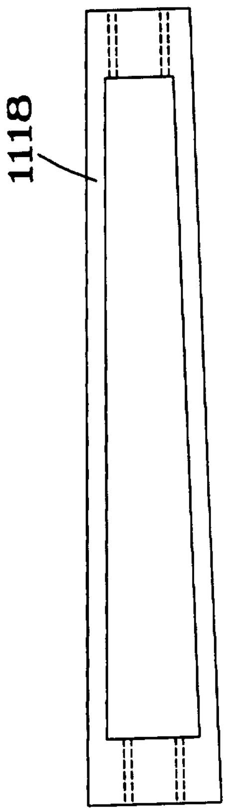

Figure 15(b)

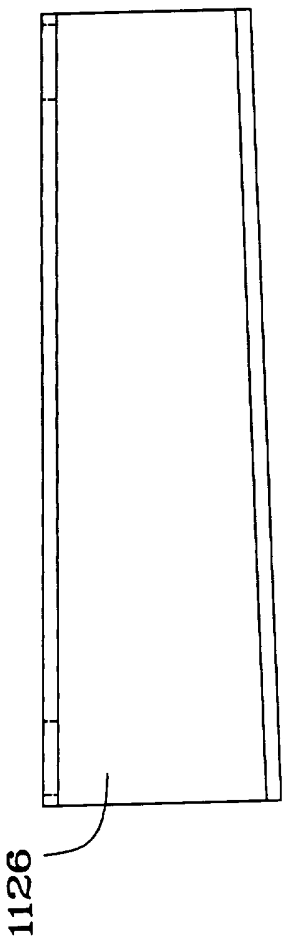

Figure 15(c)

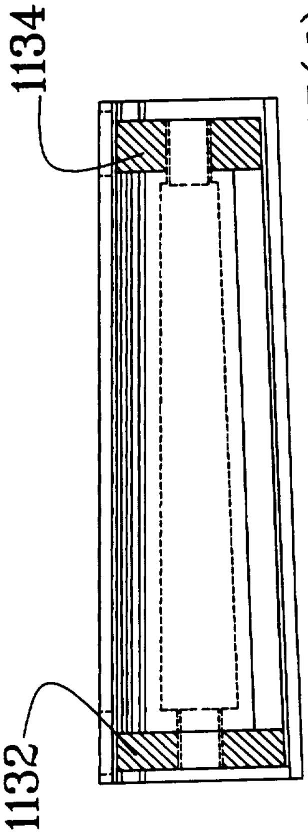

Figure 15(d)

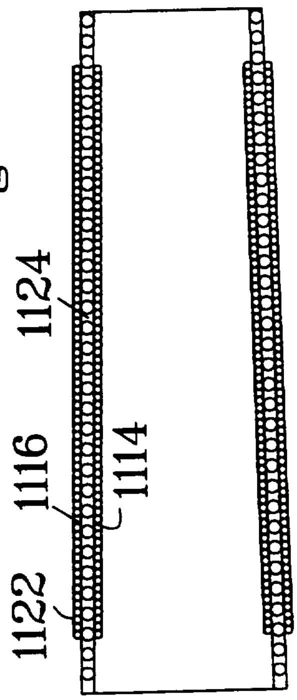

Figure 15(e)

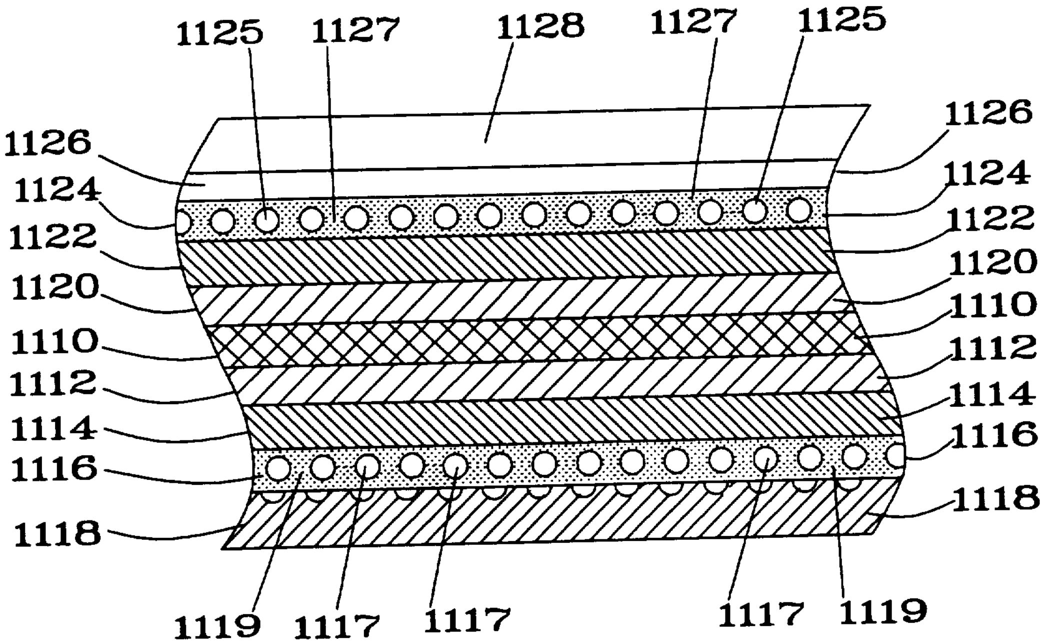
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Figure 15(f)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/09947

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 8/10, 6/00
US CL :429/31, 33, 35; 29/6232; 427/115
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/30- 34, 38-40, 94; 29/623.1, 623.2; 427/115

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,175,165 (Adlhart) 20 November 1979.	
A	US,A, 4,477,541 (Fraioli) 16 October 1984.	
A	US,A, 4,824,742 (Parry) 25 April 1989.	
A	US,A, 4,975,342 (Matsumoto) 04 December 1990	
A	US,A, 5,171,646 (Rohr) 15 December 1992.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 DECEMBER 1995	17 JAN 1996

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ANTHONY SKAPARS
Facsimile No. (703) 305-3230	Telephone No. (703) 305-9646