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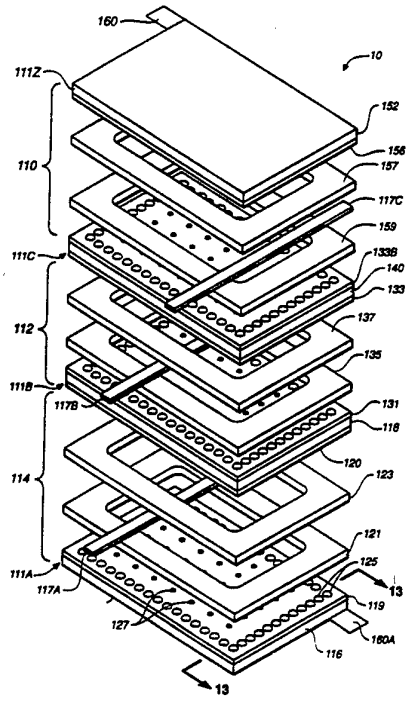
(54) Title: ENERGY STORAGE DEVICE AND METHODS OF MANUFACTURE

(57) Abstract

A dry preunit (10), includes a plurality of cells (110, 112, 114) in a true bipolar configuration, which are stacked and bonded together, to impart to the device an integral and unitary construction. Each cell (114) includes two electrically conductive electrodes (111A, 111B) that are spaced apart by a predetermined distance. The cell (114) also includes two identical dielectric gaskets (121, 123) that are interposed, in registration with each other, between the electrodes (111A, 111B), for separating and electrically insulating these electrodes. When the electrodes (111A, 111B), and the gaskets (121, 123) are bonded together, at least one fill gap (130) is formed for each cell. Each cell (114) also includes a porous and conductive coating layer (119, 120) that is formed on one surface of each electrode. The coating layer (119) includes a set of closely spaced-apart peripheral microprotrusions (125), and a set of distally spaced-apart central microprotrusions (127). These microprotrusions (125, 127) impart structural support to the cells, and provide additional insulation between the electrodes. An energy storage device (10A) such as a capacitor, is created with the addition of an electrolyte to the gap (130) of the dry preunit (10) and subsequent sealing of the fill ports.



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ENERGY STORAGE DEVICE AND METHODS OF MANUFACTURE

BACKGROUND OF THE INVENTION

Cross-Reference To Related Applications

The present application is a continuation-in-part of U.S. Application Serial No. 07/947,414, filed September 18, 1992, U.S. Application Serial No. 07/947,294, filed September 18, 1992, and U.S. Application Serial No. 07/958,506, filed October 7, 1992, all of which are incorporated by reference in their entirety.

Field of the Invention

The present invention generally relates to an energy storage device, and more particularly to a bipolar double layer capacitor-type energy storage device, and to methods for manufacturing the same.

Description of the Related Art

Energy Storage Devices -- There has been significant research over the years, relating to useful reliable electrical storage devices, such as a capacitor or a battery. Large energy storage capabilities are common for batteries; however, batteries also display low power densities. In contrast, electrolytic capacitors possess very high power densities and a limited energy density. Further, carbon based double-layer capacitors have a large energy density; but, due to their high equivalent series resistance (ESR), carbon electrodes have low power capabilities. It would therefore be highly desirable to have an electrical storage device that has both a high energy density and a high power density.

A recent review by B.E. Conway in J. Electrochem. Soc., vol. 138 (#6), p. 1539 (June 1991) discusses the transition from "supercapacitor" to "battery" in electrochemical energy storage, and identifies performance characteristics of various capacitor devices.

D. Craig, Canadian Patent No. 1,196,683, in November 1985, discusses the usefulness of electric storage devices based on ceramic-oxide coated electrodes and pseudo-capacitance. However, attempts to utilize this disclosure have resulted in capacitors which have inconsistent electrical properties and which are often unreliable.

These devices cannot be charged to 1.0 V per cell, and have large, unsatisfactory leakage currents. Furthermore, these devices have a very low cycle life. In addition, the disclosed packaging is inefficient.

M. Matroka and R. Hackbart, US Patent No. 5,121,288, discusses a capacitive power supply based on the Craig patent which is not enabling for the present invention. A capacitor configuration as a power supply for a radiotelephone is taught; however, no enabling disclosure for the capacitor is taught.

J. Kalenowsky, US Patent No. 5,063,340, discusses a capacitive power supply having a charge equalization circuit. This circuit allows a multicell capacitor to be charged without overcharging the individual cells. The present invention does not require a charge equalization circuit to fully charge a multicell stack configuration without overcharging an intermediate cell.

H. Lee, et al. in IEEE Transactions on Magnetics, Vol. 25 (#1), p.324 (January 1989), and G. Bullard, et al., in IEEE Transactions on Magnetics, Vol. 25 (#1) p. 102 (January 1989) discuss the pulse power characteristics of high-energy ceramic-oxide based double-layer capacitors. In this reference various performance characteristics are discussed, with no enabling discussion of the construction methodology. The present invention provides a more reliable device with more efficient packaging.

Carbon electrode based double-layer capacitors have been extensively developed based on the original work of Rightmire, U.S. Patent No. 3,288,641. A. Yoshida et al., in IEEE Transactions on Components, Hybrids and Manufacturing Technology, Vol. CHMT-10, #1,P-100 - 103 (March 1987) discusses an electric double-layer capacitor composed of activated carbon fiber electrodes and a nonaqueous electrolyte. In addition, the packaging of this double-layer capacitor is revealed. This device is on the order of 0.4-1 cc in volume with an energy storage capability of around 1-10 J/cc.

T. Suzuki, et al., in NEC Research and Development, No. 82, pp. 118 - 123, July 1986, discloses improved self-discharge characteristics of the carbon electric double-layer capacitor with the use of porous separator materials on the order of 0.004 inches thick. An inherent problem of carbon based electrodes is the low conductivity of the material resulting in a low current density being delivered from these devices. A second difficulty is that the construction of multicell stacks is not done in a true bipolar

electrode configuration. These difficulties result in inefficient packaging and lower energy and power density values.

Additional references of interest include, for example:

The state of solid state micro power sources is reviewed by S. Sekido in Solid State Ionics, vol. 9, 10, pp. 777-782 (1983).

M. Pham-Thi et al. in the Journal of Materials Science Letters, vol. 5, p. 415 (1986) discusses the percolation threshold and interface optimization in carbon based solid electrolyte double-layer capacitors.

Various disclosures discuss the fabrication of oxide coated electrodes and the application of these electrodes in the chlor-alkali industry for the electrochemical generation of chlorine. See for example: V. Hock, et al. US Patent No. 5,055,169 issued October 8, 1991; H. Beer US Patent no. 4,052,271 issued October 4, 1977; and A. Martinsons, et al. US Patent no. 3,562,008 issued February 9, 1971. These electrodes, however, in general do not have the high surface areas required for an efficient double-layer capacitor electrode.

It would be useful to have a reliable long-term electrical storage device, and improved methods to produce the same. It would also be desirable to have an improved energy storage device with energy densities of at least 20-90 J/cc.

Packaging of Energy Storage Devices -- As mentioned above, there has been significant research over the years regarding electrical storage devices of high energy and power density. The efficient packaging of the active materials, with minimum wasted volume, is important in reaching these goals. The space separating two electrodes in a capacitor or a battery is necessary to electronically insulate the two electrodes. However, for efficient packaging, this space or gap should be a minimum. It would therefore by highly desirable to have a method to create a space separator or gap that is substantially uniform and of small dimension (less than 5 mil (0.0127 cm).

A common way to maintain separation between electrodes in an electrical storage device with an electrolyte present (such as a battery or capacitor) is by use of an ion permeable electrically insulating porous membrane. This membrane is commonly placed between the electrodes and maintains the required space separation between the two electrodes. Porous separator material, such as paper or glass, is useful for this

application and is used in aluminum electrolytic and double layer capacitors. However, for dimensions below 1 or 2 mil (0.00254 to 0.00508 cm) in separation, material handling is difficult and material strength of the capacitor is usually very low. In addition, the open cross-sectional areas typical of these porous membrane separators are on the order of 50-70%.

Polymeric ion permeable porous separators have been used in carbon double layer capacitors as discussed by Sanada et al. in IEEE, pp.224-230, 1982, and by Suzuki et al. in NEC Research and Development, No. 82, pp. 118-123, July 1986. These type of separators suffer from the problem of a small open area which leads to increased electrical resistance.

A method of using photoresist to fill voids of an electrically insulating layer to prevent electrical contact between two electrode layers for use as a solar cell is disclosed by J. Wilfried in US Patent No. 4,774,193, issued September 27, 1988.

A process of creating an electrolytic capacitor with a thin spacer using a photosensitive polymer resin solution is disclosed by Maruyama et al in US Patent No. 4,764,181 issued August 16, 1988. The use of solution application methods described in a porous double-layer capacitor electrode would result in the undesirable filling of the porous electrode.

Additional references of general interest include U.S. Patents 3,718,551; 4,052,271; and 5,055,169. All of the applications, patents, articles, references, standards, etc. cited in this application are incorporated herein by reference in their entirety.

In view of the above, it would be very useful to have a method to produce a reliable small space separation between electrodes in electrical storage devices with a large open cross-sectional area.

SUMMARY OF THE INVENTION

The present invention relates to a novel electrical storage device that has both a high energy density and a high power density.

It is an object of the present invention to provide new methods for manufacturing the storage device.

It is also another object of the present invention to provide a reliable long-term electrical storage device, and improved methods to produce the same.

It is a further object of the present invention to provide efficient packaging of an electrical storage device by reducing the gap between the anode and cathode, which reduces the electrical resistance of the ionically conducting electrolyte.

Briefly, the foregoing and other objects are attained by an energy storage device such as a capacitor, which includes a plurality of cells in a bipolar configuration. The cells are stacked and bonded together, to impart to the device an integral and unitary construction.

Each cell includes two electrically conductive electrodes that are spaced apart by a predetermined distance. The cell also includes at least one dielectric gasket that is interposed, in relation to each other, between the electrodes, for separating and electrically insulating these electrodes.

When the electrodes, and the gaskets are bonded together, at least one fill gap is formed for each cell. Each cell also includes a high surface area (porous) electrically conductive coating layer that is formed on one (or, more) surface of each electrode. This coating layer optionally includes a set of closely spaced-apart peripheral microprotrusions, and a set of distally spaced-apart central microprotrusions. These microprotrusions are formed by novel screen printing or photolithographic printing methods. These microprotrusions impart structural support to the cells, and provide additional insulation between the electrodes.

An ionically conductive medium fills the cell gap and pores of the high surface area coating.

BRIEF DESCRIPTION OF THE FIGURES

The above and other features of the present invention and the manner of attaining them, will become apparent, and the invention itself will be best understood, by reference to the following description and the accompanying drawings, wherein:

Figure 1 is a perspective view of the preunit 10 a dry energy storage device which is constructed according to the present invention;

Figure 1A is a perspective view of the electrolyte-filled energy storage device 10A of the present invention;

Figure 2 is a cross-sectional view of the storage device of Figure 1 showing a removable cord 117A within the storage device, taken along line 2-2 thereof;

Figure 2A is another cross-sectional view of the storage device of Figure 1, taken along line 2A-2A thereof;

Figure 3 is a schematic representation of an exploded view of the preunit of Figure 1, illustrating three cells;

Figure 4 is a block diagram of the manufacture steps of the storage device 10A;

Figure 5 is a top plan view of a porous coating layer with microprotrusions which forms a part of the storage device of Figures 1 through 4;

Figure 6 is a diagrammatic illustration of a capacitive circuit, which is equivalent to the device 10A;

Figure 7 is a schematic representation of a screen printing method to produce microprotrusions on a coating layer used with the energy storage device according to the present invention;

Figure 8 is a schematic representation of an electrode holder used in the manufacture method of Figure 7;

Figure 9 is a schematic representation of a method to photolithographically produce the microprotrusions according to the present invention;

Figure 10 is a schematic isometric view of a pair of hot rollers used for laminating a photoresist to an electrode prior to photolithography;

Figure 11 is a schematic isometric view of a mask placed over the photo resist of Figure 10;

Figure 12 is a schematic isometric view illustrating the exposure of unprotected portions of the photo resist of Figures 10 and 11;

Figure 13 is a cross-sectional view of an electrode which forms a part of the energy storage device, taken along line 13-13 of Figure 3; and

Figure 14 is a schematic cross-sectional view of two bipolar electrodes with the high surface area porous coating layer on the electrically conducting substrate forming one cell.

Figure 15 is a schematic view of a frame used to hold thin support materials during the dip coating process;

Figure 15A is a schematic view of wire used in the frame of Figure 15.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Definitions

The definitions of the following terms are not intended to be exclusive:

"Cord" refers to the thin strips of material included in the method of manufacture of the dry preunit. After initial heating, the removal of the cord produces the open fill ports.

"Electrically conducting support material" refers to any electrically conducting metal or metal alloy, electrically conducting polymer, electrically conducting ceramic, electrically conducting glass, or combinations thereof. Metals and metal alloys are preferred for producing stock units. The support material should have a conductivity of greater than about 10^{-4} S/cm.

"Second electrically conducting material" (having a high surface area) refers to a porous electrode coating which may be of the same or different composition on each side of the support material. Preferred metal oxides of the present invention include those independently selected from tin, lead, vanadium, titanium, ruthenium, tantalum, rhodium, osmium, iridium, iron, cobalt, nickel, copper, molybdenum, niobium, chromium, manganese, lanthanum, or lanthanum series metals or alloys or combinations thereof, and possibly containing additives like calcium to increase electrical conductivity.

"Electrolyte" refers to an ionically conductive aqueous or non-aqueous solution or material, which enables the dry preunit to be electrically charged.

"Cab-O-Sil®" refers to silica filler available from Cabot Corporation of Tuscola, Illinois. A variety of sizes are available.

"Epoxy" refers to the conventional definition of the product which is an epoxy resin mixed with a specific curing agent, usually a polyamine. or polyepoxide mixed with a polyamine curing agent.

MYLAR® refers to a polyester of polyethylene terephthalate of DuPont, Inc. of Wilmington, Delaware. It is usually commercially available in sheet form of varying thicknesses.

"Metal oxide" refers to any electrically conducting metal oxide.

"Mixed metal oxide" refers to an electrically conducting oxide compound of two or more metal oxides.

"Photoresist" is any photo curable material. Usually, it is an epoxide or acrylate or combinations thereof.

"ConforMASK" is a negative working photopolymer available commercially from Dynachem of Tustin, California. This polymer should be used at 50% or less relative humidity.

Dry Preunit Energy Storage Device

Referring now to the drawings, and more particularly to Figures 1, 2 and 3 thereof, there is illustrated a dry preunit of energy storage device 10 which is constructed according to the present invention. The energy storage device is first an assembled dry preunit 10. After filling the present cells with an electrolyte, the surface is heated to close and to fuse the exterior surface, to form device 10A which is then electrically charged.

The device preunit 10 generally includes a plurality of cells, such as the cells 110, 112 and 114, which are formed, prepared, and stacked according to the teaching of the present invention. Figure 1A illustrates an assembled view of the electrical storage device preunit 10A, formed of twelve superposed cells. It should however be understood to those skilled in the art, after reviewing the present specification that any different number of cells can be used.

For simplicity of illustration, Figure 3 is an exploded view of the preunit 10, showing only three exemplary cells 110, 112 and 114. The cells have generally similar design and construction, and therefore, only the cells 114 and 112 will be described in detail, in relation to Figures 2, 2A, 3 and 13.

The cell 114 includes a first electrically conductive external electrode or end plate 111A, and a second internal, electrically conductive bipolar electrode 111B. Both electrodes 111A and 111B are spaced apart at the edges by means of two dielectric or electrically insulating gaskets 121 and 123.

When the first and second electrodes 111A and 111B, and the insulating gaskets 121 and 123 and the electrically conducting porous material (oxide) layers 119 and 120 are bonded together to form the cell 114, a central air filled gap 130 (Figure 2A) is formed by these elements. When the preunit 10 is ready to be used, the gap 130 is filled with an electrolyte (not shown) to produce device 10A.

For this purpose, an exemplary access or fill port 122, is shown in Figure 2A for illustration purpose only, and is formed between the gaskets 121 and 123, in order to allow the electrolyte to fill the gap 130. The fill port 122 is formed by means of a tab or cord 117A, which is inserted between the gaskets 121 and 123, prior to fusing or bonding the gaskets 121 and 123. When the gaskets 121 and 123 are heated, the cord 117A becomes surrounded by the reflow gasket material, which causes the outline of fill port 122 to be formed. The two gaskets become a fused polymer mass covering a minimum of the active electrically conducing coating layers 119 and 120.

Considering now the electrodes 111A and 111B in greater detail, the methods of manufacturing them will be described later. One difference between the electrodes 111A and 111B is that the electrode 111A optionally includes a tab 160A, for connection to a power source (not shown).

A further, but optional distinction between the electrodes 111A and 111B, is that the electrode 111A includes one porous electrically conductive coating layer 119, which is deposited on a support material or structure 116, while the bipolar electrode 111B includes two porous coating layers 120 and 131, which are deposited on either or both sides of the support material or structure 111B. As such, the electrode 111B is a true bipolar electrode. It should be understood that both sides of the electrode 111A could be coated with porous electrically conductive layers.

Yet another optional distinction between the electrodes 111A and 111B lies in the rigidity of the support structures 111A and 111B. The electrode 111A, acting as an external end plate, should preferably have a more rigid construction, so that it imparts sufficient rigidity to the overall structure of the energy storage device 10A. The electrode 111B and other similar internal electrodes do not necessarily need to be as rigid as the external electrode 111A. Nonetheless, when the device 10A is large, additional support structure is required, and the internal electrodes, i.e. 111B, are used as additional support structure. In this case, it is desirable to rigidify the internal electrodes, i.e. 111B.

As a result, the support material 116 is thicker than the support material 118. In the preferred embodiment, the support material 116 has a thickness of about 10 mils (0.0254 cm),while the support material 118 has a thickness of about 1 mil (0.00254 cm). Other values could alternatively be selected.

The electrodes 111A, 111B and the remaining electrodes of the storage device 10A, are sized and dimensioned according to the desired application, without departing from the scope of the invention. For instance, in one application, the device 10A is miniaturized, e.g. for a cardiac defibrillator. While in another application, the overall volume of the device is one cubic meter or even greater, e.g. for an electric vehicle. The dimensions of the electrodes determine the overall capacitance of the storage device 10A.

In the preferred embodiment, the electrodes, i.e. 111A and 111B, are rectangularly shaped. However, these electrodes and consequently the preunit 10 could assume various other shapes, such as circular, square, etc. An important feature of the preunit 10 is the flexibility of its design, which enables it to be used in various applications.

Considering now the coating layers 119 and 120 in greater detail, the methods of forming them will be described later. In the preferred embodiment, the coating layer 119 includes a plurality of microprotrusions, while the coating layer 120 does not include such microprotrusions. It should be understood, however, that the coating layer 120 could alternatively be designed similarly to the coating layer 119, without departing from the scope of the invention.

Figure 5 is a top plan view of the coating layer 119, which includes an array of microprotrusions, and which is deposited on the inner face or flat side of the support material 116. The coating layer 119 is porous with high surface area, electrically conductive, and relatively thin. The array includes two sets of microprotrusions. The first set includes a plurality of peripheral microprotrusions 125, and the second set includes a plurality of centrally located microprotrusions 127.

In the preferred embodiment, the peripheral and the central protrusions 125 and 127 are similarly designed, and are generally semi-spherically shaped. However, other shapes, for example a rectangular shape, are contemplated within the scope of the present invention. The diameter of each protrusion 125 or 127 is about 6 mil (0.01524 cm). Different applications of the device 10 might require that the microprotrusions 125 and 127 be differently designed. The center-to-center separation of the peripheral microprotrusions 125 is about 20 mil (0.0508 cm), while the center-to-center separation of the central microprotrusions 127 is about 40 mil (0.1016 cm).

One reason for the higher density of the peripheral microprotrusions 125, is to prevent edge shorting. One reason for the lower density of the central microprotrusions 127, is to provide separation between the electrodes 111A and 111B, with minimal masking of the electrode surfaces. For this purpose, the gasket 121 is allowed to cover at least part of the microprotrusions 125, but preferably not the microprotrusions 127.

The peripheral microprotrusions 125 are adjacently disposed along an outer periphery of the coating layer 119. While only four rows of microprotrusions are illustrated, it should be understood to those skilled in the art, that additional rows may added, depending on the size and application of the device 10. The central microprotrusions 127 are similarly adjacently disposed, in an arrayed arrangement, within a central section 132 of the coating layer 119. As illustrated in Figure 5, the central microprotrusions 127 are surrounded by the peripheral microprotrusions 125.

The microprotrusions 125 and 127 are formed on the coating layer 119 to provide added structural support to the first and second electrodes 111A and 111B.

For instance, if, the second electrode 111B starts to sag or bow toward the first electrode 111A, the microprotrusions 127 will prevent contact between these electrodes 111A and 111B.

Figure 5 further shows that the coating layer 119 further includes a plurality of spacings, i.e. 133A through 133G, where the cord, i.e., 117A, are placed, in order to ultimately form the fill port, i.e. 122. As illustrated for large electrode sizes the coved only extends partway into the central section 132. For smaller electrode sizes the coved across the electrode surface with the two ends protruding out opposite sides, thus forming simultaneously fill ports 113C and 133D. In this case the width of the cord is smaller than, or equal to the center-to-center separation between the central microprotrusions 127. However, the cord is larger than the center-to-center separation between the peripheral microprotrusions 125, to prevent the peripheral microprotrusions from pinching the cord, and preventing it from being removed the spacings are increased in the peripheral microprotrusions. Alternatively, the cord may be similar in width to the peripheral microprotrusions separation and no accommodation in the microprotrusion pattern needs to be done.

Considering now the coating layer 120, it serves a similar function as the coating layer 119, and is deposited on the side of the electrode 111B, which faces the inner side of the first electrode 111A. In the preferred embodiment, the coating layer 120 does not include microprotrusions. In an alternative embodiment of the preunit 10, the coating layers 119 and 120 are similarly constructed, and include microprotrusion layers.

Considering now the gaskets 121 and 123, the methods of producing them will be described later. The gaskets 121 and 123 are generally identical, and are arranged in registration (adjacent and superposable) with each other. For brevity, only the gasket 121 will be described in greater detail. The gasket 121 includes a solid peripheral section 143 and a hollow central section 144.

In the preferred embodiment, the cord 117A, or a part thereof, is placed between the gaskets 121 and 123, and extends across the hollow section, i.e. 144, of the gaskets, and protrudes outside the peripheral section, i.e. 143. In another embodiment, the cord does not extend across the entire width of the gaskets, and

only a part of the cord is sandwiched between the gaskets and extends beyond both edges of one side of the gasket.

Turning now to Figure 1, the next adjacent cell 112 will now be briefly described. The cell 112 is generally similar in design and construction to the cell 114. The cell 112 includes the bipolar electrode 111B, as its first electrode, and a second bipolar electrode 111C. The electrodes 111B and 111C are generally identical, and are spaced-apart, in registration with each other.

A porous coating layer 131, which is identical to the coating layer 119, is deposited on the surface of the support material 118, facing the electrode 111C. A coating layer 133, which is similar to the coating layer 120, is deposited on a support material or structure 140, which forms a part of the electrode 111C.

The cell 112 further includes two gaskets 135 and 137 that are identical to each other and to the gaskets 121 and 123 of the cell 114. A cord 117B forms a fill port 142 between the gaskets 135 and 137.

The cell 110 is substantially similar to the cell 114, and includes a first bipolar electrode 111Y, a second electrode 111Z, two gaskets 157 and 159, a cord 117C, a tab 160, and a fill port 162. It should be noted that Figure 3 does not show the inner electrode 111Y.

Turning now to Figure 6, there is illustrated a diagrammatic view of a capacitive circuit 200 which is representative of, and generally has an equivalent function to the device 10A. The circuit 200 illustrates the cell 114 as two capacitors C1 and C2; the cell 112 as two capacitors C3 and C4; and the cell 110 as two capacitors C5 and C6. As a result, the device 10 is generally equivalent to a plurality of capacitors connected in series.

The porous electrically conducting coating 119 in conjunction with an ionically conducting medium (not shown) within the cell 114, form the capacitor C1. The ionically conducting medium and the coating 120 form the capacitor C2. The coating 131 and the ionically conducting medium within the cell 112 form the capacitor C3. The ionically conducting medium within the cell 112 and the coating 133 form the capacitor C4. Similarly, the cell 110 is represented by the capacitors C5 and C6.

An important aspect of the present invention, is the bipolar configuration of the energy storage device. The use of a single electrode, such as the electrode 111B to form two back-to-back capacitors, such as the capacitors C2 and C3, result in a bipolar electrode B. This design significantly reduces the overall size of the device 10A.

While not wanting to be bound by theory, an explanation of the operation of the capacitive energy storage device, at the molecular level is helpful to understand the enormous value of the electric double layer. For simplicity, to describe Figure 14, Figure 3 can be used for reference where the same reference numbers are used (and the porous material is a mixed metal oxide).

Figure 14 is a schematic cross-sectional representation of the magnified edge of the magnified edge of the support 118 & 148A and electrically conducting coating layers (120, 131, 133, 133B).

The center support 188 is depicted as a metal but can be any material which is electrically conducting and provides the support for the coating. The coating which has high surface area provides the structure and geometry for the energy storage. As can be seen in Figure 14, layer 120, etc. has a discontinuous surface with many fissures, micropore and mesopore which create the high surface area.

Thus, the porous coatings 120 and 131 are coated onto support 118 to form bipolar electrode 111B and coatings 133 and 133B are coated onto support 148A to form bipolar electrode 111C. After the preunit 10 is assembled, the pull tabs are removed creating the fill ports and the preunit 10 is charged with electrolyte 190, the fill ports, e,g. 117D, are sealed creating device 10A.

The device 10A is then charged electrically producing the following results at the same time:

Coating 120 becomes negatively charged. Electrically conducting support 118 conducts electrons accordingly. Thus, porous coating 131 becomes positively charged. The ionically conducting electrolyte ions accordingly. An electric double layer is formed at the electrode-electrolyte interface forming the individual capacities in circuit 200. Thus, the surface of coating 133 becomes negatively charged, and the surface of coating 133B becomes positively charged. Because the porous high

surface area oxide allows the effective surface area of the electrode to become very high, the corresponding electrical storage capacity of the device increases dramatically.

Methods of Manufacturing the Energy Storage Device

Referring to Figures 1 to 5, a general description for the preferred method to produce the dry pre-unit 10 of the energy storage device 10A, is as follows:

(A) Support Material Preparation

The support material are optionally etched or cleaned by a variety of conventional pickling and cleaning procedures.

In some experiments, if the metal surface is not etched it is too smooth. This smooth surface sometimes causes inadequate adhesion of the porous coating. The etch creates a suitable rough surface.

1. Wet Etching - A preferred procedure is to contact the metal support with an aqueous inorganic strong acid, e.g. sulfuric acid, hydrochloric acid, hydrofluoric acid, nitric acid, perchloric acid or combinations thereof. The etching is usually performed at elevated temperatures of 50 to 95°C (preferably 75°C) for about 0.1 to 5 hr (preferably 0.5 hr) followed by a water rinse. Room temperature acid etching is possible. An alkaline etch or an oxalic acid etch may also used.

2. Dry Etching - The roughened support surface is obtained by sputtering, plasma treatment, and/or ion milling. A preferred procedure is Ar RF sputter etching at between around 0.001 and 1 torr with about 1 KeV energy at 13.5 Mhz. Commonly, 0.1-10 watts/cm^2 power densities for about 1-60 min. are used to clean and roughen the surface. Another procedure is to plasma etch the support with a reactive gas such as oxygen, tetrafluoromethane, and/or sulfurhexafluoride at around 0.1-30 torr for about 1-60 min.

3. Electrcchemical Etching - The roughened surface is obtained by electrochemical oxidation treatment in a chloride or fluoride solution.

(B) Coating of Support Material

The coating (e.g. oxide) is porous and composed of mostly micropores (diameter < 17Å). Large 0.1-1 μm wide cracks are present on the surface protruding to depths as thick as the coating. However, greater than 99% of the surface area

arises from these micropores. The average diameter of these micropores are around 6-12 Å.

After various post-treatments the pore structure can be altered to increase the average pore size. For example, the steam post-treatment creates a bimodal pore distribution. In addition to the micropores, a narrow distribution of mesopores (diameter < 17-1000Å) having a diameter of about 35 Å is created. These treated electrode coatings have 85-95% of the surface area arising from the micropore structure.

With alternate electrode construction methods this pore size distribution can be varied. The effective high surface area of the coating is 1,000 to 10,000 to 100,000 times larger than the projected surface area of the electrode as a monolith. The pore size, distribution, and surface area controlled with the temperature of pyrolysis and/or high temperature water treatment. In addition, the use of surfactants to create micelles or other organized structure in the coating solution increases the average pore size up to the values around 100-200 Å with only 5-10% of the surface area coming from micropores.

As illustrated in Figure 13, the electrode 111A includes a porous and conductive coating layer 119, which is formed on at least one surface of the support material 116. The support material 116 is electrically conductive, and sufficiently rigid to support the coating layer 119 and to impart sufficient structural rigidity to the device 10.

One goal of the present invention, is to optimize the energy density and power density of the device 10. The object is achieved by reducing the thickness of the support material 116, and maximizing the surface area of the coating layer 119. The power density of the device 10 is further optimized, by maintaining a low resistance.

The surface area of the coating layer 119 is determined by the BET methodology, which is well known in the art. The surface enhancement, which is an indication of the optimization of the surface area of the coating layer 119, is determined according to the following equation:

Surface enhancement = (BET Surface Area / Projected Surface Area)

In the present invention, the surface enhancement values can be as large as 10,000 to 100,000.

The coating layer 119 is porous, and its porosity could range between about five percent (5%) and ninety-five percent (95%). Exemplary porosity range for efficient energy storage is between about twenty percent (20%) and twenty-five percent (25%).

In conventional double-layer capacitors, the main device resistance is due to the carbon coating layer. In the present invention, most of the device resistance is due to the electrolyte, which has a higher resistance than that of the porous conductive coating layer.

When the preunit device 10 is filled with an electrolyte, it becomes ready to be charged to become device 10A. The main criterion for the electrolyte is to be ionically conductive and have bipolar characteristics. The boundary or interface region between the electrode and the electrolyte is referred to in the field, as the "double layer", and is used to describe the arrangement of charges in this region. A more detailed description of the double layer theory is found in "Modern Electrochemistry", by Bockris et al, volume 2, sixth print, chapter 7 (1977).

The surface area of the coating layer affects the capacitance of the device 10A. If for instance, the surface enhancement factor is between 1,000 to 20,000, and the double layer capacitance density is between about 10 to 500 microfarad per cm^2 of the interfacial surface area (i.e. the BET surface area), then surface enhancement capacitance densities of about 0.1 to 10 farads/cm^2 electrode are obtained.

While the double layer theory is described herein, it should be understood that other theories or models, such as the proton injection model, could alternatively be used.

The high surface area (porous) electrically conducting coating material is applied onto the support material.

1. Solution Methods - The porous coating material may originate from various reactive precursors in a solution or a sol-gel composition. Numerous methods of application of these precursor compositions are feasible; but not limited

to the following. A curing, hydrolysis and/or pyrolysis process usually is performed to form the coating on the support. Pyrolysis of the metal salts is usually done in a controlled atmosphere (nitrogen, oxygen, water, and/or other inert and oxidative gasses) by means of a furnace and/or an infrared source.

(a) Dip Coating - The electrode or support, is dipped into a solution or sol-gel, coating the support with a precursor coating, and subsequently cured by pyrolytic and other methods. Optionally, this process may be repeated to increase layer thickness. A preferred procedure is to dip the support material in a metal chloride/alcohol solution followed by pyrolysis at between about 250 and 500°C for 5-20 min in a 5-100% oxygen atmosphere.

This process is repeated until the desired weight of coating is obtained. A final pyrolysis treatment at 250-450°C is done for 1-10 hr. Typically about 1-30 mg/cm^2 of coating is deposited onto a support for a capacitance density of around 1-10 F per square centimeter electrode cross-sectional area. Another procedure is to create a sol-gel solution with ruthenium, silicon, titanium and/or other metal oxides and coat the support as above. By adjusting the pH, water concentration, solvent, and/or the presence of additives like oxalic acid, formamide, and/or surfactants the discharge frequency characteristics of the coating may be adjusted.

High relative humidity during the pyrolysis step can be used to complete the conversion of starting material to oxide at lower temperatures, a procedure is to pyrolyze at about 300°C without control of humidity. However, an additional procedure is to maintain the relative humidity above about 50% during this pyrolysis at temperatures below 350°C or below.

A preferred method for dip coating thin (e.g. 1 mil) support structures is to use a wire frame structure 300 to keep the support material 118 under tension (Figures 15 and 15A).

The wire frame structure 300 includes at least two (2) wires 301 and 301A of lengths larger than the width of the support material 118. Each wire 301 and 301A includes a single length of wire which is tightly coiled at each end about 360° to form two coils 302 and 303. The coils are wrapped so the ends of the coil are around 1cm above the plane of the wire. The coils 302 and 303 are placed through

holes 304 and 305, respectively, in the support materials. The holes 304 and 305 are located at two corners on an adjacent side of the support material.

Two additional wires 301B and 301C could be similarly used on the remaining two sides of the support material to provide additional support.

(b) Spray Coating - The coating solution is applied to the support by a spray method, cured, and optionally repeated to increase the thickness. A preferred procedure is to apply the coating solution to the substrate at a temperature of 0-150°C by means of an ultrasonic or other spray nozzle with a flow rate of around 0.1-5 ml/min in a carrier gas composed of nitrogen, oxygen and/or other reactive and inert gases. The coating characteristics can be controlled by the partial pressure of oxygen and other reactive gasses.

(c) Roll Coating - The precursor coating is applied by a roll coating methodology, cured, and optionally repeated to increase the thickness. The coatings described above for dip coating are usable here.

(d) Spin Coating - A spin coating methodology in the conventional art is used to apply the precursor coating, and optionally repeated.

(e) Doctor Blading - A doctor blading methodology is used to apply the precursor coating, and optionally repeated.

2. Electrophoretic Deposition - The porous coating or precursor coating is applied to the support by electrophoretic deposition techniques, and optionally repeated.

3. Chemical Vapor Deposition - The porous coating or precursor coating may be applied by chemical vapor deposition techniques known in the art.

(C) Electrode Pretreatment

It has been found that a number of pretreatments (conditioning) or combinations thereof are useful to improve the electrical characteristics of the coating (e.g. electrochemical inertness, conductivity, performance characteristics, etc.). These treatments include for example:

1. Steam - High temperature water or steam treatment controlled in atmospheres can be used to decrease the leakage current. A method procedure is to

contact the coated electrode with water saturated steam in a closed vessel at between 150 and 325°C for between 1 to 6 hr. under autogenic pressure.

2. Reactive Gas The coated electrode is contacted one or more times with a reactive gas such as oxygen, ozone, hydrogen, peroxides, carbon monoxide, nitrous oxide, nitrogen dioxide, or nitric oxide at between ambient temperature and 300°C at a reduced pressure or under pressure. A preferred procedure is to contact the coated electrode with flowing ozone at between about 5-20 weight percent in air at between ambient and 100°C and 0.1-2000 torr pressure for 0.1-3 hr.

3. Supercritical Fluid - The coated electrode is contacted with a supercritical fluid such as carbon dioxide, organic solvent, and/or water. A preferred procedure is treatment with supercritical water or carbon dioxide for 0.1-5 hrs by first raising the pressure then the temperature to supercritical conditions.

4. Electrochemical-The coated electrode is placed in a sulfuric acid electrolyte and contacted with an anodic current sufficient to evolve oxygen gas and subsequently with a cathodic current. In one embodiment the electrode is contacted with 10mA/cm^2 in 0.5M sulfuric acid for about 5 min, to evolve oxygen gas. The electrode is then switched to a cathodic current and the open circuit potential is driven back to a potential of between about 0.5V - 0.75V, preferably between 0.5 and 0.6 and more preferably about 0.5 V (vs. NHE) with out hydrogen gas evolution.

5. Reactive liquid-The coated electrode is contacted with an oxidizing liquid such as aqueous solutions of hydrogen peroxide, ozone, sulfoxide, potassium permanganate, sodium perchlorate, chromium (VI) species and/ or combinations thereof at temperatures around ambient to 100 °C for 0.1-6 hr. A preferred procedure uses a 10-100 mg/l aqueous solution of ozone at 20-50 °C for around 0.5-2 hr. followed by an aqueous wash. An additional procedure is to treat the coated electrode in a chromate or dichromate solution.

(D) Spacing between Electrodes

A number of methods are available to obtain electrical insulation and properly defined spacing between the electrodes. These methods include, for example:

1. Microprotrusions - The separator 125 and 127 between the coatings 119 and 120, includes a matrix of small (in area and height) protrusions, i.e. 125

and 127, on the surface of at least one side of the electrode. These microprotrusions may be composed of thermosets, thermoplastics, elastomers, ceramics, or other electrically insulating materials.

Several methods of applying these microprotrusions are included, but not limited to:

(a) Screen Printing - The microprotrusions are placed on the electrode surface by conventional screen printing, as described below, in greater detail, under the heading "SCREEN PRINTING". Various elastomers, thermosets, photo curable plastics, and thermoplastics are applied in this way. A preferred procedure is to use an acid resistant epoxy or VITON® solution.

(b) Chemical Vapor Deposition - Microprotrusions are also placed on the electrode surface by depositing silica, titania and/or other insulating oxides or materials through a mask.

(c) Photolithography - Microprotrusions are also produced by means of a photolithographic methods, as is described later, in greater detail, under the heading "PHOTOLITHOGRAPHIC PRODUCTION OF MICROPROTRUSIONS".

2. Physically thin separator sheet - The separator between the electrodes is a thin, substantially open structure material such as glass. A preferred material is 0.001-0.005 in (0.00254 to 0.01270 cm) porous glass sheet available from Whatman Paper Ltd located in Clifton, NJ.

3. Casting a separator - The separator between the porous material is also obtained by casting a thin, substantially open structure film such as for example NAFION®, polysulfones, or various aero- and sol-gels.

4. Air space - The separator between the electrodes is also an air space which is subsequently occupied by the non-aqueous or aqueous electrolyte.

(E) Gasketing

The materials used for the gaskets, such as the gaskets 121, 123, 135, 137, 157 and 159, at the edge of the active electrode surface include any organic polymer which is stable in the electrical/chemical environment, and to the processing conditions. Suitable polymers include, for example polyimide, TEFZEL®, polyethylene (high and low density), polypropylene, other polyolefins, polysulfone, KRATON®

other fluorinated or partly fluorinated polymers or combinations thereof. The gasket may be applied as a preformed material, screen printed, or by other methods.

(F) Cord for Fill Port

The cord (117A, 117B and 117C) for the creation of the fill ports, such as the fill ports 122 and 142, is of any suitable material having some specific properties, e.g., it is different from the gasket materials, has a higher melting temperature (Tm) than the gasket material, and does not melt, flow or adhere to the gasket material under the heating conditions described herein. Generally, glass, metal, ceramic, and organic polymers or combinations thereof are used.

(G) Stacking

A stack is created by starting with an endplate and alternating gasket material, cord, electrode, gasket, cord electrode until the desired number of cells are created finishing with a second endplate, and optionally with a gasket material on the top outside of the stack.

(H) Assembling (heating and cooling)

The stack is heated under pressure to cause reflow of the gasket material, adhering and sealing the perimeter of the electrode materials to the adjacent electrode in the stack; thereby, creating isolated cells and an assembled stack unit. This is done in an inert atmosphere.

(a) Radio Frequency Induction Heating (RFIH) is used to heat the stack to cause reflow of the gasket material.

(b) Radiant Heating (RH) is used to uniformly heat the stack to cause reflow of the gasket material. A preferred method is to use 1-100 μm radiation at 0.5-10 watts/cm^2 for 1-20 min.

(c) Conductive and/or convective heating in a furnace, optionally in an inert atmosphere, is used to heat the stack to cause reflow of the gasket material.

(I) Creating the fill port

The cords are pulled to remove them from the assembled unit to create a dry preunit having at least one fill port per a cell.

(J) Post-Conditioning

1. A number of post-conditioning reactive gas treatments of the stack or assembled stack or combinations thereof are useful to improve the overall and long term electrical characteristics of the electrode and resulting device. These include either before step (H) and/or after step (I) treatment with hydrogen, nitric oxide, carbon monoxide, ammonia, and other reducing gasses or combinations thereof at between ambient temperature and the Tm of the gasket material at a reduced pressure or under pressure.

2. A second post conditioning commonly done is to adjust the open circuit potential of the electrode after step (F) and stack the electrode in an inert atmosphere (e.g. Ar, N_2). This is done by using a cathodic current without hydrogen evolution.

(K) Filling of Dry Preunit

The dry preunit is filled with an ionically conducting aqueous or non-aqueous electrolyte.

A preferred electrolyte is approximately 30% sulfuric acid in water due to the high conductivity. Non-aqueous electrolytes based on propylene and ethylene carbonate are also used to obtain larger than 1.2V/cell potentials.

A preferred procedure for filling the dry preunit with liquid electrolyte is to place the preunit in a chamber, evacuate the chamber between about 1 torr to 1 microtorr, preferably about 250 mtorr to less than 1 torr, and introduce the electrolyte; thereby, filling the cell gaps with electrolyte through the fill ports. Alternatively, the preunit may be placed in the electrolyte and a vacuum pulled; thereby causing the gas in the cell gaps to be removed and replaced by the electrolyte.

In addition, non liquid based electrolytes (e.g. solid and polymer) may be used. In those cases the electrode is coated with the electrolyte before reflow and a fill port is not required.

(L) Sealing of Fill Ports

The fill ports are sealed by reflowing an additional film of polymer the same or different over the openings to create a sealed device. This is commonly done with an induction heater, which locally heats the film over the fill port opening.

(M) Burn-In

The device is brought to full charge usually by charging the device in 0.1 V/cell steps at a charging current of about 4 mA/cm^2.

(N) Testing

Termination Methods -- Several methods are used to make electrical connections to the ultracapacitor endplates, and are described below.

1. Endplate Tabs (160 and 160A) - The endplates (111A and 111Z) themselves have been cut to extend out beyond the normal gasket perimeter. These extensions allow attachment of a wire or ribbon. Typically, the extension is a stub from which all oxide material is removed down to the bare support material; 5 mil (0.0127 cm) thick nickel ribbon is spot welded to the stub.

2. Silver Epoxy - The oxide coating is removed from the exposed faces of the endplates or the endplates may be coated only on one side. Clean nickel foil leads or copper plates make electrical connection to the exposed faces by bonding them together with a conductive silver epoxy. Optionally, the oxide coating is present.

3. Lugs - Threaded titanium nuts are welded to the thick titanium endplates before coating. Electrical connection to the titanium nuts is achieved by screw attachment.

4. Press Contacts - The oxide is removed or the endplates may be coated only on one side from the exposed side of the endplates before assembly into the device stack. The bare support material e.g. titanium, is reverse sputtered to clean the surface, being careful not to overheat the substrate. The clean surface is then sputtered with titanium to lay down a clean adhesion layer, followed by gold. The gold acts as a low contact resistance surface to which electrical contact can be made by pressing or by wire bonding.

5. Deposition of a compatible medium such for example aluminum, gold, silver, etc. outside by CVD or other means.

The device resistance is measured at 1 kHz. The device capacitance is determined by measuring the coulombs needed to bring the device to full charge at a

charging rate of around 4 mA/cm^2 of electrode area. Leakage current is measured as the current needed to maintain a full charge after 30 min. of charging.

These devices may be made in various configurations depending on the desired application. By adjusting the device voltage, cell voltage, electrode area, and/or coating thickness in a rational manner, devices made to fit defined and predetermined specifications are constructed.

The electrode capacitance density (C' in units of F/cm^2) is roughly 1 F/cm^2 for every 10 μm of coating. Therefore, for large capacitance values a thicker coat is used. The device capacitance (C) is equal to the electrode capacitance density times the electrode area (A in units of cm^2) divided by two times the number of cells (n) (equation 1).

The leakage current (i") is proportional to the electrode area, while the equivalent series resistance (ESR) is inversely proportional to the electrode area (eqn. 2). Typical values for i" are less than 20 μA/cm^2.

The total number of cells in a device (n) is equal to the cell voltage (V') divided by the total device voltage (V) (eqn. 3). Cell voltages up to about 1.2 V can be used with aqueous based electrolytes.

The device height (h), based on a cell gap (h') and a support thickness (h"), is determined from the number of cells and the electrode capacitance density in units of cm by equation 4.

The device ESR is a function of the number of cells times the cell gap (h') times the resistivity of the electrolyte (r) times a factor of about 2 divided by the area (equation 5).

eqn. 1 $C = C'A/2n$

eqn. 2 $i'' \propto A \propto 1/ESR$

eqn. 3 $n = V/V'$

eqn. 4 $h/cm = n(0.002C' + h' + h'')$

eqn. 5 $ESR \approx 2nh'r/A$

Devices are constructed to meet the requirements of various applications by considering the voltage, energy, and resistance requirements. The following examples are not meant to be limiting in any way:

For electric vehicle applications about a 100 KJ to 3 MJ device is used. A large voltage (about 100 to 1000 V) large energy (1-5 F/cm^2) storage device is used with an electrode area of about 100 to 10,000 cm^2.

For electrically heated catalyst applications for reduction of automobile cold start emissions about a 10 to 80 KJ device is used. This device is about 12 to 50 V constructed with around 100 to 1000 cm^2 area electrodes of 1-5 F/cm^2. Optionally, a device consisting of several devices in parallel can be constructed to meet the electrical requirements.

For defibrillator applications about a 200-400 V device with 0.5 to 10 cm^2 area electrodes of 1-3 F/cm^2 are used.

For uninterruptable power source applications various series/parallel device configurations may be used.

Screen Printing

Considering now a screenprinting method 250, with respect to Figures 7 and 8, the focus of the method 250, is to produce a series of microprotrusions 125 and 127 on the surface of the coating layers, to act as a space separator in electrical storage devices, such as a capacitor or a battery, in general, and in the dry preunit energy storage device 10, in particular.

The substrate is usually a thin metal such as titanium, zirconium, or alloys thereof. The substrate is usually in the shape of a thin metal plate as is conventional in the capacitor art.

The substrate is coated on one or both sides with a porous carbon compound or a porous oxide coating. This step is accomplished by methods conventional in the art. The oxide coating serves as the charge storage area for the device.

Alternately, a stacked set of battery electrodes (e.g., lead for lead acid) or electrolytic capacitor electrodes (e.g., alumina and tantalum) may be fabricated.

It is important that the flat surfaces of adjacent coated substrates or electrodes do not contact each other and further be of a uniform separation. The epoxy microprotrusions accomplish the desired uniform separation.

Sample Holding -- The coated thin flat substrate needs to be secured (or held), so that the formation of the microprotrusions is precise and accurate on the

flat surface of the substrate. For thin metal sheets (0.1 to 5 mil (0.000254 to 0.0127 cm), especially about 1 mil (0.00254 cm)) an electrode holder 275 is particularly important. If a strong vacuum is pulled on a thin sheet, often reverse dimples are formed in the thin sheet which cause significant undesirable changes in the physical and electrical properties of the final device.

The electrode holder 275 includes a porous ceramic holder 276, which is useful because the pore size is small enough that the dimples do not appear when a mild or stronger vacuum is pulled. The flat ceramic surface of the ceramic holder 276 must be in intimate contact with the surface of the electrode 111A, under conditions which do not deform the metal or disrupt the coating present. The vacuum used with the porous ceramic is at least 25 in mercury. Preferably the vacuum is between about 25 and 30 in., especially 26 and 29 in.

Further, the ceramic substrate needs to be flush with the surface of any mechanical holder to assure that uniform extrusion of the epoxy through the screen openings occurs. Flush in this context means that the flat surface of the holder and the surface of the coating for electrical storage differ from each other by between about ± 5 mil (0.0127 cm) deviation or less from level per 6 linear in.

The electrode holder 275 further includes a metal frame 277, which should also be as flush (flat) as possible so that uniformly sized protrusions are formed from one end of the electrode to the other.

The electrode holder 275 can be purchased from a number of commercial sources for example from Ceramicon Designs, Golden, Colorado. Alternatively, the sample holder 276 can be manufactured using commercially available metals, alloys or ceramics.

Usually, a 5 in (12.7 cm) by 7 in (17.78 cm) coated sheet electrode is formed.

The metal holder 277 has a plurality of strategically located pins, such as the three pins 278, 279 and 280, which are used to align and position the electrode 111A, using a plurality of corresponding holes 281, 282 and 283, respectively. The holes 281, 282 and 283 are usually as close to the peripheral edges of the electrode

111A, as possible to conserve useful electrode surface. Alternatively, no alignment holes are used, and the pins are used to align the electrode edges.

A stencil (not shown) having a predetermined open pattern, is stretched and secured in a conventional screen printing frame (not shown). The screen mesh is removed.

The epoxy components are mixed and the fluid epoxy is placed on the surface of the stencil, then spread to obtain an even applied coat. This can be accomplished using a pressure bar, doctor bar or a squeegee.

Usually, constant temperature and humidity are important to obtain an even coat.

The stencil is then carefully removed leaving the fluid epoxy protrusions on the surface of the oxide. The epoxide protrusions are then cured using ambient, accelerated heat at from between 100 to 150°C. or light.

The electrode having microprotrusions is then combined with other electrodes, and assembled in a wet process or a dry process. If a dry process is used, the dry unit 10 is then back filled with electrolyte, when it is to be charged.

It is important that the cured epoxy does not react with the liquid electrolyte eventually used in the fabrication of the capacitor having multiple layers of electrodes.

The cured microprotrusions then perform their function by keeping the spacing between the electrodes uniform.

As can be seen from Figure 6, the edges of the flat surface of the electrode have protrusions 125 that are closer together than those protrusions 127 in the active or central portion of the electrode. These protrusions 125 increase the support at the edges to maintain uniform separations. Alternatively, bars may be used.

It is apparent that from these teachings the following are possible:

Increasing or decreasing the substrate electrode thickness will allow an increase or decrease in the microprotrusion spacing due to changes in support rigidity.

Other thermosets, thermoelastomers, or photo curable epoxies or epoxy derivatives conventional in the art can be used.

Other microprotrusion pattern elements can be used such as squares, lines, crosses, etc. Specifically, bars on the perimeter can add mechanical support.

Optionally the screen may be heated, if necessary to bring the resin flowable epoxy to a temperature when its viscosity becomes suitable for printing for a short time.

This heating step followed by screen printing of the flowable epoxy resin must be performed quickly because the working time for the epoxy is significantly reduced.

The electrical storage devices produced having the microprotusions 125 and 127 are useful as batteries, capacitors and the like.

Photolithographic Production of Microprotrusions

The focus of the present method is to produce a series of microprotrusions on the surface, or alloys of the electrode substrate, using photolithography, with respect to Figures 10, 11 and 12. The substrate is usually in the shape of a thin metal plate as is conventional in the capacitor art.

A photo resist film 381 is applied to the surface of the electrode 111A, either by vacuum lamination using the commercially available Dynachem ConforMASK film applicator, and Dynachem vacuum applicator Model 724/730, or by passing the photo resist film 381 and electrode 111A through a pair of heated rollers 384 and 385.

Exposure is done using a standard 1-7kW UV exposure source, such as mercury vapor lamps 389.

The ConforMask film applicator is developed using standard conditions such as 0.5-1.0% sodium or potassium carbonate monohydrate in either a developing tank or a conveyorized aqueous developer. Optionally, after developing the electrode with microprotrusions may be neutralized in a dilute 10% sulfuric acid solution. This removes all the unwanted unreacted film to leave the reacted microprotrusions adhered to the electrode surface.

To obtain optimum physical and electrical performance properties the resulting material is put through a final curing process involving both UV irradiation and thermal treatment utilizing conventional UV curing units and convection air ovens.

The multiple electrodes are assembled to produce for instance a capacitor, as described above. The microprotrusions accomplish the desired uniform separation.

COMMERCIAL APPLICATIONS

The energy storage device 10A has a multitude of applications, as a primary or back up power supply, and/or as a capacitor. The size is from 0.1 volt to 100,000 volts or $0.1cm^3$ to 10^6 cm^3. Typical voltage ranges may include combinations of uses in automotive and other applications.

Among these applications are the following:

Automobile Applications	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
Airbags & Seat Restraints	1-100	1-1000
Seat Warmers	1-100	1-100
Electronically Heated Catalyst	1-1000	1-1,000,000
Electric Vehicle Propulsion	100-1000	100-1,000,000
Hybrid Electric Vehicle Propulsion	1-1000	10-100,000
Internal Combustion/Ultra Capacitor Propulsion	1-1000	100-100,000
Power Steering	1-1000	1-100
Regenerative Braking/Shock Absorption	1-1000	5-100
Starting Lighting and Ignition with battery	1-1000	2-100
Starting Lighting and Ignition stand alone	1-100	1-100
Medical Applications		
Cardiac Defibrillators	10-500	0.1-100
Pacemakers	1-300	0.1-300
Neuro stimulators and like	0.1-300	0.1-300
Implantable and external devices	0.1-300	0.1-300
Surgical Power Tools	10-700	1-10

	Medical Applications (cont)	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
	Ambulatory Monitoring Equipment	1-100	1-100
5	Automatic Liquid Chromatography	1-100	1-20
	Automated Clinical Lab Analysis	1-100	1-20
	Computerized Tomography (CT) Scanners	1-1000	1-100
	Dental Equipment	1-200	1-10
	Digital Radiography Equipment	1-500	1-1000
10	Electrosurgical Instruments	1-200	1-10
	Fiberoptics	1-100	1-100
	Examination Scopes	1-100	1-10
	Hearing Aids	1-10	0.1-1.0
	Infusion Devices	1-100	0.1-10
15	Magnetic Resonance Imaging (MRI)	1-1000	1-1000
	Nuclear Medical Diagnostic Equipment	1-1000	1-100
	Electric Patient Monitoring Systems	1-200	1-100
	Respiratory Therapy Equipment	1-500	1-100
	Surgical Lasers	1-1000	1-1000
20	Electric Surgical Support Systems	1-100	1-1000
	Ultrasonic Diagnostic Equipment	1-100	1-100
	Mobile Propulsion Systems		
	Fork lifts	1-1000	100-10,000
	Golf carts	1-1000	100-10,000
25	Farm Implements Trains Subways	1-1000	100-100,000
	Regenerative Braking	1-1000	1-100
	Business/Commercial Electronics Applications		
	Calculators	1-120	0.5-10
	Cellular Telecommunications	1-120	1-100
30	Commercial Audio Amplifiers	1-1000	1-10
	Commercial Flash/Strobe Lights	1-1000	1-10
	Commercial Power Tools	1-1000	1-100

Business/Commercial Electronics (cont)	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
Commercial Video Cameras	1-120	1-10
Computers	1-120	1-10
Copiers	1-120	1-10
Dictation Equipment	1-100	1-1000
Electric Motors	1-1000	1-1000
Electronic Locks	1-120	1-10
Electronic Organizers/PDAs	1-100	1-5
Emergency Lighting Systems	1-440	1-1000
Facsimile Equipment	1-120	1-10
Microphones	1-120	1-3
Pagers	1-120	1-2
Printers	1-120	1-10
Security Systems	1-120	1-100
Slide Projectors	1-120	1-100
Uninterruptible Power Supplies	1-1000	1-100,000
Surge Protectors	1-1000	1-100,000
Wireless Networks	1-1000	1-1000
Consumer Electronics Applications		
Audio Systems:		
Compact/Home	1-120	1-10
Portable Tape/CD	1-120	1-5
Walkman/Personal Stereo	1-120	1-5
CB Radios	1-120	1-10
HAM Radios	1-120	1-100
Camcorders	1-120	1-10
Home Satellite Dishes	1-120	1-10
Microphones	1-120	1-3
Monitors and Cathode Ray Tubes	1-1000	1-100
Photo Flash	1-1000	1-3

	Consumer Electronics Applications (cont)	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
	Receivers, Transceivers	1-1000	1-10
	Telephone answering devices	1-120	1-5
5	Cellular, cordless phones	1-120	1-3
	Toys & Games	1-120	1-10
	Television sets	1-1000	1-10
	Home	1-1000	1-10
	Portable	1-1000	1-10
10	VCRs	1-120	1-10
	Video Disk Players	1-120	1-10
	Video Games	1-120	1-10
	Watches/Clocks	1-120	1-100
	Consumer Electric Housewares Applications		
15	Air Purifiers	1-120	1-100
	Bag Sealers	1-500	1-100
	Blenders	1-120	1-10
	Clocks-Total	1-120	1-100
	Alarm & Desk	1-120	1-10
20	Coffee Grinders	1-120	1-10
	Coffee Makers	1-120	1-10
	Convection Ovens	1-1000	1-1000
	Corn Poppers	1-120	1-10
	Curling Irons/Brushes	1-120	1-5
25	Deep Fryers	1-230	1-100
	Electric Blankets	1-120	1-10
	Flashlights	1-100	1-10
	Floor Polishers	1-220	1-100
	Food Processors	1-120	1-10
30	Hair Dryers	1-120	1-5
	Heating Pads	1-120	1-5

(Cont) Consumer Electric Housewares Applications	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
Home Security Systems	1-120	1-100
Irons	1-120	1-5
Knives	1-120	1-3
Massagers	1-120	1-5
Mixers	1-120	1-5
Microwave Ovens	1-230	1-10
Power Tools	1-230	1-100
Security Systems	1-230	1-100
Shavers	1-120	1-3
Smoke Detectors	1-120	1-5
Timers	1-120	1-3
Toasters/Toaster Ovens	1-120	1-5
Toothbrushes (Electric)	1-120	1-3
Vaporizers	1-120	1-10
Water Pulsators	1-120	1-10
Whirlpools (Portable)	1-120	1-100
Consumer Major Appliances		
Compactors	1-120	1-10
Dishwashers	1-220	1-100
Dryers	1-120	1-100
Freezers	1-220	1-100
Ranges	1-220	1-1000
Refrigerators	1-120	1-100
Washers	1-220	1-100
Water Heaters	1-220	1-100
Outdoor Appliances		
Bug Killers	1-120	1-10
Outdoor Grills	1-120	1-100
Power Mowers	1-220	1-100

Outdoor Appliances (cont)	TYPICAL Volt RANGE	TYPICAL SIZE(cm^3)
Riding Mowers	1-1000	1-1000
Riding Tractors	1-1000	1-10,000
Rotary Tillers	1-1000	1-10,000
Snow Plows/Blowers	1-220	1-1000
Weed Trimmers	1-220	1-100
Other Applications		
Electro-expulsive Deicing	1-1000	1-100
Electronic Fuses	1-1000	1-10
Lasers	1-1000	1-100
Phased-Array radar	1-1000	1-1000
Rail Gun	1-1000	1-10,000

Multiple devices are placed is series and/or parallel for specific applications to achieve desired performance.

Fabrication of Dry Preunit

The following examples are presented to be descriptive and explanatory only. They are not to be construed to be limiting in any manner.

EXAMPLE 1

Fabrication of A Dry Preunit

(A) Coating Method

The support structure is prepared by etching a 1 mil (0.00254 cm) titanium sheet with 35% HNO_3/1.5 % HF at 60°C for 5 min. The end plates are 5 mil (0.0127 cm) titanium.

The oxide coating solution is 0.2 M ruthenium trichloride trihydrate and 0.2 M niobium pentachloride in tert-butanol (reagent grade).

The etched Ti sheets are dip-coated by immersion into the solution at ambient conditions. The coated sheet is submerged into the solution, held for about 1 sec and then removed.

After each coating, the oxide is dried at 70°C for 10 min, pyrolyzed at 350°C for 10 min and removed to cool to ambient temperature all in ambient atmosphere.

The dip-coating steps are repeated for 10 coats (or any desired number) rotating the Ti sheet so as to dip with alternate sides down. A thickness of about ten microns is achieved.

The fully coated sheet is final annealed at 350°C for 3 hrs in ambient atmosphere.

(B) Electrode Pretreatment

The coated electrode is contacted with saturated steam in a closed vessel at 280°C for 3 hrs under autogenic pressure.

(C) Spacing

Microprotrusions are screen printed on one side of the electrode, as described below, in greater detail, under the heading "SCREEN PRINTING". The epoxy compound is EP21AR from Masterbond, of Hackensack, New Jersey.

The epoxy protrusions are cured at 150°C for 4 hr. in air. The coated electrodes are next die-stamped to the desired shape.

(D) Gasket

A modified high density polyethylene (HDPE, improved puncture resistance and adhesion) 1.5 mil (0.00381 cm) thick by 30 mil (0.0762 cm) wide with outside perimeter the same as that of the electrode is placed on the electrodes on the same side as the microprotrusions and impulse heat laminated. The HDPE is grade PJX 2242 from Phillips-Joanna of Ladd, Illinois.

(E) Cord

One cord (Dupont T^2 TEFZEL® film 90ZM slit in machine direction) 0.9 mil (0.00229 cm) thick by 10 mil (0.0254 cm) wide is placed across the narrow dimension of the gasket and electrode surface and aligned between microprotrusions. The location of the cord is one of three positions centered, left of center, or right of center.

A second HDPE gasket is placed on the first gasket sandwiching the cord between the two gaskets.

The second gasket is impulse heated to adhere to the first gasket and to fix the cord in place.

(F) Stacking

Electrode/microprotrusion/gasket/cord/gasket units are stacked in a non-metallic (ceramic) alignment fixture beginning with a 5 mil (0.0127 cm) end plate unit to the desired number of cells and ending with a plain 5 mil (0.0127 cm) end plate with the cords arranged such that the location is staggered-left, center, right in a three unit repeating cycle (end perspective). Light pressure is applied to the top of the stack through a ceramic piston block to maintain uniform alignment and contact throughout the stack.

(G) Reflow

A radio frequency induction heater (2.5 kW) is used to heat the stack. The stack was placed centrally in the three turn, 3 in (7.62 cm) diameter coil and heated for 90 seconds at a power setting of 32 %. The fused unit is allowed to cool to ambient temperature.

(H) Cord Removal

The cords are removed by carefully pulling the exposed ends of the cord to leave the open fill ports.

EXAMPLE 2

Alternative Fabrication of Dry Preunit

(A) Coating Method

The support structure is prepared by etching a 1 mil (0.00254 cm) titanium sheet with 50% HCl at 75°C for 30 min. The end plates are 2 mil (0.00508 cm) titanium.

The oxide coating solution is 0.3 M ruthenium trichloride trihydrate and 0.2 M tantalum pentachloride in isopropanol (reagent grade).

The etched Ti sheets are dip-coated by immersion into the solution at ambient conditions. The coated sheet is submerged into the solution, held for about 1 sec and then removed.

After each coating, the oxide is dried at 70°C for 10 min. in ambient atmosphere, pyrolyzed at 330°C for 15 min in a 3 cubic feet per hrs. flow of 50 vol.

% oxygen and 50 % nitrogen, and removed to cool to ambient temperature in ambient atmosphere.

The dip-coating steps are repeated for 30 coats (or any desired number) rotating the Ti sheet so as to dip with alternate sides down.

The fully coated sheet is final annealed at the above conditions for 3 hr.

(C) Spacing

VITON® microprotrusions are screen printed on one side of the electrode, as described below, in greater detail, under the heading "VII. SCREEN PRINTING".

The VITON® protrusions are cured at 150°C for 30 min. in air. The coated electrodes are next die-stamped to the desired shape.

(D) Gasket

A modified high density polyethylene (HDPE, improved puncture resistance and adhesion) 1.0 mil (0.00254 cm) thick by 20 mil (0.0508 cm) wide with outside perimeter the same as that of the electrode is impulse heat laminated to both sides of the electrode. The HDPE is grade PJX 2242 from Phillips-Joanna of Ladd, Illinois.

(E) Cord

One cord, 1 mil (0.00254 cm) diameter TEFLON® coated tungsten wire is placed across the narrow dimension of the gasket and electrode surface and aligned between microprotrusions. The location of the cord is one of three positions centered, left of center, or right of center.

(F) Stacking

Electrode/microprotrusion/gasket/cord/gasket units are stacked beginning with a 2 mil (0.00508 cm) end plate unit to the desired number of cells and ending with a plain 2 mil (0.00508 cm) end plate with the cords arranged such that the location is staggered-left, center, right in a three unit repeating cycle (end perspective).

(G) Reflow

The HDPE gasket is reflowed in nitrogen at 125°C for 120 min to reflow the thermoplastic. The unit is cooled in nitrogen to ambient temperature.

(H) Cord Removal

The cords are removed by pulling the exposed ends to leave the open fill ports.

EXAMPLE 3

Alternative Fabrication of Dry Preunit

(A) Coating Method

The support structure is prepared by etching a 1 mil (0.00254 cm) titanium sheet with 50% Hcl at 75°C for 30 min. The end plates are 10 mil (0.0254 cm) titanium.

The oxide coating solution is 0.2 M ruthenium trichloride trihydrate and 0.2 M tantalum pentachloride in isopropanol (reagent grade).

The etched Ti sheets are dip-coated by immersion into the solution at ambient conditions. The coated sheet is submerged into the solution, held for about 1 sec and then removed.

After each coating, the oxide is dried at 70°C for 10 min, pyrolyzed at 300°C for 5 min and removed to cool to ambient temperature all in ambient atmosphere.

The dip-coating steps are repeated for 10 coats (or any desired number) rotating the Ti sheet so as to dip with alternate sides down.

The fully coated sheet is final annealed at 300°C for 3 hrs in ambient atmosphere.

(B) Electrode Pretreatment

The coated electrode is contacted with saturated steam in a closed vessel at 260°C for 2 hrs under autogenic pressure.

(C) Spacing

Microprotrusions are screen printed on one side of the electrode, as described below, in greater detail, under the heading "SCREEN PRINTING". The epoxy compound is grade EP21AR from Masterbond, Hackensack, NJ.

The epoxy protrusions are cured at 150°C for 4 hr. in air. The coated electrodes are next die-stamped to the desired shape.

(D) Gasket

A modified high density polyethylene (HDPE, improved puncture resistance and adhesion) 1.5 mil (0.00381 cm) thick by 30 mil (0.0762 cm) wide with outside perimeter the same as that of the electrode is placed on the electrodes on same side

as the microprotrusions and impulse heat laminated. The HDPE® is grade PJX 2242 from Phillips-Joanna of Ladd, Illinois.

(E) Cord

One cord (TEFZEL®) 1 mil (0.00254 cm) thick by 10 mil (0.0254 cm) wide is placed across the narrow dimension of the gasket and electrode surface and aligned between microprotrusions. The location of the cord is one of three positions centered, left of center, or right of center.

A second HDPE® gasket is placed on the first gasket sandwiching the cord between the two gaskets.

The second gasket is impulse heated to adhere to the first gasket and to fix the cord in place.

(F) Stacking

Electrode/microprotrusion/gasket/cord/gasket units are stacked beginning with a 10 mil (0.0254 cm) end plate unit to the desired number of cells and ending with a plain 10 mil (0.0254 cm) end plate with the cords arranged such that the location is staggered-left, center, right in a three unit repeating cycle (end perspective).

(G) Reflow

The gasket is reflowed in nitrogen at 160°C for 45 min to reflow the thermoplastic. The unit is cooled in nitrogen to ambient temperature.

(H) Cord Removal

The cords are removed by carefully pulling the exposed ends to leave the open fill ports.

EXAMPLE 4

Alternative Fabrication of Dry Preunit

(A) Coating Method

The support structure is prepared by etching a 1 mil (0.00254 cm) titanium sheet with 50% HCl at 75°C for 30 min. The end plates are 5 mil (0.0127 cm) titanium.

The oxide coating solution is 0.2 M ruthenium trichloride trihydrate and 0.2 M Ti(di-isopropoxide)bis 2,4-pentanedionate in ethanol (reagent grade).

The etched Ti sheets are dip-coated by immersion into the solution at ambient conditions. The coated sheet is submerged into the solution, held for about 1 sec and then removed.

After each coating, the oxide is dried at 70°C for 10 min, pyrolyzed at 350°C for 5 min in oxygen and removed to cool to ambient temperature all in ambient atmosphere.

The dip-coating steps are repeated for 30 coats (or any desired number) rotating the Ti sheet so as to dip with alternate sides down.

The fully coated sheet is final annealed at 350°C for 3 hrs in an oxygen atmosphere.

(C) Spacing

Microprotrusions are thermally sprayed through a mask on one side of the electrode. The thermal spray material is TEFLON® from E.I. DuPont de Nemours & Co., Wilmington, Delaware.

The TEFLON® protrusions are cured at 300°C for 0.5 hr. in air. The coated electrodes are next die-stamped to the desired shape.

(D) Gasket

A modified high density polyethylene (HDPE, improved puncture resistance and adhesion) 1.5 mil (0.00381 cm) thick by 30 mil (0.0762 cm) wide with outside perimeter the same as that of the electrode is placed on the electrodes on same side as the microprotrusions and impulse heat laminated. The HDPE is grade PJX 2242 from Phillips-Joanna of Ladd, Illinois.

(E) Cord

One cord (TEFZEL®) 1 mil (0.00254 cm) thick by 10 mil (0.0254 cm) wide is placed across the narrow dimension of the gasket and electrode surface and aligned between microprotrusions. The location of the cord is one of three positions centered, left of center, or right of center.

A second HDPE® gasket is placed on the first gasket sandwiching the cord between the two gaskets.

The second gasket is impulse heated to adhere to the first gasket and to fix the cord in place.

(F) Stacking

Electrode/microprotrusion/gasket/cord/gasket units are stacked beginning with a 5 mil (0.0127 cm) end plate unit to the desired number of cells and ending with a plain 5 mil (0.0127 cm) end plate with the cords arranged such that the location is staggered-left, center, right in a three unit repeating cycle (end perspective).

(G) Reflow

The gasket is reflowed in nitrogen at 190°C for 30 min. to reflow the thermoplastic. The unit is cooled in nitrogen to ambient temperature.

(H) Cord Removal

The cords are removed by carefully pulling the exposed ends to leave the open fill ports.

EXAMPLE 5

Alternative Fabrication of Dry Preunit

(A) Coating Method

The support structure is prepared by etching a 0.8 mil (0.002032 cm) zirconium sheet with 1%HF/20% HNO_3 at 20 °C for 1 min. The end plates are 2 mil (0.00508 cm) zirconium.

The oxide coating solution is 0.2 M ruthenium trichloride trihydrate and 0.1 M tantalum pentachloride in isopropanol (reagent grade).

The etched Ti sheets are dip-coated by immersion into the solution at ambient conditions. The coated sheet is submerged into the solution, held for about 1 sec and then removed.

After each coating, the oxide is dried at 85°C for 10 min, pyrolyzed at 310°C for 7 min and removed to cool to ambient temperature all in ambient atmosphere.

The dip-coating steps are repeated for 10 coats (or any desired number) rotating the Ti sheet so as to dip with alternate sides down.

The fully coated sheet is final annealed at 310°C for 2 hrs in ambient atmosphere.

(C) Spacing

Microprotrusions are thermally sprayed through a mask on one side of the electrode. The thermal spray material is TEFLON® from E.I. DuPont de Nemours & Co., Wilmington, Delaware.

The TEFLON® protrusions are cured at 310°C for 1.0 hr. in air. The coated electrodes are next die-stamped to the desired shape.

(D) Gasket

A polypropylene gasket 1.5 mil (0.00381 cm) thick by 30 mil (0.0762 cm) wide with outside perimeter the same as that of the electrode is placed on the electrodes on same side as the microprotrusions and impulse heat laminated.

(E) Cord

One cord, 1 mil (0.00254 cm) diameter TEFLON® coated tungsten wire, is placed across the narrow dimension of the gasket and electrode surface and aligned between microprotrusions. The location of the cord is one of three positions centered, left of center, or right of center.

A second polypropylene gasket is placed on the first gasket sandwiching the cord between the two gaskets.

The second gasket is impulse heated to adhere to the first gasket and to fix the cord in place.

(F) Stacking

Electrode/microprotrusion/gasket/cord/gasket units are stacked beginning with a 2 mil (0.00508 cm) end plate unit to the desired number of cells and ending with a plain 2 mil (0.00508 cm) end plate with the cords arranged such that the location is staggered-left, center, right in a three unit repeating cycle (end perspective).

(G) Reflow

The gasket is reflowed in nitrogen at 195°C for 60 min. to reflow the thermoplastic. The unit is cooled in nitrogen to ambient temperature.

(H) Cord Removal

The cords are removed by pulling the exposed ends to leave the open fill ports.

EXAMPLE 6

Filling of the Cell Gap Space

A dry preunit 10 may be filled with an electrolyte with the following procedure. Any of many possible dry preunit configurations may be used.

(H) Back Fill

The cords are removed manually to open the fill port. The stacked unit is placed into an evacuation chamber and evacuated to < 35 mtorr for 5 to 60 min. The liquid electrolyte 3.8 M H_2SO_4 de-airated with nitrogen is introduced into the chamber and fills the evacuated space between the electrodes.

(I) Seal Fill Port Openings

The electrolyte filled preunit is removed from the chamber. It is rinsed with deionized water to remove excess electrolyte and dried. HDPE film (1.5 mil (0.00381 cm) thick) is placed over the fill port openings and impulse heat sealed over the ports.

(J) Conditioning

The device is charged up to full charge beginning at 0.1 V/cell increasing by 0.1 V/cell until 1 V/cell is obtained.

(K) Testing

The device is tested in the conventional manner, having 1 V/cell with leakage current of less than 25 $\mu A/cm^2$, and a capacitance density per a cell of greater than about 0.1 F/cm^2. A 10 V device has a height of no more than 0.05", a 40 V device has a height of no more than 0.13", and a 100 V device has a height of no more than 0.27".

Performance characteristics for various device geometries and configurations based on a sulfuric acid electrolyte are presented in Table 1.

Table 1

Ultracapacitor Device Performance Characteristics

Area/cm^2	2	2	2	2	25	25
volt	10	40	100	100	100	100
C/mF	26	6.7	2.6	10	150	753
ESR/mohm	100	330	780	780	62	70
vol/cc	0.29	0.73	1.6	1.6	11	32
J/cc	4.5	7.4	8.1	31	69	111A

watt/cc	860	1660	2000	2000	3670	1100

EXAMPLE 7

Alternative Backfill of Dry Preunit

A dry preunit 10 may be filled with an electrolyte with the following procedure. Any of many possible dry preunit configurations may be used.

(H) Back Fill

The cords are removed to open the fill port. The stacked unit is placed into an evacuation chamber and evacuated to < 35 mtorr for 5 to 60 min. The liquid non-aqueous electrolyte 0.5 M KPF_6 in propylene carbonate de-airated with nitrogen is introduced into the chamber and fills the evacuated space between the electrodes.

(I) Seal Fill Port Openings

The electrolyte filled preunit is removed from the chamber and excess electrolyte is removed. HDPE film (1.5 mil (0.00381 cm) thick) is placed over the fill port openings and impulse heat sealed over the ports.

(J) Conditioning

The device is charged up to full charge beginning at 0.1 V/cell increasing by 0.1 V/cell until 1.5 V/cell is obtained.

(K) Testing

The device is tested in the conventional manner, having 1.5 V/cell with leakage current of around 100 $\mu A/cm^2$, and a capacitance density of around 4 Mf/cm^2 for a 10 cell device.

EXAMPLE 8

DEVICE POST-TREATMENT CONDITIONS

The following is a list of the electrical properties (Table 3) of devices using various gas postconditioning techniques to adjust the electrode rest potential so that charging to at least 1 V/cell on multicell devices filled with 4.6 M sulfuric acid electrolyte is possible and reduced leakage currents are observed. This treatment is done before, during, and/or after reflow of the gasket material. For gas treatment at temperatures below that used for gasket reflow the atmosphere was exchanged with an inert gas such as nitrogen or argon during reflow. For treatment after reflow of

the gasket material the tabs were removed before treatment. During treatment the atmosphere is evacuated and filled with the reactive gas periodically.

TABLE 3

Device characteristics for various postconditioning.

gas	T/°C	t/min.	i"/μA/cm^2	V/cell
H_2	50	20	8	1.0
CO	100	170	40	1.0
CO	90	103	12	1.0
CO	90	165	20	1.0
CO	80	120	25	1.1
NO	75	20	27	1.0
NO	95	140	21	1.1
NH_3	85	30	26	1.0

FORMATION OF MICROPROTRUSIONS BY SCREEN PRINTING

EXAMPLE 9

Application of Epoxy Microprotrusions by Screen Printing onto a Porous Coating on a Thin Substrate

(A) Screen Preparation - A 325 mesh stainless steel screen is stretched on a standard screen printing frame. To this screen is edge glued (Dexter Epoxy 608 clear) to a smaller 1-1.5 mil (0.00254 to 0.00381 cm) thick brass sheet which has holes (6.3 mil (0.016 cm) diameter) drilled or etched to the desired pattern. The screen mesh is removed from the area covered by the brass sheet leaving the brass sheet edge glued to the screen mesh attached to the frame.

(B) Sample Holding - A vacuum is pulled on a porous alumina holding plate of 10 μm average pore diameter is used to hold the 1 mil (0.00254 cm) thick porous oxide coated material during the printing.

(C) Epoxy - A two component epoxy Master Bond EP21AR is modified to the desired viscosity (thixotropic, 300,000 to 400,000 cps) by the addition of a silica filler. The filled epoxy having the desired viscosity is available by purchase order from Master Bond, Inc. of Hackensack, New Jersey. The epoxy is prepared as per instructions. The useful lifetime as a flowable fluid is about 30 min.

(D) Screen printer parameters --

squeegee speed: 1-2 in/s

snap off: 20-30 mil (0.0508 to 0.0762 cm)

Constant temperature and humidity of the epoxy are important to assure an even applied coat. Typical conditions are about 40-70% relative humidity and a temperature of about 20-25°C.

(E) Printed epoxy pattern -- An array of epoxy bumps essentially 1 mil (0.00254 cm) in height and about 7.5 mil (0.019 cm) in diameter are produced. A typical pattern on an electrode consists of an array of microprotrusions deposited on 40 mil (0.1016 cm) center-to-center spacing. In addition, the density of microprotrusions at the perimeter of the electrode is increased by decreasing their center-to-center spacing to 20 mil (0.508 cm). The screen printed epoxy configuration is cured at 150°C for a minimum of 4 hr.

EXAMPLE 10

Screen Print Formation of Epoxy Microprotrusions

(A) Screen Preparation -- A 230 or 325 mesh screen (8x10 in stainless steel) without an emulsion on the surface, mounted on a standard printing frame, is used as the base piece. An etched, drilled or punched stencil (6.0 x 8.5 molybdenum) is edge glued using Dexter Epoxy 608 Clear from Dexter located to the back side of the screen. MYLAR® is placed over the stencil-screen unit and pressure applied to smooth the epoxy into a uniform layer.

The screen is then flipped, epoxy applied to the top side of the screen, a MYLAR® sheet placed over the area and the epoxy smoothed. The MYLAR® sheet on the top side of the screen is then removed. The screen-stencil assembly is then placed into a 120°C oven with ambient atmosphere for 5 min to cure the epoxy. Alternatively, the epoxy can be cured by setting at ambient temperature for 30-60 min.

After removal of the screen-stencil from the oven, the MYLAR® on the back side is carefully peeled away immediately. The mesh screen on the top side is then cut away using a sharp edge, with care being taken to prevent cutting of the stencil. Upon removal of the mesh over the stencil pattern, any heat stable thermoset adhesive (e.g. an epoxy resin) is applied to the cut mesh-stencil perimeter, covered with MYLAR®, and

the epoxy smoothed to ensure edge attachment of the screen to the stencil. The epoxy is cured in the oven for 5 min. The resulting item is a stencil stretched taut by the screen, ready for printing.

(B) Sample Holding - A porous ceramic holding (e.g. Fig. 8) plate (Ceramicon Designs, Golden, Colorado, P-6-C material) of 4.5-6μ pore diameter with a porosity of 36.5% (30-60% porosity is acceptable) is used to hold the 1 mil (0.00254 cm) thick porous oxide coated material during the printing by pulling a vacuum through the porous ceramic plate. The ceramic plate is cut to the appropriate dimensions (the size and shape of the substrate to be printed). This ceramic plate then is inserted into an aluminum (steel, etc) frame 277 and epoxy or other adhesive) that can be mounted to a screen printer. The ceramic plate is then carefully ground flush to the metal frame as flat as possible. Locating pins 278, 279 and 280 are then added to hold the substrate 111A in appropriate location using holes 281, 282 and 283.

(C) Epoxy - The Master Bond EP 21 ART® (a two component epoxy (of polyamine hardener, 33 weight percent and a liquid epoxy resin, 67 weight percent) about with a viscosity of 150,000 to 600,000 cps). The epoxy is prepared as per the product instructions. The useful lifetime as a flowable fluid is about 30 min.

(D) Screen Printing Parameters -

Squeegee Speed	1-2 in/s (depends upon epoxy viscosity)
Snap Off	20-30 mil (0.0050 to 0.0076 cm) (Related to screen tension; and adjusted accordingly)

(E) Printed epoxy pattern - An array of epoxy bumps essentially about 1 to 1.25 mil (0.00254 to 0.00316 cm) in height and about 7.5 mil (0.019 cm) in diameter are produced. A typical pattern on an electrode consists of an array of microprotrusions deposited on 40 mil (0.1 cm) center-to-center spacing. In addition, the density of microprotrusions around the perimeter of the electrode is increased by decreasing their center-to-center spacing to 20 mil (0.0508 cm). The screen printed epoxy configuration is cured at 150°C for 4 to 12 hrs. in an ambient atmosphere.

EXAMPLE 11

ALTERNATIVE SCREEN PRINTING PARAMETERS

(A) Separator Bumps -- Separator bumps range in height from .001 to .004 in. (.00254 to 0.01016 cm) and widths of .006 to .012 in. (.01524 to .03038 cm). Separator bumps may take the form of dots, squares, rectangles or a composite of these shapes. The widths of the bumps increase as the bump height is increased.

(B) Separator Pattern -- Two patterns are utilized on an electrode substrate, the Active Field Area and the Bounding Border Area. The AFA has the separator bumps located on .040 by .040 in. (.1016 by .1016 cm) center to center spacing and are normally dots. The BBA has an increased bump density with a .020 by .020 in. (.0508 by .0508 cm) center to center spacing. Rows of rectangles alternate between arrays of dots.

(C) Screen Preparation -- Design of the separator configuration is performed on a CAD (Computer Aided Drafting) system. The CAD electronic data is converted to a Gerber plot file. This plot data is used by the screen manufacture to create the artwork to produce the desired thickness stencil for the screen printer. The screen is sent ready to use by SMT (Screen Manufacturing Technologies of Santa Clara, California).

(D) Electrode Vacuum Plate (Workholder) -- A porous ceramic plate (Ceramicon Designs, Golden, Colorado, P-6-C material) trimmed .050 smaller than the electrode perimeter is fitted and epoxied into an aluminum plate designed to fit the screen printer. The top and bottom surfaces are ground flush and parallel. Multiple pins are inserted around the centered electrode edge creating a corner stop for placement of the electrode substrate.

(E) Epoxy -- A two component epoxy Master Bond EP21AR is modified to the desired viscosity (thixotropic, 300,000 to 400,000 cps) by the addition of a silica filler. The filled epoxy having the desired viscosity is available by purchase order from Master Bond, Inc. of Hackensack, New Jersey. The epoxy is prepared as per instructions. The useful lifetime as a flowable fluid is about 30 min.

(F) Screen Printing Parameters

Thick Film Screen Printer	
Squeegee Durometer	45 to 100 Type A

Squeegee Speed	1-2 in/s
Squeegee Pressure	10 to 15 lbs.
Squeegee Down Stop	.010 to max. in.
Snap Off	.010 to .030 in. (.0254 to .0762 cm.)

FORMATION OF MICROPROTRUSIONS BY PHOTOLITHOGRAPHY

EXAMPLE 12

Hot Roller Photolithographic Production of Microprotrusions

(A) The ConforMASK® 2000 high conformance solder mask of 1.5 mil (0.0038 cm) in thickness is cut to the same size as the electrode.

(B) The photo resist film 381 is applied by placing the ConforMASK® film on the electrode material surface 111A, after removing a release sheet 382 between the photo resist film 381 and the electrode 111A, and passing the laminate through heated rollers (384 and 385), at 150°F, to adhere the photoresist film 381 to the electrode surface 111A. A polyester cover sheet 382A on the outside of the photo resist film 381 is then removed.

(C) A dark field mask 387 containing rows of transparent holes (openings 388) is placed on the photo resist 381. A typical pattern consists of an array of holes 6 mil (0.0212 cm) in diameter 40 mil (0.1 cm) center-to-center spacing with a higher density (20 mil (0.0508 cm) center-to-center) for three rows on the perimeter of the electrode.

(D) The film 381 is exposed through the holes 388 and the mask 387, for about 20 seconds, to a conventional UV light source, i.e. mercury vapor lamps 389. The mask is then removed.

(E) The unexposed area of the photo resist is developed or stripped by placing it in a tank with 1% potassium carbonate for 1.5 min.

(F) The electrode surface with the microprotrusions (standoffs) are then washed with de-ionized water, placed in a tank with 10% sulfuric acid, for 1.5 min and a final de-ionized water rinse.

(G) First, the microprotrusions 13 are exposed to UV light. A final cure of the microprotrusions (standoffs) is done in a convection air oven at 300°F for 1 hr.

The finished electrode 111A is used directly, or is treated, as described above.

EXAMPLE 13

Vacuum Lamination of Photo resist

(A) The ConforMASK® 2000 high conformance solder mask of 2.3 mil (0.0058 cm) in thickness is cut slightly larger than the electrode.

(B) The photo resist film is 381 vacuum laminated to the electrode 111A, and onto a supporting backing plate using standard operating conditions (160°C, 0.3 mbars) using a Dynachem vacuum applicator model 724 or 730. The polyester cover sheet 382A is removed.

(C) The dark field mask 387 containing rows of transparent holes 388 is placed on the photo resist film 381. A typical pattern includes an array of holes 6 mil (0.0015 cm) in diameter 40 mil (0.102 cm) center-to-center spacing with a higher density (20 mil (0.0054 cm) center-to-center) for three rows on the perimeter of the electrode.

(D) The film is exposed for 20 to 40 seconds to a non-collimated UV light source of 3-7 KW power.

(E) The unexposed area of the photo resist film is developed or stripped by using 0.5% potassium carbonate in a conveyorized spray developing unit, followed by a de-ionized water rinsing and turbine drying.

(F) A final cure of the microprotrusion standoffs is done in a two step process. First, the microprotrusions are exposed to UV light in a Dynachem UVCS 933 unit and then placed in a forced air oven at 300-310°F for 75 min.

The finished electrode is used directly or further treated as described above.

EXAMPLE 14

Surfactants for Porosity Control

32g of cetyltrimethyl ammonium bromide was added to 1 ℓ of iso-propanol with stirring and slight heat. After approximately one hour 73 g of $TaCl_5$ and 47 g of $RuCl_3 \cdot H_2O$ was added to the clear solution. The standard coating procedure was performed with interim pyrolysis at 300°C or 5 min. and a final pyrolysis at 300°C for 3 hours. The average pore diameter of the coating increased to around 45 Å. After

post-treatment in steam at 260°C at 680 psi for 2 hr. the average pore diameter increased to 120 Å.

A 25 wt % cetyltrimethyl ammonium chloride in water solution may also be used to modify the pore diameter of the resulting coating.

EXAMPLE 15

Thermal Elastomeric Gasket

An alternative construction methodology is to sandwich a thermal elastomer gasket (e.g. KRATON®) between the two HDPE gaskets. Device characteristics are similar to those previously described.

EXAMPLE 16

Inclusion of Second Material to Accommodate Electrolyte Volume Increases

A porous hydrophobic material is added to each cell to accommodate any volume increase of the electrolyte due to an increase in temperature.

This material is placed in the cell as either a gasket material inside the perimeter HDPE gasket, or as a disk replacing part of the separator material.

A common material used is a PTFE material from W.L. Gore & Associates, Inc. 1-3 mil thick. Preferably, the PTFE material has water entry pressures from 20 to 100 psi.

EXAMPLE 17

Alternate Electrode Pretreatment

After the electrodes have microprotrusions, gaskets, and pull cards (after step E), the electrodes are placed in 1M sulfuric acid and the open circuit potential is adjusted to about 0.5V (vs HHE) using cathodic current with no hydrogen evolution. The electrodes are transferred submerged in deionized water to an inert atmosphere (e.g. Ar) where they are dried and assembled.

While only a few embodiments of the invention have been shown and described herein, it will become apparent to those skilled in the art that various modifications and changes can be made in the improved method to produce an electrical storage device such as a battery or a capacitor having improved lifetime and charge/recharge characteristics and low leakage current, and the device thereof without departing from

the spirit and scope of the present invention. All such modifications and changes coming within the scope of the appended claims are intended to be carried out thereby.

WE CLAIM:

1. A dry preunit for an energy storage device comprising:

at least a first cell for storing energy, said first cell comprising, in combination:

a. a first electrically conductive electrode;

b. a second electrically conductive electrode, said first and second electrodes being spaced apart by a first predetermined distance; and

c. first dielectric gasket means interposed between said first and second electrodes, for separating and electrically insulating said first and second electrodes;

whereby, when said first electrode, said second electrode and said first gasket means having a centrally located opening are bonded together to form said first cell, an air filled fill gap is formed therebetween.

2. The dry preunit according to claim 1, wherein said first cell further includes:

a. a first high surface area electrically conducting coating layer formed on one surface of said first electrode, such that said first coating layer is interposed between said first electrode and said gasket means; and

b. a second electrically conducting high surface area coating layer formed on one surface of said second electrode, such that said second coating layer is interposed between said second electrode and said first gasket means;

c. a layer which includes a plurality of protrusions on the first coating layer, the second coating layer, or combination thereof; and

wherein said protrusions impart structural support to said first cell, and provide additional insulation between said first and second electrodes.

3. The dry preunit according to claim 2, wherein said first cell further includes a first fill port formed by said gasket means, in order to allow an electrolyte to flow into said fill gap.

4. The dry preunit according to claim 3, wherein said first cell further includes a first cord which is inserted within said first fill port; and

wherein when said first cord is removed, said first fill port is opened and said fill gap becomes accessible.

5. The dry preunit according to claim 1 or 4, further including at least a second cell, and wherein said first cell and said second cell are stacked and connected, in order to impart an integral unitary structure to the dry preunit.

6. The dry preunit according to claim 5, wherein said second electrically conductive electrode is a bipolar electrode, which is shared by said first and second cell; and

wherein said second cell further includes a third electrically conductive electrode which is oppositely disposed relative to said second electrically conductive electrode; and

wherein said first and second electrically conductive electrodes are spaced apart, by a second predetermined distance.

7. The dry preunit according to claim 6, wherein a third coating layer is formed on the second flat surface of said second electrode, such that said second coating layer is interposed between said second electrode and said second gasket means; and

wherein said second cell includes a plurality of discrete protrusions located on either electrode surface.

8. The dry preunit according to claim 7, wherein said second cell further includes a high surface area and electrically conductive coating which is formed on one surface of said third electrode; and

wherein said fourth coating layer is interposed between said third electrode and said second gasket means.

9. The dry preunit according to claim 8, wherein said second cell further includes a second fill port that is formed within said second gasket means.

10. The dry preunit according to claim 9, further including exterior tab means for connection to a power source.

11. The dry preunit according to claim 8, wherein each of said first and third coating layers includes an additional layer having a set of peripheral protrusions, and a set of central discrete protrusions that are disposed in an arrayed arrangement.

12. The dry preunit according to claim 11, wherein the diameter of each protrusion is about 6 mil (0.015 cm);

wherein the center-to-center separation of said peripheral protrusions is about 20 mil (0.0508 cm);

wherein the center-to-center separation of said central protrusions is about 40 mil (0.102 cm); and

wherein said peripheral and central protrusions have a dielectric composition.

13. The dry preunit according to claim 6, wherein said first and second predetermined distances are equal.

14. The dry preunit according to claim 1 or 5, wherein each of said first and second gasket means includes two dielectric gaskets, which are disposed in registration with each other; and

wherein said first cord is disposed between said gaskets to form said first fill port.

15. The dry preunit according to claim 6, wherein said first, second and third electrodes are similarly and rectangularly shaped.

16. A capacitor preunit including at least a first cell, the capacitor comprising:

a. a first electrically conductive electrode;

b. a second electrically conductive electrode, said first and second electrodes being spaced apart by a first predetermined distance; and

c. first dielectric peripheral gasket means interposed between said first and second electrodes, for separating and electrically insulating said first and second electrodes;

whereby, when said first electrode, said second electrode and said first gasket means are bonded together to form the first cell, a fill gap is formed therebetween.

17. The capacitor preunit according to claim 16, wherein the first cell further includes:

a. a first high surface area coating layer formed on one surface of said first electrode, such that said first coating layer is interposed between said first electrode and said gasket means; and

b. a second high surface area coating layer formed on one surface of said second electrode, with the proviso that said second coating layer is interposed between said second electrode and said first gasket means;

c. a layer having a plurality of discrete protrusions; and

wherein said protrusions impart structural support to the first cell, and provide additional insulation between said first and second electrodes.

18. The capacitor preunit according to claim 17, further including at least a second cell;

wherein the first and second cell are stacked and bonded, in order to impart an integral unitary structure to the capacitor;

wherein said second electrically conductive electrode is a bipolar electrode, which is shared by said first and second cell;

wherein said second cell further includes a third electrically conductive electrode which is oppositely disposed relative to said second electrically conductive electrode; and

wherein said first and second electrically conductive electrodes are spaced apart, by a second predetermined distance.

19. An electrically conductive high surface area porous coating layer for use in a dry preunit for an energy storage device, such as a capacitor or like devices.

20. The coating layer according to claim 19, wherein the porous layer comprises a metal oxide or a mixed metal oxide, having a large effective surface area consisting essentially of micro and meso pores, is coated on a support.

21. A method for storing energy using the dry preunit according to any one of claims 1 through 20, wherein said preunit is charged with an ionically conducting electrolyte, sealed, and electrically charged.

22. A method for making a dry preunit comprising the steps of forming the device according to any one of claims 1 through 20.

23. A method for making a dry preunit comprising the steps of forming at least a first cell by:

a. spacing apart a first electrically conductive electrode and a second electrically conductive electrode, by a first predetermined distance; and

b. placing a first dielectric gasket means between said first and second electrodes, for separating and electrically insulating said first and second electrodes;

whereby, when said first electrode, said second electrode and said first gasket means are bonded together to form said first cell, a fill gap is formed therebetween.

24. A method for making a capacitor preunit comprising the steps of forming at least a first cell by:

a. spacing apart a first electrically conductive electrode and a second electrically conductive electrode, by a first predetermined distance; and

b. placing a first dielectric gasket means between said first and second electrodes, for separating and electrically insulating said first and second electrodes;

whereby, when said first electrode, said second electrode and said first gasket means are bonded together to form said first cell, a fill gap is formed therebetween.

25. A method for making a capacitor preunit comprising the steps of forming at least a first cell by:

a. spacing apart a first electrically conductive layer means and a second electrically conductive layer means, by a first predetermined distance; and

b. placing a first dielectric gasket means between said first and second conductive layer means, for separating and electrically insulating said first and second conductive layer means;

whereby, when said first electrically conductive layer for storing electrical charge, said second conductive layer means for storing electrical charge, and said first gasket means for separating the electrode surfaces are bonded together to form said first cell, a fill gap is formed therebetween.

26. The method for making an dry preunit according to claim 23, further including the steps of:

a. forming a first porous, high surface area, and conductive coating layer on one surface of said first electrode, such that said first coating layer is interposed between said first electrode and said gasket means;

b. forming a second porous, high surface area, and conductive coating layer on one surface of said second electrode, such that said second coating layer is interposed between said second electrode and said first gasket means; and

c. forming a plurality of discrete microprotrusions on said first coating layer, wherein said microprotrusions impart structural support to said first cell,

and provide additional insulation between said first and second electrodes.

27. A method of producing an array of substantially uniform microprotrusions on a surface as a separator useful in the construction of single or multiple layer electrical charge storage devices, which method comprises:

(a) obtaining an electrically insulating material which is essentially inert to electrolyte conditions to produce a thixotropic composition at between ambient temperature to about 75°C and ambient pressure;

(b) obtaining a thin electrode material comprising a thin flat electrically conducting metal sheet center coated on one or both sides with electrically conducting carbon, porous metal oxide, porous mixed metal oxide or other porous coating and securing the flat electrode in a suitable holder;

(c) placing a thin flat screen or stencil having small openings over the flat thin electrode;

(d) contacting the top exterior thin screen surface with the flowable composition of step(a) so that small portions of the composition extrude through the pattern and contact the exterior surface of the thin electrode and optionally penetrate the exterior surface of the porous electrode coating, when a squeegee is brought across the screen surface to cause contact of the screen with the electrode surface;

(e) removing the sample from the screen printer; and

(f) curing the applied material whereby the discrete microprotrusions essentially retain their shape and dimensions.

28. The method of claim 27, wherein the device is selected from a capacitor or a battery.

29. An improved method to produce a dry preunit of an electrical storage device for storage of electrical charge in a condition to have the electrode surfaces contacted with a non-aqueous or aqueous electrolyte, which method comprises:

(a) preparing a thin in thickness substantially flat sheet of electrically conducting support material coated on each flat side with the same or different thin layer of a second electrically conducting material having a high surface area, optionally with the provision that both flat sides of the electrically conducting support is a sheet having the perimeter edge surfaces either:

(i) having a thin layer of second electrically conducting material,

(ii) are partly devoid of second electrically conducting material, or

(iii) are devoid of second electrically conducting material;

(b) creating an ion permeable or semipermeable space separator stable to the aqueous or non-aqueous electrolyte obtained by:

(i) depositing substantially uniform in height groups of electrically insulating microprotrusions, on the surface of at least one side of the thin layer of second electrically conducting material,

(ii) placing a thin precut ion permeable or semipermeable separator on one surface of the second electrically conducting material, or

(iii) casting an ion permeable or semipermeable thin layer on the surface of at least one side of the electrically conducting material, or

(iv) creating a thin air space as separator;

(c) contacting the perimeter edge surface of one or both sides of the thin sheet of step (b) with one or more thin layers of synthetic organic polymer as a gasket material selected from the group consisting of a thermoplastic, thermoelastomer, and a thermoset polymer;

(d) placing on or within the gasket material and optionally across the thin sheet at least one thin cord of a different material which cord has a higher melting point (T_m) greater than the gasket polymer material and does not melt, flow, or permanently adhere to the gasket under the processing conditions;

(e) producing a repeating layered stack of the thin flat articles of sheet coated with high surface area coating and separator produced in step (d) optionally having the end sheets consisting of a thicker support;

(f) heating the stack produced in step (e) at a temperature and applied pressure effective to cause the synthetic gasket material to flow, to adhere to, and to seal the edges of the stack creating a solid integral stack of layers of alternating electrically conductive sheet coated with second electrically conducting material and the ion permeable separator, optionally such that the gasket material creates a continuous integral polymer enclosure;

(g) cooling the solid integral stack of step (f) optionally in an inert gas under slight pressure; and

(h) removing the at least one thin cord of different material between each layer creating at least one small opening between the layers of electrically conducting sheet coated with second electrically conducting material.

30. The method of claims 26 or 29, wherein said microprotrusions comprise ceramics, organic elastomers, thermoplastics, or thermosets, or combinations thereof.

31. The method of claims 30, wherein either

after step (e) and before step (f) or after step (h), the integral stack is treated by:

(j) evacuating the dry preunit to substantially remove residual gases;

(k) contacting the dry unit with one or more reducing gases at near ambient pressure;

(l) heating the unit and reducing gas to between about 20 to 150°C for between about 0.1 and 5 hr;

(m) evacuating the dry preunit;

(n) replacing the reducing atmosphere with inert gas; and

(o) optionally repeating steps (j), (k), (l), (m), and (n) at least once.

32. The method of claim 29, wherein either after step (e) and before step (f) or after step (h), the integral stack is treated by:

(j) evacuating the dry preunit to substantially remove residual gases;

(k) contacting the dry unit with one or more reducing gases at near ambient pressure;

(l) heating the unit and reducing gas to between about 20 to 150°C for between about 0.1 and 5 hr;

(m) evacuating the dry preunit;

(n) replacing the reducing atmosphere with inert gas; and

(o) optionally repeating steps (j), (k), (l), (m), and (n) at least once.

33. The method according to claim 31 or 32, wherein the vacuum in steps (j), (m) and (o) is between about 1 torr to 1μtorr.

34. The method according to claim 32 or 33, wherein the reducing gas is selected from hydrogen, carbon monoxide, nitric oxide, ammonia or combinations thereof; and

the inert gas is selected from helium, neon, nitrogen, argon or combinations thereof;

and the one or more reducing gases and one or more inert gases are contacted with the unit in a sequential manner.

35. The method according to claim 29, wherein:

in step (b) gasket material is placed on the top of the device and the gasket material between the electrodes is of sufficient excess in volume so that upon heating in step (f) excess gasket material extrudes about the perimeter edges of the support to create a seamless sealed integral surface at the edge of the stack unit.

36. The method according to claim 29, wherein

in step (a) the support has second electrically conducting material on the perimeter edge surfaces,

in step (b) the microprotrusions are on the surface of the second electrically conducting material,

in step (c) the gasket material is a thermoplastic,

in step (e) the end sheets are a thicker support material,

in step (f) the gasket material is in excess to create a continuous integral sealed enclosure,

in step (g) the stack is cooled to ambient temperature, and in step (h) the cord comprises a metal, ceramic, organic polymer or combinations thereof.

37. An improved method to produce an electrical storage device for storage of electrical charge, which method comprises:

evacuating the dry preunit of claims 29 to 36,

contacting the evacuated dry preunit with an electrolyte selected from either an aqueous inorganic acid or a non-aqueous organic ionically conducting medium for a time sufficient to backfill the space between the support sheets using the fill port,

removing any exterior surface electrolyte, and

closing and sealing the fill port openings.

38. An improved method to produce a dry preunit of an electrical storage device for storage of electrical charge in a condition to have the electrode surfaces contacted with a non-aqueous or aqueous electrolyte, which method comprises:

(a) obtaining a thin in thickness flat metal sheet support wherein the metal is selected from titanium, zirconium, iron, copper, lead, tin, nickel, zinc or combinations thereof, having a thickness of between about 0.1 and 10 mil coated on each flat surface with a thin porous layer of at least one metal oxide having a high surface area independently selected from metal oxides of the group consisting of tin, lead, vanadium, titanium, ruthenium, tantalum, rhodium, osmium, iridium, iron, cobalt, nickel, copper, molybdenum, niobium, chromium, manganese, lanthanum or lanthanum series metals or alloys or combinations thereof, possibly containing small percentage of additives to enhance electrical conductivity,

wherein the thin metal oxide layer has a thickness of between about 0.1 and 100 microns,

optionally with the provision that both flat surfaces of the electrically conducting sheet have the perimeter edge surfaces devoid of metal oxide;

(b) creating an ion permeable space separator which is stable to the aqueous or non-aqueous electrolyte selected from:

(i) depositing a substantially uniform in height array of electrically insulating discrete microprotrusions which are stable to an aqueous or non-aqueous electrolyte having a height of between about 0.1 and 10 mil on the surface of one or both sides of the thin layer of porous metal oxide,

(ii) placing a thin precut ion permeable electrically insulating separator having a thickness of between about 0.1 and 10 mil on one flat surface of the metal oxide layer;

(iii) casting an ion permeable or semipermeable separator having a thickness of between about 0.1 and 10 mil on at least one surface of the second electrically conducting material; or

(iv) creating a thin air space as a separator;

(c) contacting the perimeter edge surface of one or both sides of the thin electrically conducting sheet of step (b) with one or more thin layers of synthetic organic polymer as a gasket material wherein the polymer is selected from polyimides, TEFZEL®, KRATON®, polyethylenes, polypropylenes, other polyolefins, polysulfone, other fluorinated or partly fluorinated polymers or combinations thereof;

(d) placing on or within the gasket material and optionally across the thin flat sheet at least one thin cord of a different material which has a higher melting temperature (T_m) than the polymeric gasket material, which cord does not melt, flow or adhere to the gasket material under the processing conditions described herein;

(e) assembling a repeating layered stack of the thin flat articles of sheet coated with metal oxide and separator produced in step (d) optionally having end sheets having only one side coated and/or being made of thicker support material;

(f) heating the layered stack of step (e) at 0 to 100°C greater than T_m of the gasket material causing the gasket material to flow, to adhere to, and to seal the edges of the layered stack creating a solid integral layered stack of sheet and separator optionally enclosing and sealing the stack in an integral polymer enclosure;

(g) cooling to ambient temperature the solid integral stack of step (f) in an inert environment; and

(h) removing the at least one thin cord between each layer creating at least one small opening into the fill gap located between the porous electrode layers.

39. The method according to claim 38, wherein:

in step (b) gasket material is placed on the top of the device and the gasket material between electrodes is of sufficient excess in volume so that upon heating in step (f) excess gasket material extrudes about the perimeter edges of the support to create a seamless sealed integral surface at the edge of the stack unit.

40. The method according to claim 38, wherein:

in step (a) the support has second electrically conducting material on the perimeter edge surfaces,

in step (b) the microprotrusions are on the surface of the second electrically conducting material,

in step (c) the gasket material is a thermoplastic,

in step (e) the end sheets are a thicker support material,

in step (f) the gasket material is in excess to create a continuous integral enclosure,

in step (g) the stack is cooled to ambient temperature,

in step (h) the cord comprises a metal, ceramic, organic polymer or combinations thereof.

41. The energy storage obtained by using the preunit device according to any one of claims 29 or 35 and

adding an electrolyte to fill the evacuated fill gap regions,

sealing the fill port openings, and

electrically charging the electrical storage device wherein said device has uses as an electrical source of power for applications independently selected from:

providing peak power in applications of varying power demands and be recharged during low demand (i.e. serving as means for a power conditioner, placed between the electrical generator and the electrical grid of the users;

providing power in applications where the electrical source may be discontinued and additional power is needed to power in the interim period or for a period to allow for a shutdown providing means for uninterruptable power source applications, comprising computer memory shutdown during electrical grey and brown outs, or power during periodic black outs as in orbiting satellites;

providing pulse power in applications requiring high current and/or energy comprising means for a power source to resistively heat catalysts, to power a defibrillator or other cardiac rhythm control device, or to provide pulse power in electric vehicle where in a battery or internal combustion engine could recharge the device;

providing power in applications that require rapid recharge with prolonged energy release comprising surgical instruments with out an electrical cord; or

providing a portable power supply for appliance and communication applications.

42. A photolithographic method to produce microprotrusions on a high surface area substrate to maintain space separation in an electrical storage device, which method comprises:

(a) obtaining an unexposed photo resist film which is essentially inert to subsequent electrolyte conditions and is electrically insulating when cured;

(b) obtaining a thin electrode material comprising a thin flat electrically conducting metal sheet center coated on one or both flat sides with electrically conducting porous metal oxide, mixed metal oxide or carbon;

(c) applying the photo resist film to one or to both flat sides of the electrode material;

(d) placing a mask having a plurality of small holes over the photo resist;

(e) exposing the photo resist to a light source of an intensity and for a time effective to substantially cure the light exposed photo resist material through the holes in the mask to create cured microprotrusions followed by removing the mask;

(f) developing the photo resist film to leave the cured multiple, discrete microprotrusions on the surface of the electrode material and remove unreacted film; and

(g) further curing the remaining exposed material whereby the microprotrusions essentially retain their shape and dimensions.

43. The method according to claim 42, wherein:
in step (b) the metal oxide coats both sides of the electrode,
in step (c) the film is applied to one flat side using a hot roller technique,
in step (f) developing using dilute aqueous base and
in step (g) using light, heat or a combination thereof to cure the microprotrusions.

44. The method according to claim 43, wherein in step (c) the photo resist is vacuum laminated.

45. The dry preunit according to claim 1 or 5, wherein said first electrode includes a first electrically conductive, high surface area, porous coating layer, which is formed on one surface thereof, such that said first coating layer is interposed between said first electrode and said gasket means; and
wherein said second electrode is a bipolar electrode.

46. The dry preunit according to claim 45, wherein said second electrode includes a first electrically conductive, high surface area, porous coating layer formed on one surface thereof, such that said second coating layer is interposed between said second electrode and said first gasket means.

47. The dry preunit according to claim 46, wherein said first electrode further includes spacer means formed on said first coating layer, for maintaining said first and second electrodes closely spaced apart.

48. The dry preunit according to claim 47, wherein said second electrode further includes a second electrically conductive, high surface area, porous coating layer formed on another surface thereof.

49. The dry preunit according to claim 47, wherein said first coating layer of said first electrode, and said first and second coating layers of said second electrode are selected from a group consisting of metal oxides, mixed metal oxides, metal nitrides, and polymers.

50. The dry preunit according to claim 47, wherein said spacer means includes a plurality of protrusions; and

wherein said protrusions impart structural support to said first cell, and provide additional insulation between said first and second electrodes.

51. An energy storage device according to any of claims 1 through 50 further including an ionically conductive medium, within the cell gaps of the dry preunit, wherein the fill ports are sealed.

52. The further inclusion of porous hydrophobic polymeric material within the fill gap of each cell during construction of claims 1 or 38 to mitigate the increase of hydrostatic pressure with an increase in temperature.

53. The porous hydrophobic polymeric material of claim 52 wherein the material comprise polytetrafluoroethylene and has water entrance pressures of between 760 and 7600 torr.

54. The method of claim 27 wherein the screen printable material is a thermal-or photo-curable epoxy resin.

55. The method of claims 38 wherein

in step (a) the porous electrode formed is conditioned by contact with:

(a) steam at a temperature of between about 150 and 300°C for between about 0.5 and 4 hr,

(b) a reactive gas or a reactive liquid at a temperature of between about 80 to 140°C for between about 0.2 and 2 hr, or

(c) an anodic current sufficient to evolve oxygen for between about 1 to 60 min,

then contacted with a cathodic current without hydrogen gas evolution until the open circuit potential is adjusted to between about 0.5V to 0.75V (vs. normal hydrogen electrode).

56. The method of claim 2 after step (c) or claim 38 between steps (d) and (e) conditioning the porous coating by

contact with a cathodic current until the open circuit potential is adjusted to between about 0.5V to 0.75V (vs. normal hydrogen electrode).

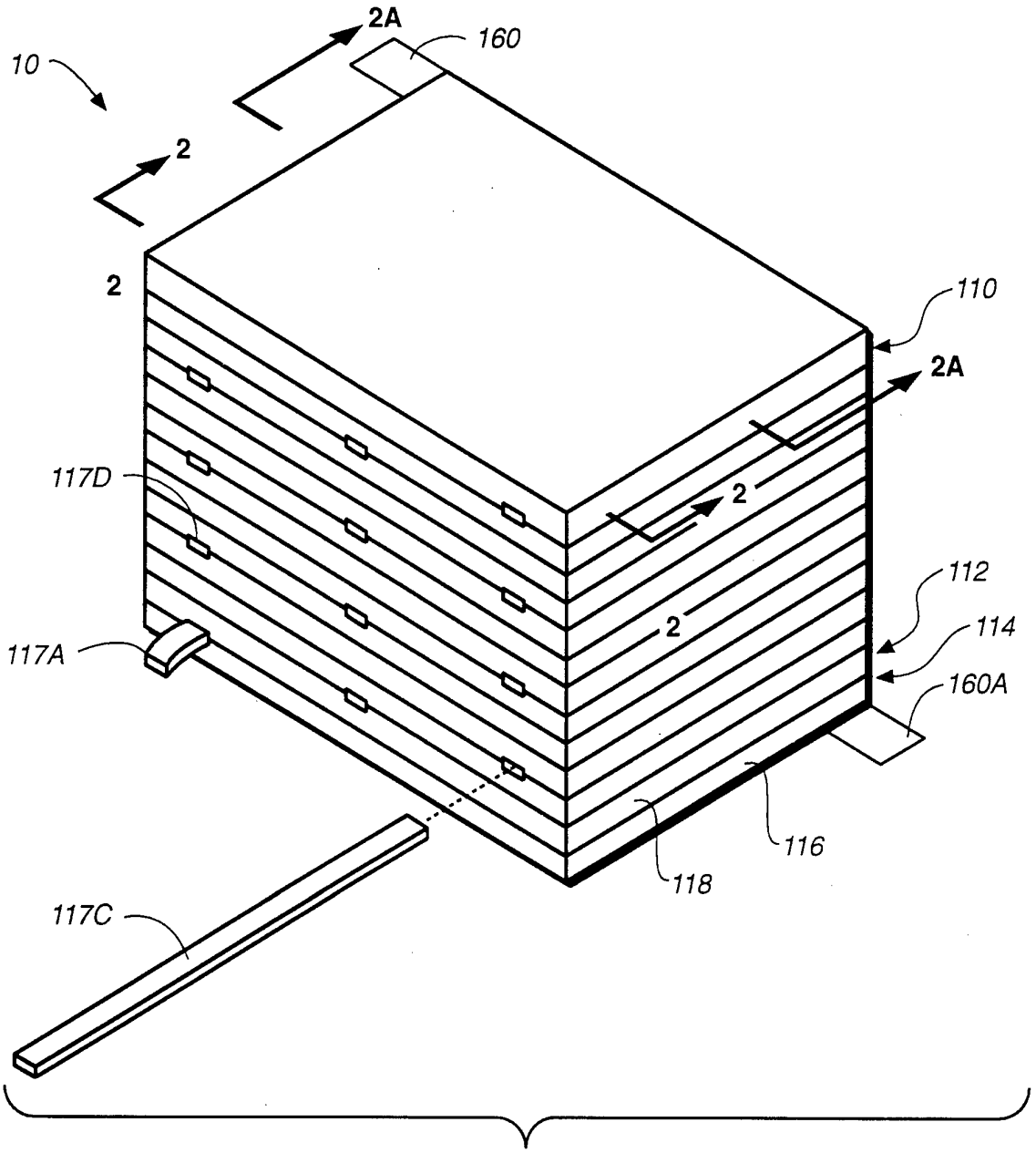

FIG._1

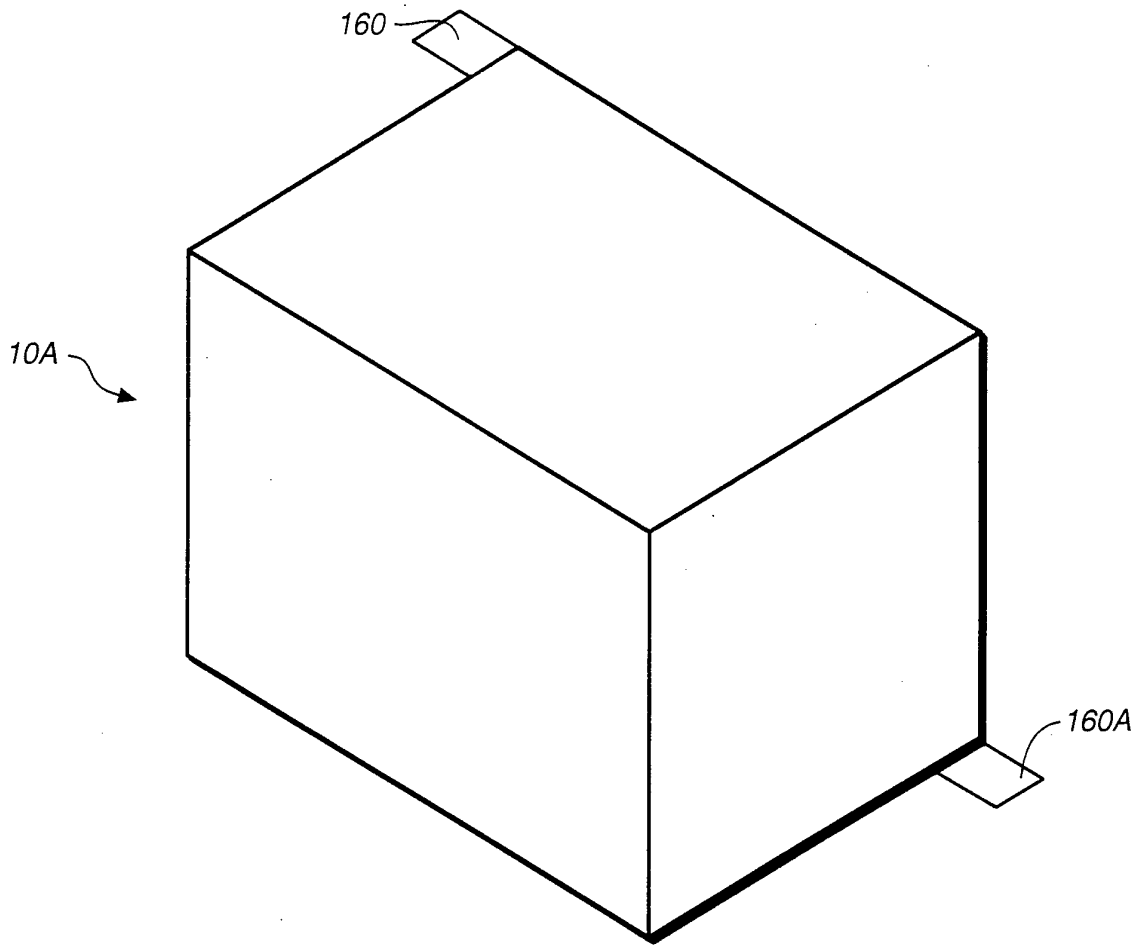

FIG._1A

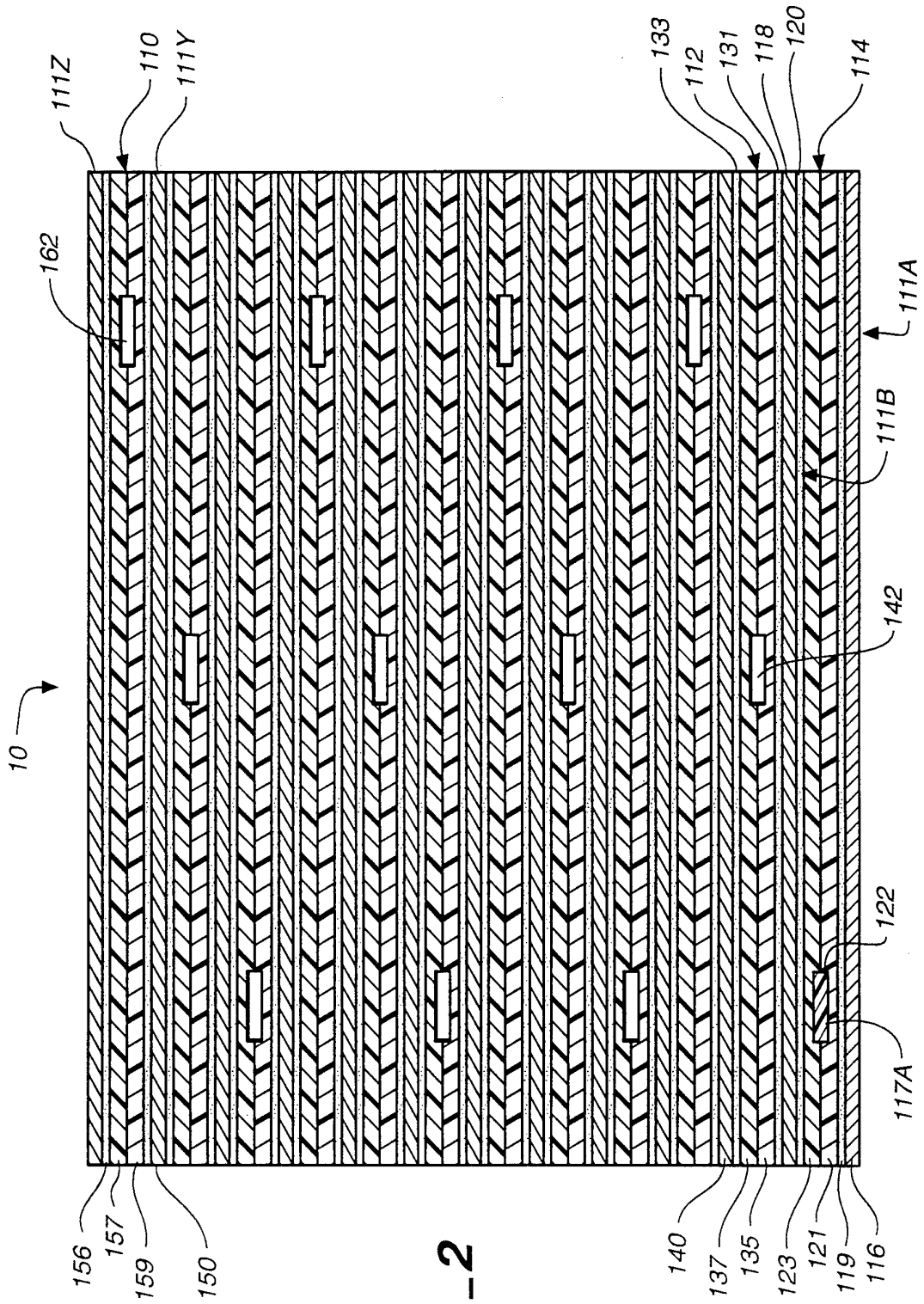
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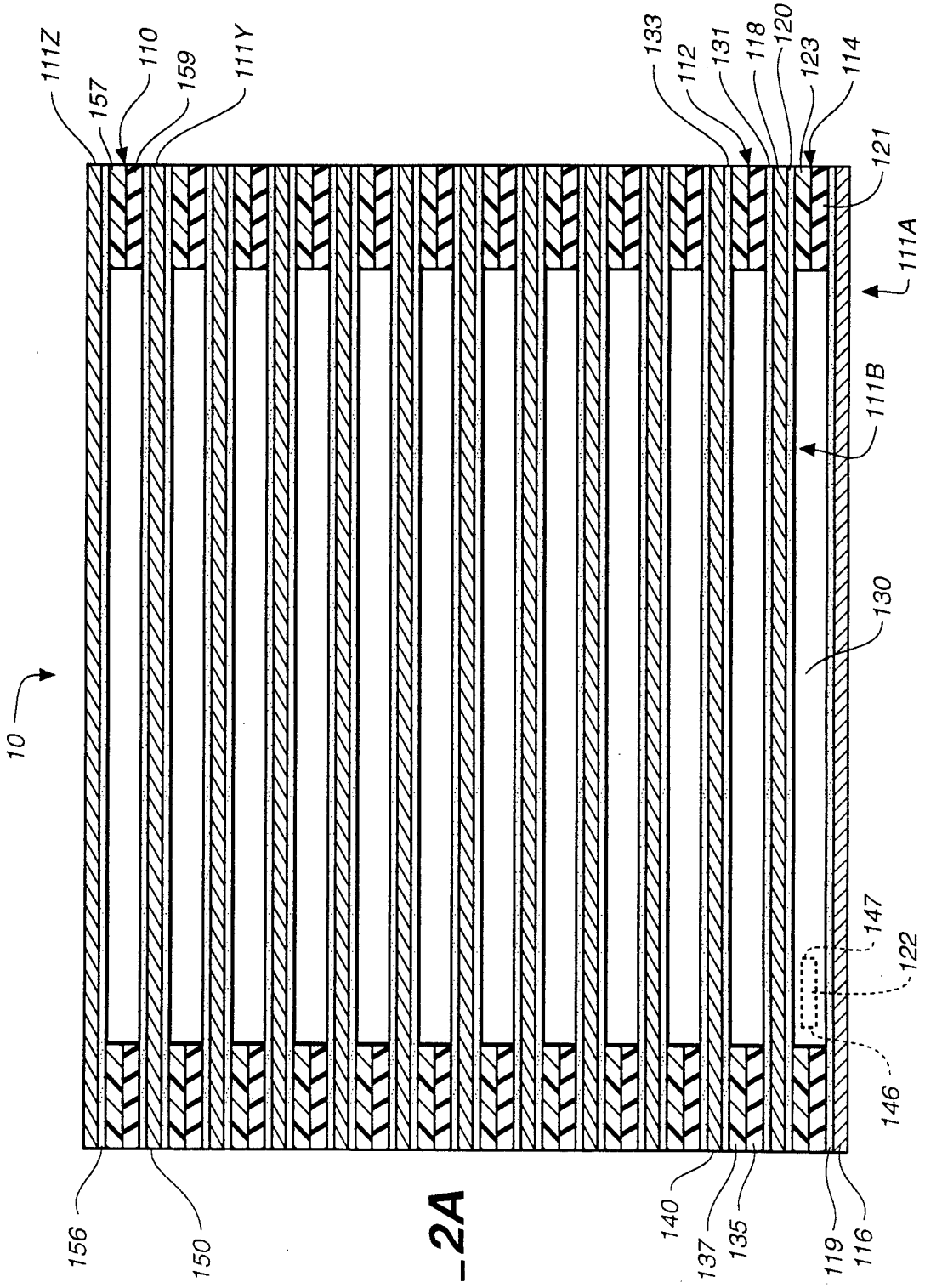
FIG._2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116

FIG._2A

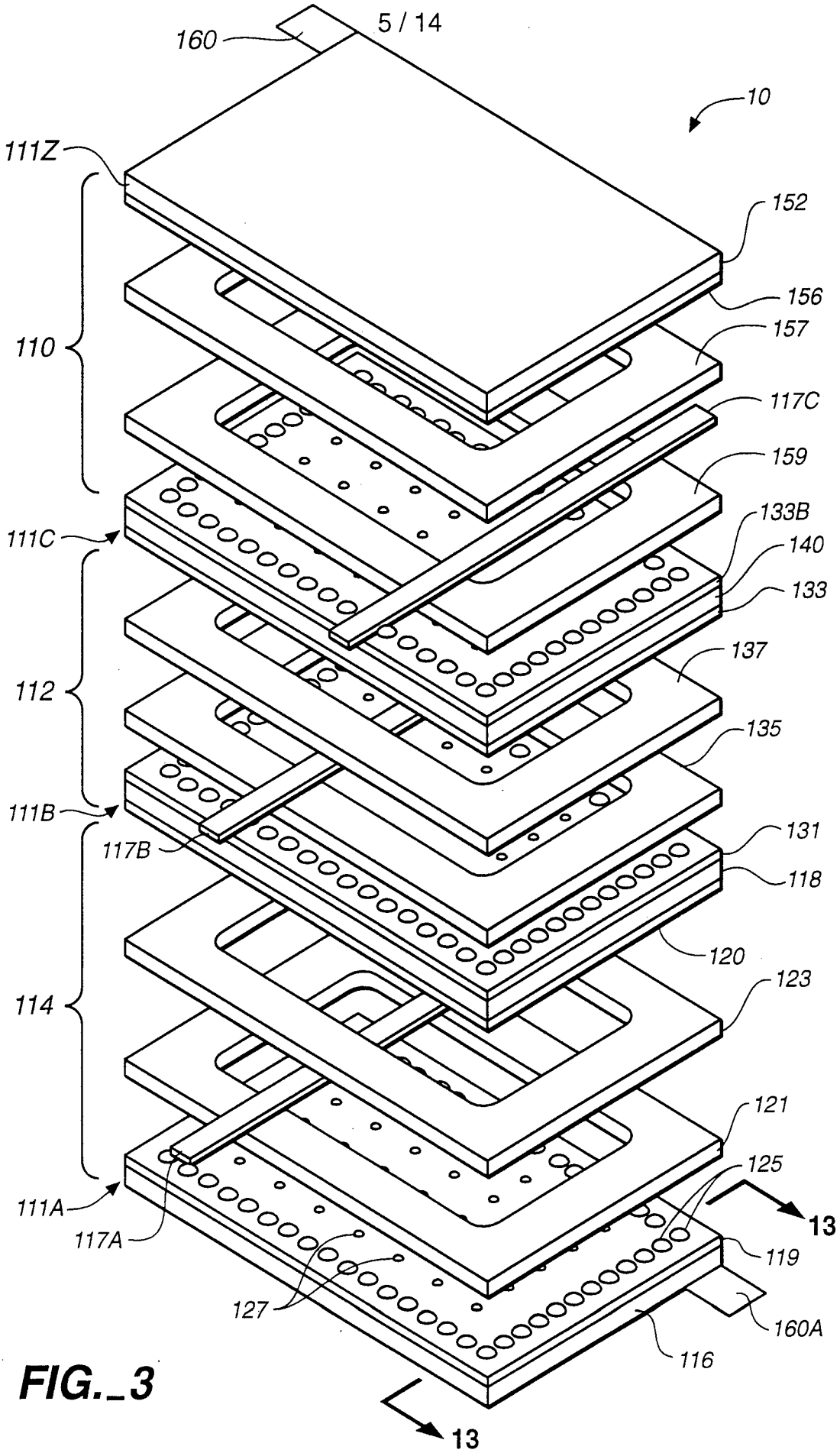

160
10
111Z
152
156
157
110
117C
159
133B
111C
140
133
137
112
135
111B
131
117B
118
120
114
123
121
111A
125
13
117A
119
127
160A
116
13

FIG._3

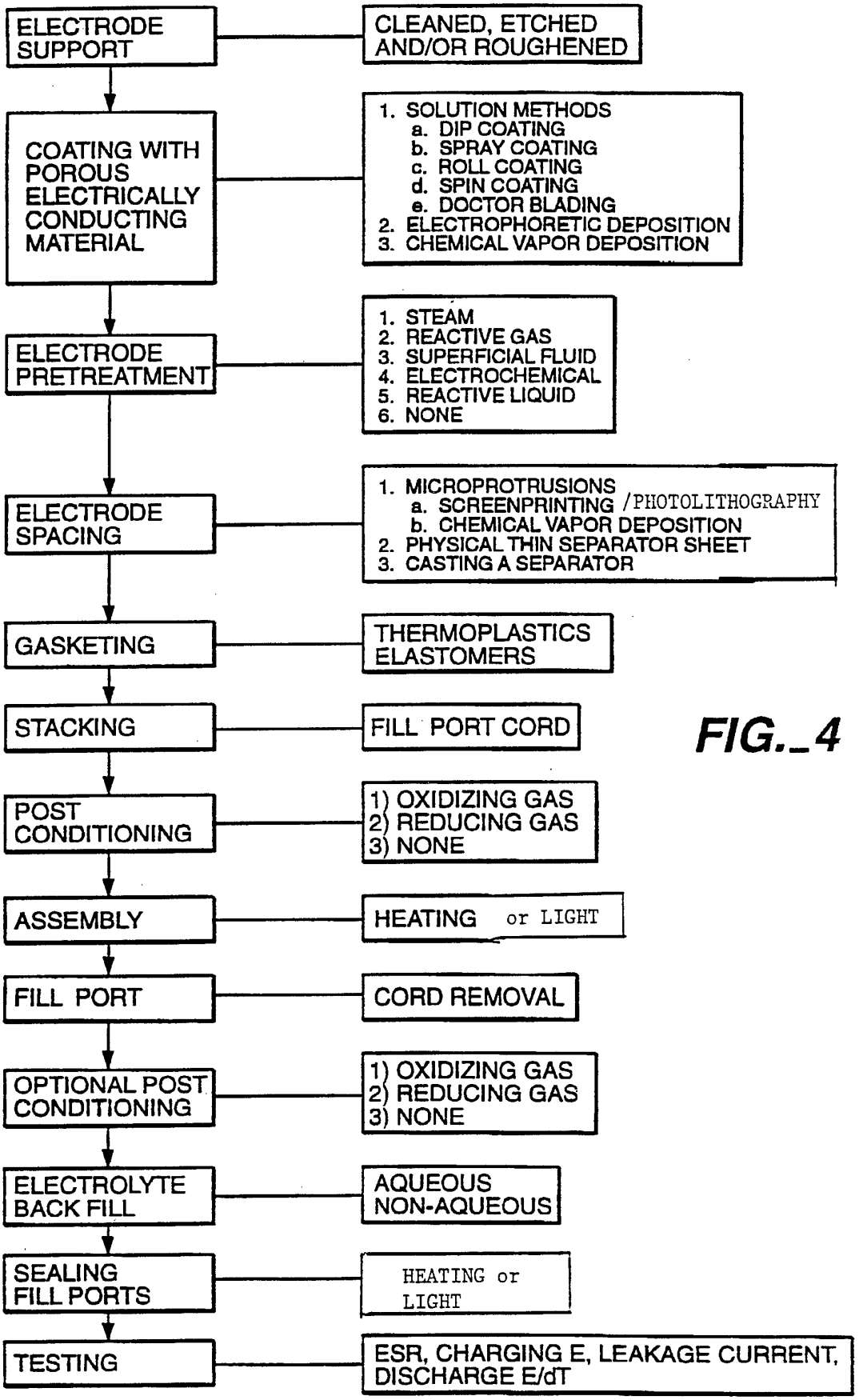
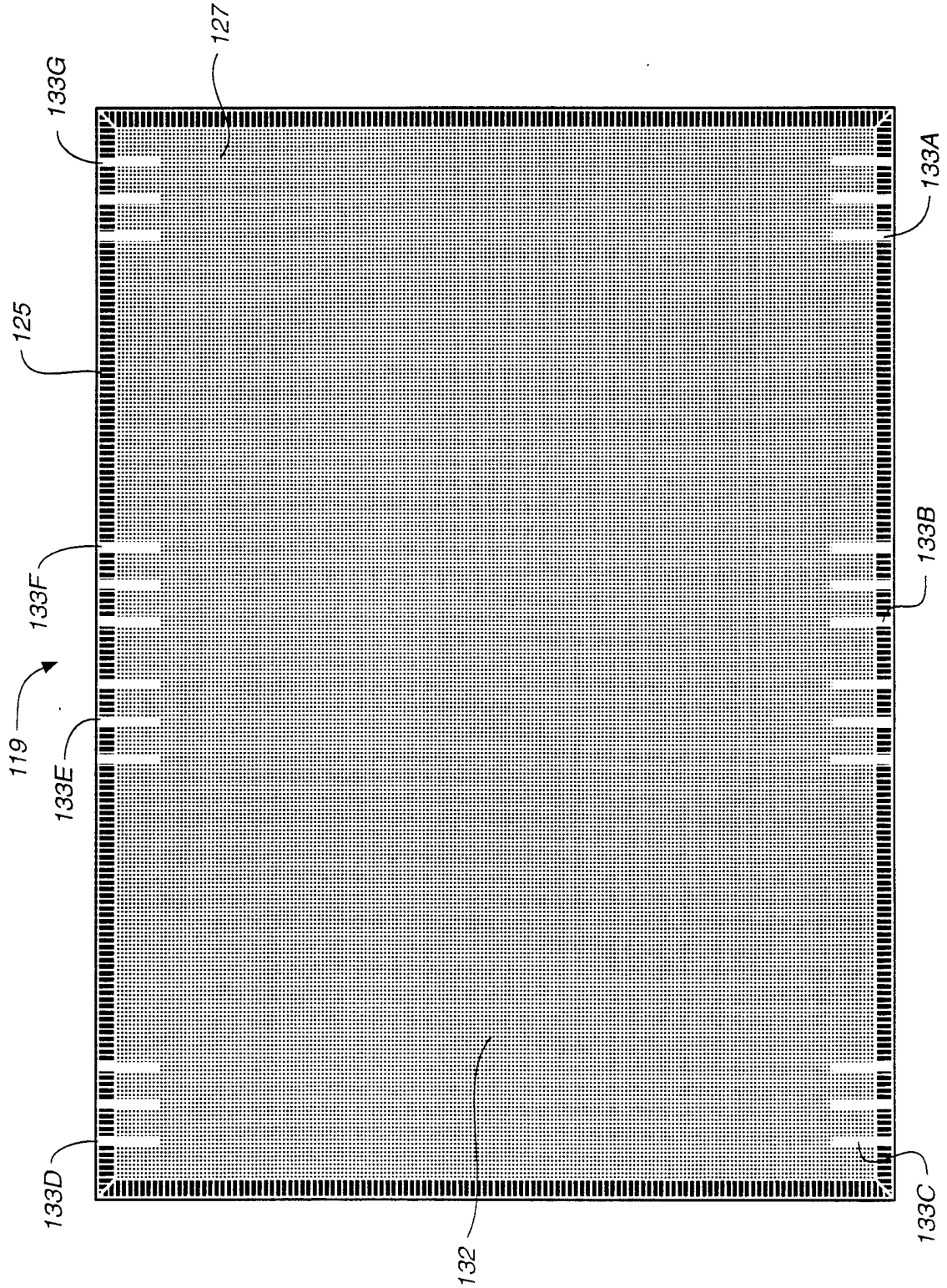

ELECTRODE SUPPORT
CLEANED, ETCHED AND/OR ROUGHENED
COATING WITH POROUS ELECTRICALLY CONDUCTING MATERIAL
1. SOLUTION METHODS
a. DIP COATING
b. SPRAY COATING
c. ROLL COATING
d. SPIN COATING
e. DOCTOR BLADING
2. ELECTROPHORETIC DEPOSITION
3. CHEMICAL VAPOR DEPOSITION
ELECTRODE PRETREATMENT
1. STEAM
2. REACTIVE GAS
3. SUPERFICIAL FLUID
4. ELECTROCHEMICAL
5. REACTIVE LIQUID
6. NONE
ELECTRODE SPACING
1. MICROPROTRUSIONS
a. SCREENPRINTING /PHOTOLITHOGRAPHY
b. CHEMICAL VAPOR DEPOSITION
2. PHYSICAL THIN SEPARATOR SHEET
3. CASTING A SEPARATOR
GASKETING
THERMOPLASTICS ELASTOMERS
STACKING
FILL PORT CORD
POST CONDITIONING
1) OXIDIZING GAS
2) REDUCING GAS
3) NONE
ASSEMBLY
HEATING or LIGHT
FILL PORT
CORD REMOVAL
OPTIONAL POST CONDITIONING
1) OXIDIZING GAS
2) REDUCING GAS
3) NONE
ELECTROLYTE BACK FILL
AQUEOUS NON-AQUEOUS
SEALING FILL PORTS
HEATING or LIGHT
TESTING
ESR, CHARGING E, LEAKAGE CURRENT, DISCHARGE E/dT

FIG._4

FIG._5



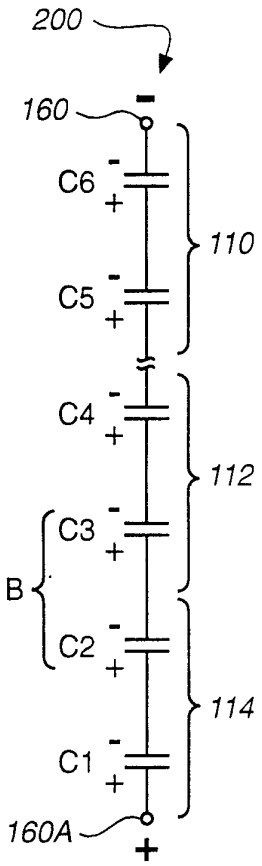

200
160
C6
C5
110
C4
112
C3
B
C2
114
C1
160A

FIG._6

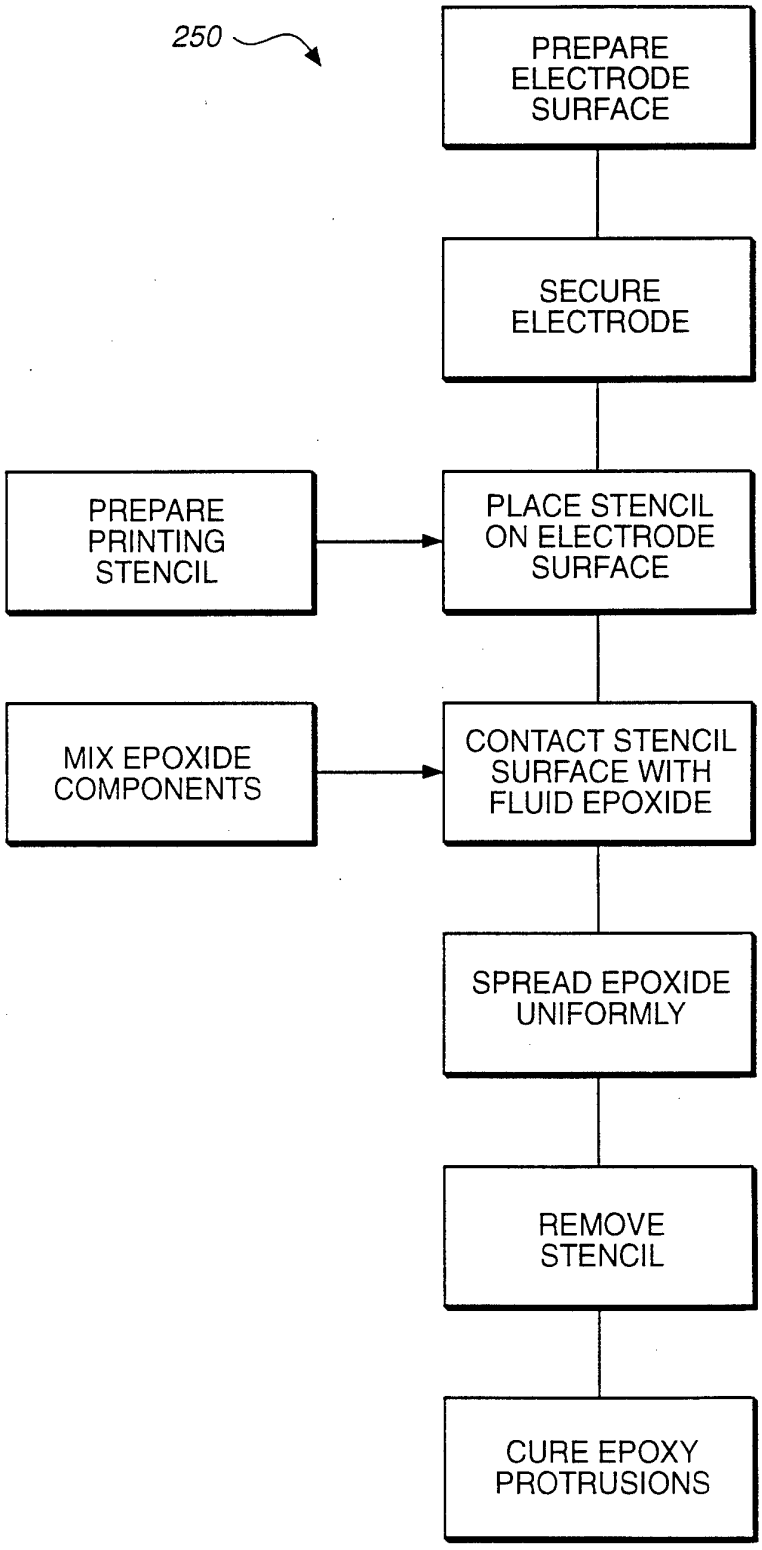
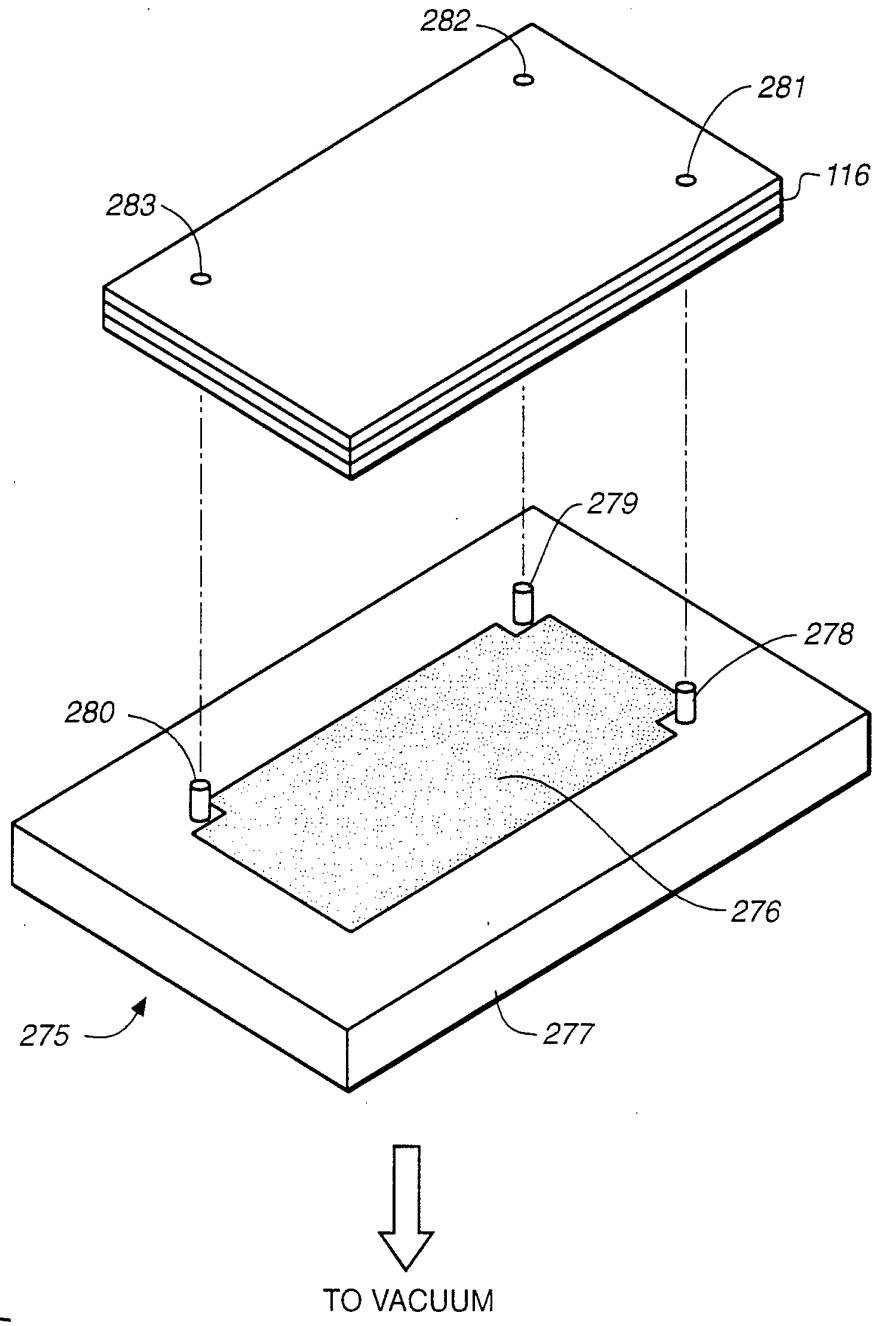

250
PREPARE ELECTRODE SURFACE
SECURE ELECTRODE
PREPARE PRINTING STENCIL
PLACE STENCIL ON ELECTRODE SURFACE
MIX EPOXIDE COMPONENTS
CONTACT STENCIL SURFACE WITH FLUID EPOXIDE
SPREAD EPOXIDE UNIFORMLY
REMOVE STENCIL
CURE EPOXY PROTRUSIONS

FIG._7

FIG._8



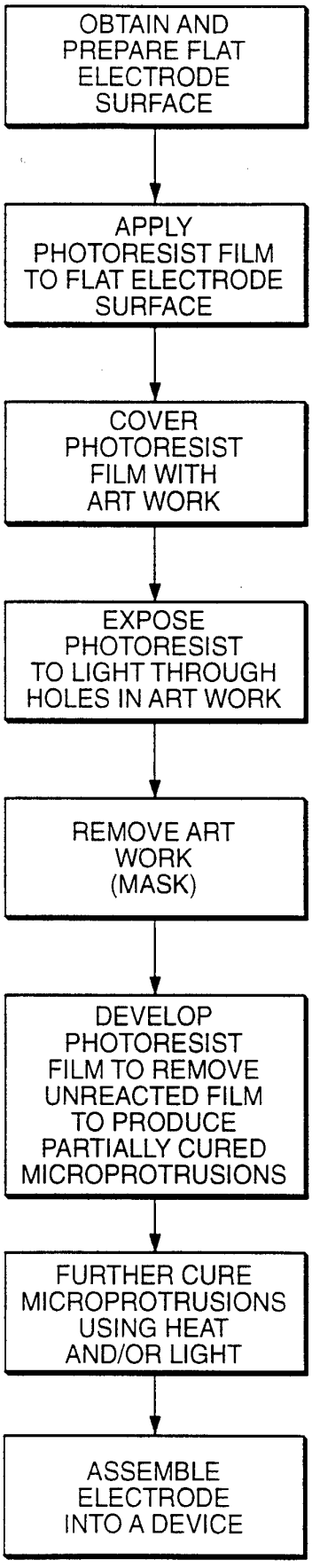

OBTAIN AND PREPARE FLAT ELECTRODE SURFACE
APPLY PHOTORESIST FILM TO FLAT ELECTRODE SURFACE
COVER PHOTORESIST FILM WITH ART WORK
EXPOSE PHOTORESIST TO LIGHT THROUGH HOLES IN ART WORK
REMOVE ART WORK (MASK)
DEVELOP PHOTORESIST FILM TO REMOVE UNREACTED FILM TO PRODUCE PARTIALLY CURED MICROPROTRUSIONS
FURTHER CURE MICROPROTRUSIONS USING HEAT AND/OR LIGHT
ASSEMBLE ELECTRODE INTO A DEVICE

FIG._9

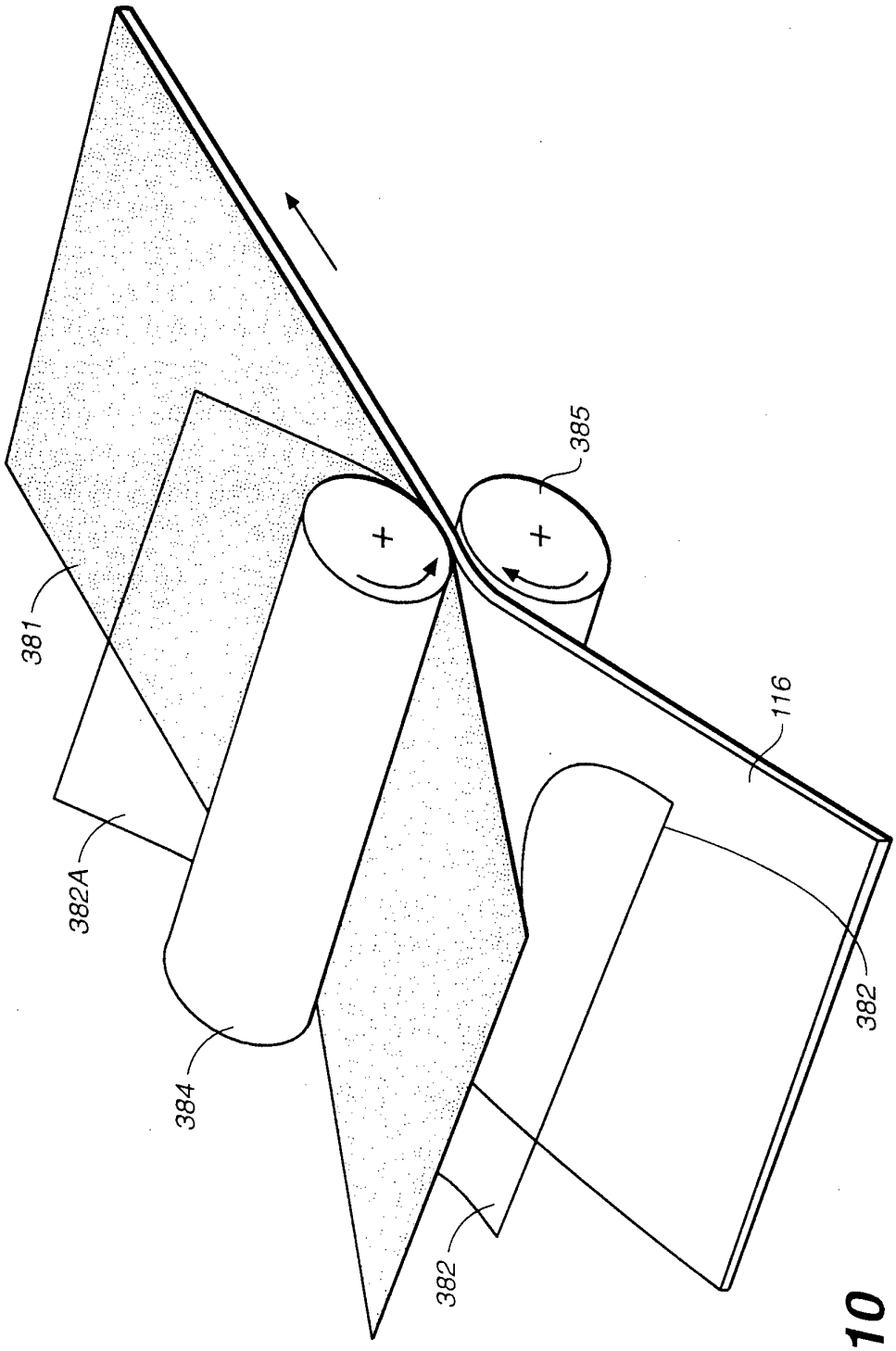


FIG._10

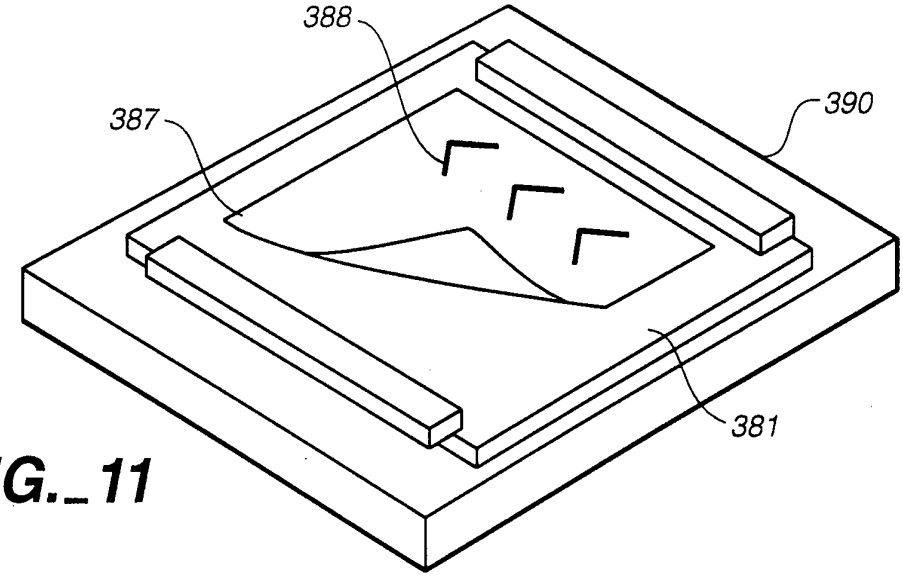
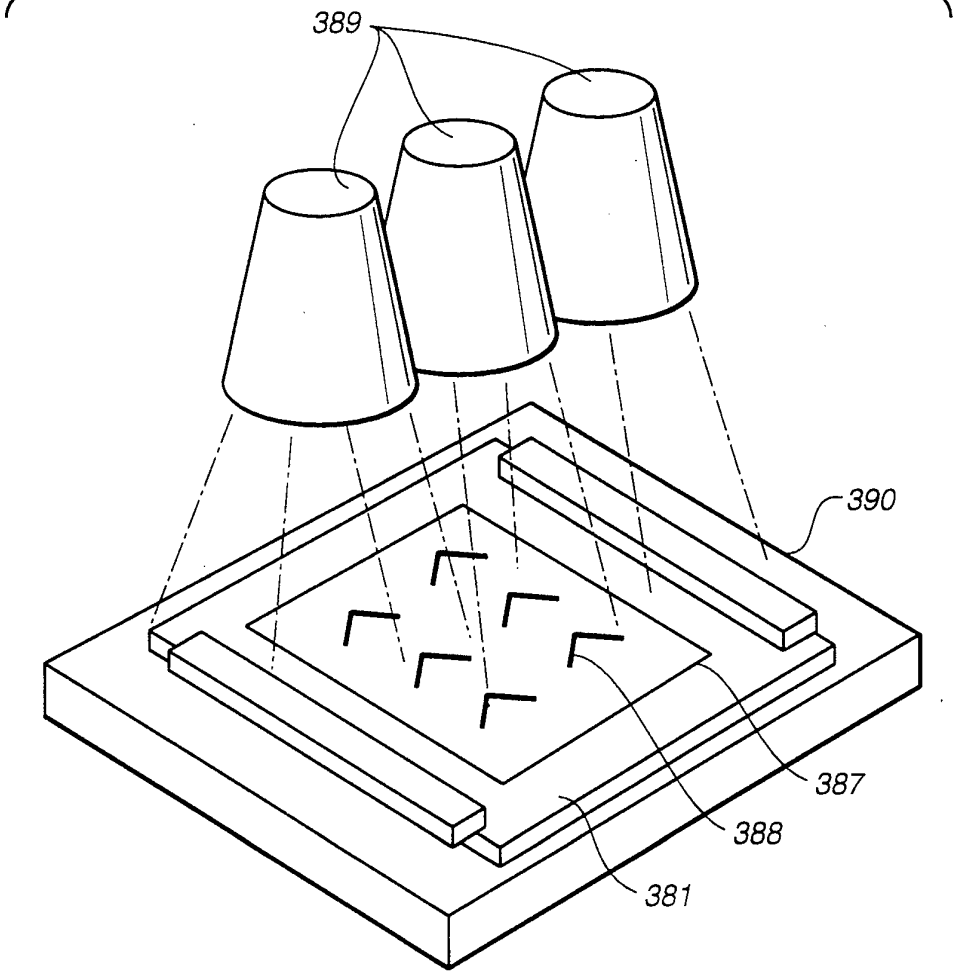


FIG._11

FIG._12



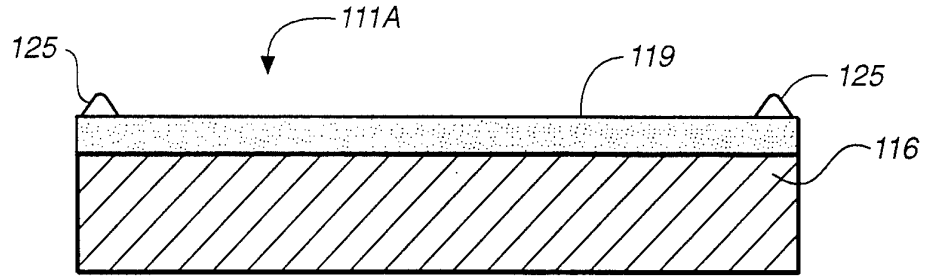


FIG._13

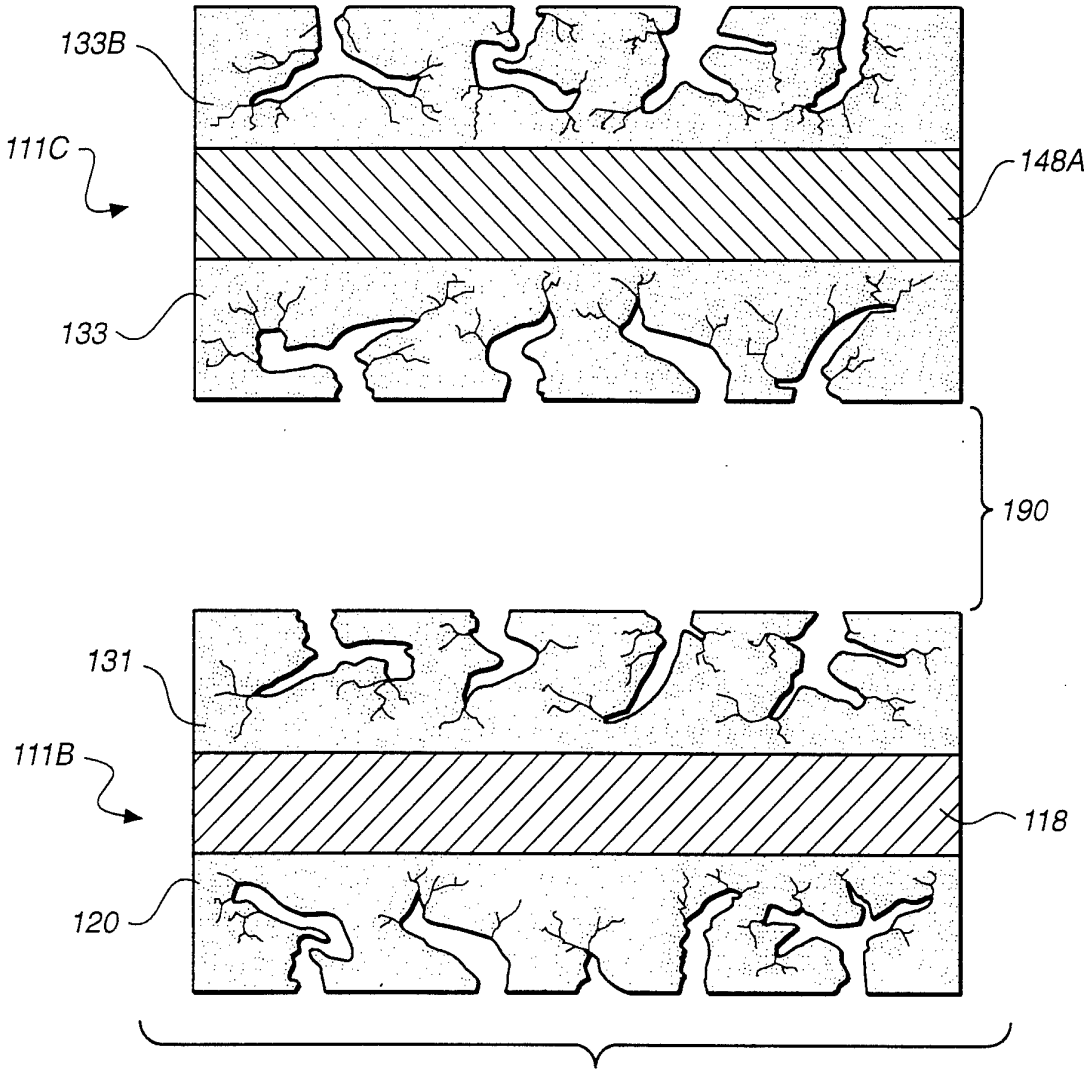


FIG._14

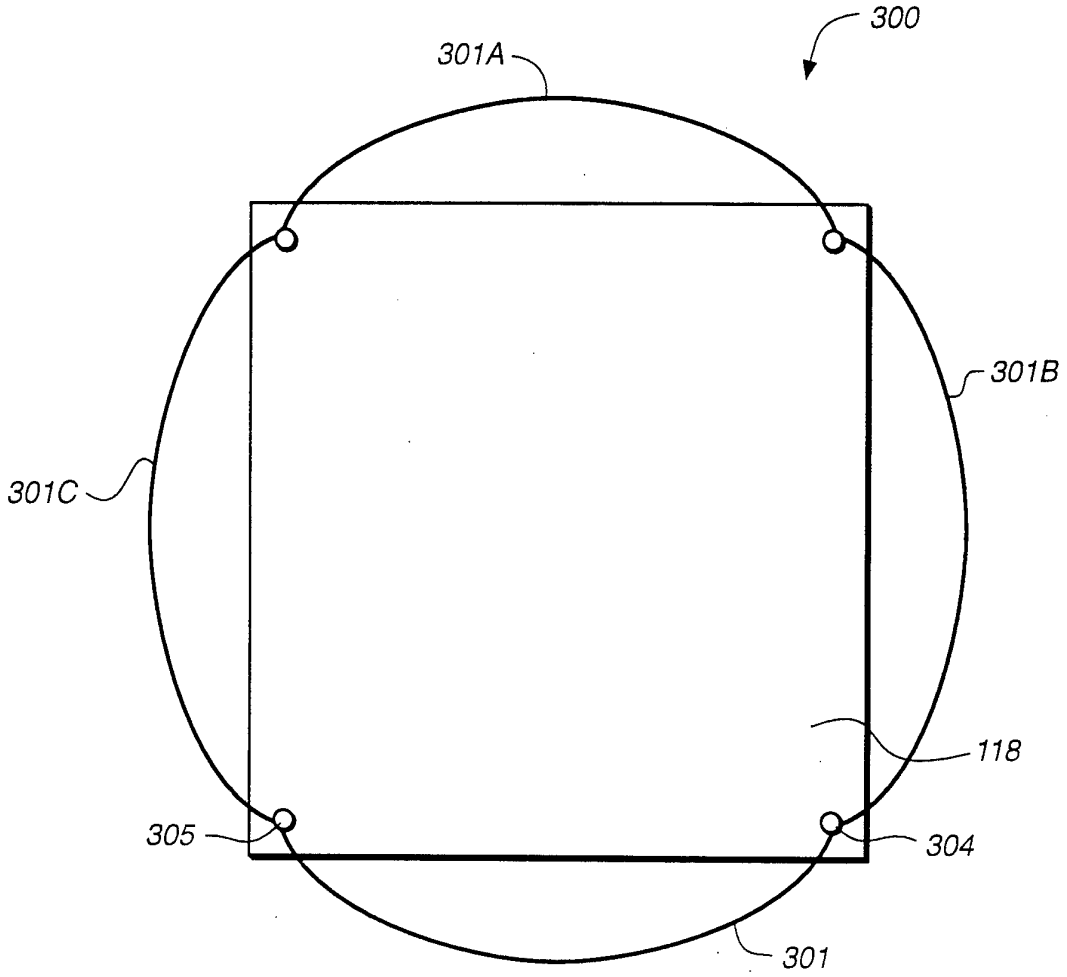


FIG._15

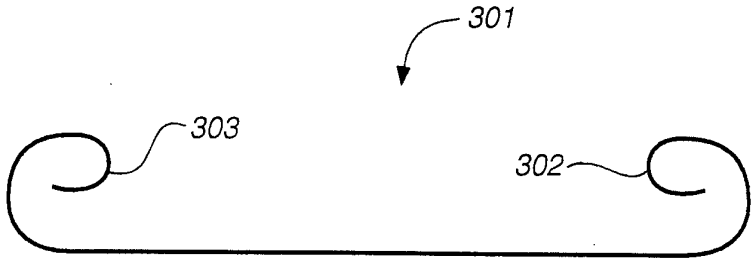


FIG._15A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/08803

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01M 2/08, 2/18, 6/12, 6/32; H01G 9/04; B05D 1/32
US CL :429/118, 130, 162, 185; 29/25.03; 427/282
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. : 429/118, 130, 162, 185; 29/25.03; 427/282; 437/919

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.
Y	US, A, 4,557,983 (Sauer) 10 December 1985, col. 2 line 18, to col. 3 line 13.	1-13, 15-18, 23-26, 29-32, 35,36, 38-44, 52, 53, 55
Y	US, A 5,116,701 (Kalisz) 26 May 1992, col. 3 line 18, to col. 5 line 35.	19,20
Y	US, A, 4,800,142 (Bish et al) 24 January 1989, col. 3 line 35, to col. 6 line 31.	1-13, 15-18, 23-26, 29-32, 35,36, 38-44, 52, 53, 55
Y	US, A, 4,052,271 (Beer) 04 October 1977, col. 1, lines 24-58.	27-28,54

[X] 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 part 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
15 November 1993

Date of mailing of the international search report
07 DEC 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

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Authorized officer
for KEVIN PICARDAT

Telephone No. (703) 308-1097

Form PCT/ISA/210 (second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/08803

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 14,21,22,33,34,37,45-51
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/08803

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,032,426 (Sumner, Jr.) 16 July 1991, col. 3, lines 32-35.	27-28, 54
Y	US, A, 4,572,843 (Saito et al) 25 February 1986, col. 5 line 49, to col. 8 line 55.	27-28, 54
A	US, A, 4,862,328 (Morimoto et al) 29 August 1989, entire document.	
A	US, A, 4,663,824 (Kenmochi) 12 May 1987, entire document.	
A	US, A, 4,555,745 (Westermeir et al) 26 November 1985, entire document.	
A	US, A, 4,548,880 (Suzuki et al) 22 October 1985, entire document.	
A	US, A, 5,116,695 (Rao et al) 26 May 1992, entire document.	
A	US, A, 5,072,335 (Kurabayashi et al) 10 December 1991, entire document.	