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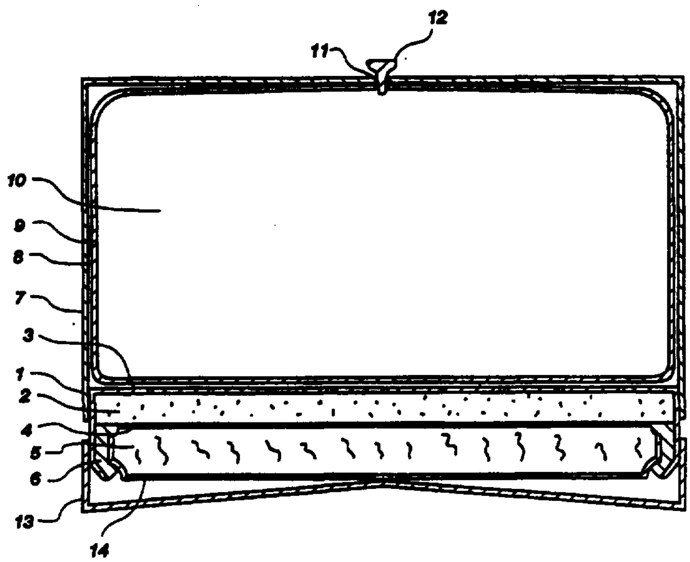

(57) Abstract

A self-contained device which dispenses a packaged fluid (9) is disclosed. The device is suited for applications where several months may lapse before performance is manually initiated, after which a steady flow is required until the packaged fluid (9) is exhausted and for applications where ease of fabrication is important. The device utilizes an electrochemically-generated gas to pressurize the packaged fluid (9) to dispense it. A gas can be electrochemically released from a solid anode material (2) to migrate across an ion conducting electrolyte (4) and be reduced at the cathode (14). The released gas pressurizes a chamber (8) resulting in fluid contained in the flexible bladder (9) within the chamber (8) to be forced through an outlet (11). Depending on the selection of anode (2) and cathode (14) materials, the device will be self-driven or a battery will be required to provide a driving force.

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GAS RELEASING ELECTROCHEMICAL CELL FOR FLUID DISPENSING APPLICATIONS

BACKGROUND OF THE INVENTION

Field of the Invention: This invention relates to a dispensing device, in particular a device where the active fluid is oxygen or nitrogen gas which has been released from a solid state electrochemical cell, and where the pressure increase resulting from the release of such gas pushes fluid from a bladder within a pressure-tight chamber through an outlet in a steady continuous flow until the fluid contents of the bladder are exhausted.

State of the Art: Richter in U.S. Pat. No. 3,894,538 disclosed a device for dispensing medicines to man or beast. The medicine was contained in a flexible container which became compressed as fluid was electro-osmotically or electrolytically introduced into an adjacent flexible chamber. The rate of medicine discharge was regulated by using a potentiometer.

Maget in U.S. Pat. No. 4,522,698 disclosed electrochemical prime movers. Embodiments of the invention include a device for dispensing pharmaceuticals to a human body over a substantial period of time at a sustained very low rate, where a battery provides the driving force to transport an electrochemically active gas from a precharged chamber to a second chamber through an ion-exchange membrane. Oxygen from air was disclosed as moving across an ion-exchange membrane to pressurize a chamber. Pressure in a chamber increases as electroactive gas transports across the membrane, this increase in pressure drives a piston which forces the contained pharmaceutical fluid to flow through an outlet. The invention requires electrodes which are electrically conductive and act as catalyst to convert molecules to ions; titanium-palladium alloy or palladium black are recommended materials. A controller is utilized to control the magnitude and time pattern of current and voltage applied to the membrane as well as to turn current on and off. To function, the invention requires either exposure to air or precharging with an electroactive gas.

Maget in U.S. Pat. No. 4,886,514 disclosed electrochemically driven drug dispensers. A potential from an external power source drives an electrochemically active gas such as hydrogen or oxygen to be transported across a membrane from a fixed volume chamber to a chamber which has a variable volume. The volume of the chamber varies by either flexing an expansible diaphragm type wall or by displacing a sliding wall, said wall is shared by a second variable volume chamber which contains a fluid drug to be administered. As the electrochemically active gas is transported to the first variable volume chamber, the drug is forced out of the second variable volume chamber through an outlet. Countering the electrochemical transport of gas across the membrane, the gas diffuses in the opposite direction across the membrane in accordance to the pressure gradient and diffusivity properties of the membrane. A controller compensates for the gas diffusion rate and varies the voltage and current to achieve the desired drug delivery rate in a steady or intermittent mode. To function, the invention requires precharging with an electroactive gas.

Maget et al. in U.S. Pat. No. 4,902,278 disclosed a fluid delivery micropump. The pump utilizes an air-actuated battery in a fixed closed circuit with an electrochemical cell which drives the transport of oxygen in air across a membrane. The transport applies external pressure to a collapsible reservoir filled with fluid, as a result, fluid is expelled from the reservoir through an outlet. The membrane is preferably a Nafion material (a perfluoro sulfonic polymer) which has been coated with platinum black/10% Teflon. Electrodes are preferably titanium screens. To control the current, a resistor is utilized. The device is activated by removing a protective peel tab to expose air inlet ports to the battery cathode. A disadvantage of this type of system is that shelf life of the device is dependent on the integrity of the seals which prevent air leakage to the battery. If the seals are not perfect, the battery will slowly discharge before the desired time of use. To function, the invention requires exposure to air.

The prior art includes several devices which are capable of performing the general function of the device presently disclosed; however, the prior art has not satisfied a demand which exists for a device which 1) has a design which can dispense a fluid over a nearly constant rate for an extended period of time, 2) has a simple design which is conducive to fabrication, 3) does not require exposure to air, fluid or the precharging of an electrochemically active gas to function, 4) does not utilize polymeric ion-exchange membranes which typically must remain hydrated to some degree to function and which are affected by humidity, which can cause changes in conductivity, gas flow and dispensing rates.

SUMMARY OF THE INVENTION

An invention is disclosed which provides a self-powered, low cost device which has a long shelf life and which dispenses a fluid at a slow, steady, predictable rate over an extended period of time. The fluid itself may have beneficial attributes or it may contain chemicals or nutrients which provide a benefit or which inhibit something undesirable to a system or living organism. The fluid can be delivered to a specific site through appropriate tubing and connections, or the fluid can be delivered to an external portion of the device where it is allowed to evaporate into a room, vehicle, container or other environment surrounding the dispenser. The dispenser may be embodied in a form intended to be stationary, sitting upon something or hung from something, or may be embodied in a form to be worn on a person or animal in the form of a pendant, a clothing attachment, a collar attachment for an animal, or in a form to be hung from a tree or other type of plant. A significant aspect of the invention is that some embodiments of the gas-generating electrochemical cell also act as a battery so that a separate power source is not required, in contrast to prior art devices.

The present device is delivered to consumers in a disabled condition so that no drain on the battery or electroactive components occurs when the device is on the shelf, waiting to be used. Activation occurs when the consumer completes an electric circuit. This may be accomplished in various ways, for example, by snapping electronically conducting components of the device together or by removing a temporary insulator from between two electronic contacts. In addition, the user typically unseals the fluid sack outlet by removing a plug, or by cutting or by puncturing the sack. Thus, neither the power supply nor the fluid contents will be compromised before the device is to be utilized.

A novel solid state electrochemical cell releases oxygen or nitrogen gas which is the working substance, i.e., pumping gas in the device. Released gas flows into a gas-tight chamber which encloses a flexible bladder containing the fluid to be dispensed. As gas is transported into a gas-tight chamber, the resulting increase in pressure compresses the bladder such that the fluid flows through an outlet to the desired destination or to a site on the dispenser where the fluid can evaporate or disperse.

Oxygen is a suitable pressurizing gas and can be electrochemically released from a solid anode material of the general form A_xO_y. The value of x is 1 to 3 and y is 1 to 4. Nitrogen also may be a suitable pressurizing gas. It can be electrochemically released from a solid anode material of the general form $A'_\alpha N_\beta$. The value of α is 1 to 3 and β is 1 to 3. In each of the above instances, an ion migrates across a suitable ion conducting electrolyte. The migrating ion may be, respectively, A ions or A′ ions. A and A′ are cations such as silver, copper and the like in a positive valence state, while A′ is an alkali metal such as sodium, lithium and the like in a positive valence state. The migrating ion (cation) allows the anion (O^{-2} or N^{-3}) to combine with a similar anion to form a gas (O_2 or N_2) concomitant with the release of electrons. At the cathode, several possibilities may occur, examples include ones in which the migrated cations are reduced to their elemental state, or where a solid material R_2 wherein R is a halogen is ionizable to R^-, or solid material, R′, where R′ is a group VIB element reducible to R'^{-2} or where cathode material CR_x is reduced to $C+XR^-$. A typical CR_x is a fluorocarbon such as a CF_x which is readily available. In the above formulas, X and x are equivalent and have a value of about 0.8 to about 1.2. The driving force powering the device is either provided by the electrochemical reactions occurring during operation of the cell, or by a battery.

The micropumps of the instant invention are characterized by a fluid dispensing chamber wherein the chamber has a fluid reservoir and a gas space. The gas space and fluid reservoir are separated by a flexible material, e.g., a membrane or a bladder, such that as the gas space expands due to incoming gas, the fluid reservoir is caused to shrink which causes fluid, generally liquid, to be discharged from a discharge port in the reservoir.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a plot of current density versus time of an Ag_2O/S cell;

FIG. 2 shows a plot of current versus time of an Ag_2O/I_2 cell;

FIG. 3 shows a plot of current versus time of two Li_3N/I_2 cells;

FIG. 4 shows a plot of current versus time of a Li_3N/CF_x cell;

FIG. 5 is a perspective sectional view of a fluid dispensing micropump embodying features of the present invention;

FIG. 6 shows a perspective sectional view of an embodiment of the invention which is a variation of what was shown in FIG. 1;

FIG. 7 shows a perspective sectional view of an embodiment of the invention which features a battery integrated into the design;

FIG. 8A schematically illustrates an electrochemical cell of the invention in a pre-discharged condition;

FIG. 8B schematically illustrates a discharging cell; and

FIG. 8C schematically illustrates a cell which does not require a discrete electrolyte member.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention employs anode materials wherein an electrochemical decomposition occurs at the anode to release an anion such as O^{-2} or N^{-3} which, upon release of electrons, combine to form O_2 and N_2 gases which can be used for pressurizing purposes. The anode materials generally comprise a compound formed of a metal cation, typically monovalent, and a divalent or trivalent anion such as O^{-2} or N^{-3}. The cathode material is one which electrochemically reacts with the cation species from the anode material after its transport through an appropriate electrolyte. The electrolyte may be solid, liquid or a solid dissolved in a liquid. If the electrolyte is not solid, a separator such as the microporous separators used in the battery industry may be used to prevent direct contact of the anode and cathode materials. If a separator is used, electrolyte is absorbed into the pores of the separator. Battery separators are typically a microporous sheet of polyolefin such as ethylene vinyl alcohol copolymers having a pore size less than 1.0 micron. The copolymer has a linear-type olefin portion with a vinyl alcohol content of between 20 and 90%. The alcohol portion may also be hydrolyzed. Other typical battery separators include those described in the patent literature such as cellophane with a grafted polymer U.S. Pat. No. 3,330,702; cellulosic material or paper coated with a resin U.S. Pat. 3,893,871 and 3,976,502; cellophane with a grafted copolymer U.S. Pat. No. 3,330,702; methacrylic acid-divinyl benzene copolymer U.S. Pat. No. 3,684,580; phenol-resorcinol-formaldehyde resin U.S. Pat. No. 3,475,355; and polyacrylamide U.S. Pat. No. 3,018,316. Several examples of a polyolefin-homo or copolymer film with fillers are U.S. Pat. Nos. 3,870,586; 3,955,014; 3,985,580; and Pat. No. 4,024,333. The use of polytetrofluoroethylene is described in U.S. Pat. No. 3,475,222 and Pat. No. 3,661,645, while other polyvinyl compositions are found in U.S. Pat Nos. 3,585,081; 3,766,106; 3,875,270 and 3,907,601. Silicone rubber-vinyl copolymer is still yet another example of a battery separator described in U.S. Pat. No. 3,585,081. The gas producing electrochemical cell is sealed from the external environment.

Since no gaseous materials are involved in the cathode chamber, the cathode or cathode current collector need not be porous. A preferred cathode is one which is sealed from the environment and has a combination of properties such that unreacted cathode and reacted cathode materials have adequate ionic and/or electronic conductivity such that the voltage drop across the zone does not increase significantly relative to the rest of the cell as the cell discharges. Suitable cathodes are set forth in the following examples.

In prior gas producing cells, it was typical for the cathode and anode chamber to contain an element common to each. For example, in Maget patent ('698), the cathode contained O_2 and the anode contained oxygen in combined form, H_2O, to form an O_2/H_2O redox couple with a proton transported through an electrolyte so that the reaction on opposite sides of the electrolyte were the reverse of one another. The total redox energy involved is zero, however, because of internal cell resistance, electrode polarization, and differences in oxygen partial pressure, a battery (power source) had to be used in such cells. Also, in such a cell, a gas is present at both electrodes, thereby requiring porous electrodes.

In the instant invention, many cells have completely different materials, i.e., no common elements, in the cathode and anode chambers. Thus, in many instances a net energy production (positive voltage) occurs so that the cell is self-powered.

The device disclosed herein is particularly distinguished from the prior art in that the device can function while completely sealed from its external environment, excluding the outlet port through which the fluid will be dispensed, and without requiring an internal reservoir of gas to be pumped. Unlike the devices described in the prior art, an organic ion-exchange membrane is not utilized in this device, and since the device is sealed, this device is not sensitive to changes in ambient humidity. Also, the device does not rely on access to air or other gas to operate. Further, because the device is simply structured and is comprised of readily available, easily fabricated materials, it is disposable.

The following examples illustrate different possibilities of the device where the anode and cathode couple, in effect, create a galvanic cell such that an additional battery is not required:

EXAMPLE 1

An example of an oxygen releasing, solid, self-driving cell is one in which the active anode material is Ag_2O and the active cathode material is solid I_2 or a combination solid I_2 and poly(2-vinylpyridene) (P2VP) or poly 2 vinylquinoline (P2VQ) which combine to form a material both electronically and ionically conductive. Several silver ion conductors are suitable as solid electrolytes for this application including Ag_4RbI_5, AgI/Al_2O_3 and Ag-Nasicon; however the preferred electrolyte in this case is AgI which reactively forms at the interface between the anode (Ag_2O) and cathode (I_2) layers. This electrolyte forms spontaneously as an interfacial reaction, requires no preparation, and conforms to any irregularities in the interface. The electrochemical reactions are:

Anodic: $Ag_2O \rightarrow 2Ag^+ + \frac{1}{2}O_2 + 2e^-$

Cathodic: $2Ag^+ + I_2 + 2e^- \rightarrow 2AgI$

Overall: $Ag_2O + I_2 \rightarrow 2AgI + \frac{1}{2}O_2$

Such a cell has a standard potential, E°, of 0.96V; therefore, in this case, no battery or other applied voltage source is required to drive the process. Once the electrical circuit is completed between the cathode and the anode, electrons and ions begin to flow and the device is operable. Other materials which would release oxygen when properly coupled with I_2 include Na_2O, K_2O, Na_2O_2, Ag_2O_2, K_2O_2, Rb_2O and Rb_2O_2. A cell of this type is schematically illustrated in FIG. 8. The cell remains dormant until an electron conductor is connected between the anode and cathode materials.

EXAMPLE 2

Another example of an oxygen releasing, solid cell which is self-driving is one in which the anode material is Ag_2O and the cathode material is solid S or a combination of solid S and Ag_2S which together form a material both electronically and ionically conductive. A suitable electrolyte is Ag_4RbI_5. The electrochemical reactions are:

Anodic: $Ag_2O \rightarrow 2Ag^+ + \frac{1}{2}O_2 + 2e^-$

Cathodic: $2Ag^+ + S + 2e^- \rightarrow Ag_2S$

Overall: $Ag_2O + S \rightarrow Ag_2S + \frac{1}{2}O_2$

Such a cell has a standard potential, E°, of 0.16V. Other materials which could be used in the place of S are Se and Te.

EXAMPLE 3

An example of a nitrogen releasing, solid, self-driving cell is one in which the anode material is Li_3N and the cathode material is solid I_2 or a combination of solid I_2 and poly(2-vinylpyridene) which combine to form a material both electronically and ionically conductive. Several lithium ion conductors are suitable as solid electrolytes for this application including LiI/Al_2O_3 and Li-Nasicon; however, the preferred electrolyte in this case is LiI which forms at the interface between the anode and cathode layers. This electrolyte, similarly to AgI, forms spontaneously, requires no preparation, and conforms to any irregularities in the interface. The electrochemical reactions are:

Anodic: $Li_3N \rightarrow 3Li^+ + \frac{1}{2}N_2 + 3e^-$

Cathodic: $3Li^+ + 3/2I_2 + 3e^- \rightarrow 3LiI$

Overall: $Li_3N + 3/2I_2 \rightarrow 3LiI + \frac{1}{2}N_2$

Such a cell has a standard potential, E°, of 2.16V; therefore, in this case, no battery or other applied voltage source is required to drive the process. Once the anode and cathode are electronically connected, the cell will begin to function.

EXAMPLE 4

Another example of a nitrogen releasing, solid, self-driving cell is one in which the anode material is NaN_3 and the cathode material is solid I_2 or a combination of solid I_2 and poly(2-vinylpyridene) which combine to form a material both electronically and ionically conductive. Several sodium ion conductors are suitable as solid electrolytes for this application including NaI/Al_2O_3 and Nasicon; however the preferred electrolyte in this case is NaI which forms at the interface between the anode and cathode layers. This electrolyte forms spontaneously, requires no preparation, and conforms to any irregularities in the interface. The electrochemical reactions are:

Anodic: $NaN_3 \rightarrow Na^+ + 3/2N_2 + e^-$

Cathodic: $Na^+ + ½I_2 + e^- \rightarrow 3LiI$

Overall: $NaN_3 + ½I_2 \rightarrow NaI + ½N_2$

Such a cell has a standard potential, E°, of 4.05V; therefore, in this case, no battery or other applied voltage source is required to drive the process.

The following examples illustrate different possibilities of the device where the solid anode and cathode couple require an applied voltage to drive the gas releasing reaction, such an applied voltage can be provided by one or more batteries:

EXAMPLE 5

Another example of a nitrogen releasing cell which is self driving is one in which the anode material is Li_3N and the cathode material is polycarbon monofluoride of CF_x (where x is 0.8 to 1.2). An example of such a material is a product of Allied Chemical under the trade name Accuflor™. A suitable electrolyte is a 1:1 mixture of ethylene glycol dimethyl ether and propylene carbonate containing 1 M $LiBF_4$. This electrolyte is used with a thin microporous separator comprised of polypropylene or polyolefin. Such a separator is electronically insulative but has high ion permeability. The cell is similar to the Li-CF_x battery described in Modern Battery Technology by C.D.S. Tuck, pp. 337-348, except that in the case of this invention, the lithium anode is replaced by a lithium nitride anode so that gas is released electrochemically as the cell discharges. The electrochemical reactions are:

Anodic: $x\ Li_3N \rightarrow 3x\ Li^+ + x/2\ N_2 + 3x\ e^-$

Cathodic: $3x\ Li^+ + 3\ CF_x + 3x\ e^- \rightarrow 3x\ LiF + 3\ C$

Overall: $x\ Li_3N + 3\ CF_x \rightarrow 3x\ LiF + 3\ C + x/2\ N_2$

Such a cell has a standard potential, E°, of approximately 2.7V; therefore, in this case, no battery or other applied voltage source is required.

EXAMPLE 6

Another example of a oxygen releasing cell which is self driving is one in which the anode material is Ag_2O and the cathode material is polycarbon monofluoride of CF_x (where x is 0.8 to 1.2). An example of such a material is a product of Allied Chemical under the trade name Accuflor™. A suitable electrolyte is 1:1 mixture of ethylene glycol dimethyl ether and propylene carbonate containing 1 M $AgBF_4$. This electrolyte is used with a thin microporous separator comprised of polypropylene or polyolefin.

EXAMPLE 7

Another example of a oxygen releasing cell which is self driving is one in which the anode material is a paste consisting of Ag_2O silver nitrate and sodium hydroxide solution and the cathode material is a paste consisting of solid S, carbon, and silver nitrate, and where the anode and cathode are separated by a solid polymer electrolyte which has been exchanged with silver ion containing solution such as silver nitrate.

EXAMPLE 8

An example of an oxygen releasing, solid cell which is not self-driving and which would require a battery or other applied voltage source is one in which the anode material is Cu_2O and the cathode material is porous copper or graphite or carbon. Several copper ion conductors are suitable as solid electrolytes for this application including $Rb_4Cu_{16}I_7Cl_{13}$ or Cu-Nasicon or a mixture of CuI and Al_2O_3. The electrochemical reactions are:

Anodic: $Cu_2O \rightarrow 2Cu^+ + \frac{1}{2}O_2 + 2e^-$

Cathodic: $2Cu^+ + 2e^- \rightarrow 2Cu$

Overall: $Cu_2O \rightarrow 2Cu + \frac{1}{2}O_2$

Such a cell has a standard potential, E°, of -0.77V. Other oxygen releasing solid couples include Cu_2O/I_2, Li_2O/I_2, Na_2O/S, K_2O_2/S.

Regardless of whether the cell is self-driven or driven with a battery or other applied voltage source, the rate of fluid dispensing is directly proportional to the rate of oxygen or nitrogen, in the above stated examples, released at the anode which is directly proportional to the electrical current. The electrical current required to dispense the fluid is very low, about 183μA per ml fluid per day at standard conditions for the oxygen releasing cells mentioned above assuming no leakage occurs from the gas chamber. To determine actual fluid delivery at conditions other than standard for those cells, the following relationship can be used:

ml actual per day = 0.00349 x Z x C x T / P;

where:
- Z = Number of electrons which must pass though the device circuit per molecule of gas released. Typically Z= 4 for O_2 release, Z=6 for N_2 release.
- C = Current in μA (microamps),
- T = Temperature in degrees K
- P = Pressure in Torr

Many applications involving concentrated chemicals will require substantially less than 1 ml per day to be effective, thus total current flow in the range of five to 500μA would be typical for this device although the device is not limited to this range. Such a current range would provide fluid delivery ranges from 0.03-2.7 ml per day. Thus, this device is effective when operating at low current densities. If a self-driven cell is selected, resistors and controllers to restrict or otherwise control current flow may be utilized or may be avoided by adjusting cement density through cell design.

Without complicating the present device, several strategies can be taken to make adjustments in construction such that the desired substance dispensing rate is achieved. Some strategies relate to adjustments which would affect the current density and hence the rate of fluid flow. The area of the electrolyte surface can be predetermined or the thickness of the electrolyte may be varied in a particular cell to give a desired gas discharge rate and consequently a desired fluid flow. The rate of cell discharge can be increased by adding constituents to the anode which would improve the electronic and ionic conductivity. For example, the addition of Ag_2S and/or $RbAg_4I_5$ to the anode has been found to dramatically improve cell discharge rates. A combination of 20% by weight of each was very effective. Other concentrations are also effective. Addition of electrolytes dissolved in non-aqueous electrolytes to either anode or cathode have similar effects and help prevent polarization. The addition to the anode of a small amount of oxygen evolution catalyst such as 0.5% RuO2 or IrO2 can increase the discharge rate by an order of magnitude. Larger and smaller amounts of these oxides also may be effectively used.

Further advantages of the invention will become apparent from the drawings and more detailed description below.

FIG. 1 shows a plot of current density versus time of a Ag_2O/S cell. Finely divided AgI (40%) and high surface area Al_2O_3 (60% by weight) were heated to 500°C to form a very ionically conductive electrolyte. A small amount of this electrolyte was pressed to form a thin membrane in a 0.625" diameter die. An anode mixture of Ag_2O powder, graphite powder, and $AgI+Al_2O_3$ electrolyte was added to one side of the membrane, a cathode mixture of sulfur powder, graphite powder, and $AgI+Al_2O_3$ electrolyte was added to the other side of the membrane. The entire cell was pressed into a three layer pellet at a pressure of 537,800 kiloneutons per square meter (KNT/m^2) (78,000 psi). A perforated stainless steel plate was used for the anode contact and an un-perforated stainless steel plate was used for the cathode contact. Total height of the cell was about 0.635 meters (0.25 inches). The cell circuit was completed by contacting an electronic resistor to the anode and cathode contacts. A resistor of approximately 10000 ohms was used in the circuit.

FIG. 2 shows a plot of current versus time of a Ag_2O/I_2 cell where the anode was approximately 60% Ag_2O, 20% Ag_2S, 20% Ag_4RbI_5 and 0.5% RuO_2 while the cathode was 6.7% P2VP with the balance consisting of I_2. Percents stated are percents by weight. The cathode mixture was heated slightly to form a semi-plastic paste. First the anode mixture was pressed in a 1.9 centimeters (0.75 inches) diameter die at about 138,000 KNT/m^2 (20,000 psi). The electrolyte between the anode and cathode was AgI which formed in situ when the anode and cathode were pressed together. The reaction continues until a continuous, impervious layer of AgI is formed, which sets as a separator between the reactive materials.

A perforated stainless steel plate was used for the anode contact and an un-perforated stainless steel plate was used for the cathode contact. Total height of the cell was about 0.508 centimeters (0.2 inches). The cell circuit was completed by contacting an electronic resistor to the anode and cathode contacts. Resistors of 10000 ohms, 5000 ohms and 1000 ohms were used in the circuit.

FIG. 3 shows a plot of current versus time of two Li_3N/I_2 cells. In the first cell approximately 33% graphite powder was mixed with a balance of Li_3N. Some of this mixture was pressed in a 1.9 centimeters (0.75 inches) diameter die at approximately 138,000 KNT/m^2 (20,000 psi). A cathode mixture of 5% P2VP with balance I_2 was mixed in a ball mill with alumina balls overnight. This cathode mixture was not heated. Some of this mixture was pressed onto the cathode. A continuous, thin LiI electrolyte layer formed in situ between the anode and cathode when they were pressed together.

A perforated stainless steel plate was used for the anode contact and an un-perforated stainless steel plate was used for the cathode contact. Total height of the cell was about 0.508 centimeters (0.2 inches). The cell circuit was completed by contacting an electronic resistor of 16,200 ohms to the anode and cathode contacts. In a second Li_3N/I_2 cell, approximately 33% graphite powder was mixed with a balance of Li_3N powder. Some of this mixture was pressed in a 1.9 centimeters (0.75 inches) diameter die at approximately 138,000 KNT/m^2 (20,000 psi). Next a layer of Li_3N powder without graphite was pressed onto the previous layer. On this layer was pressed a cathode mixture of 5% P2VP with balance I_2 which had been mixed in a ball mill with alumina balls overnight. A thin, continuous LiI electrolyte layer formed spontaneously in situ between the anode and cathode when they were pressed together. Again, a perforated stainless steel plate was used for the anode contact and an un-perforated stainless steel plate was used for the cathode contact. Total height of the cell was about 0.508 centimeters (0.2 inches). The cell circuit was completed by contacting an electronic resistor of 10000 ohms to the anode and cathode contacts.

FIG. 4 illustrates the current versus time characteristics for a Li_3N - CF_x cell all in which the anode material was a mixture of 75 wt% lithium nitride (Li3N, Aldrich, Milwaukee, Wisconsin) and 25 wt% carbon black (Vulcan). To prepare anode material, powders of Li3N and carbon were dry mixed in a ball mill under N2 atmosphere, and then passed through a sieve with a mesh size of 200 microns before pressing into anode pellet (15 mm dia. x 3 mm thick).

Cathode material was a mixture of 77 wt% carbon monofluoride (CF_x, x between 0.8 to 1.2, Allied Signal Chemicals, Morristown, NJ), 13 wt% carbon black (Vulcan), and 10 wt% poly-tetrafluoroethylene (PTFE, Aldrich, Milwaukee, Wisconsin). For preparing the cathode material, powders of CFx, PTFE and carbon were slurried in an isopropanol solution. The slurry was well mixed, heated at 90°C to coagulate PTFE, and then dried at 100°C and passed through a sieve with a mesh size of 200 microns before pressing into a cathode pellet (15 mm dia. x 5 mm thick).

Liquid electrolyte was 1 M lithium fluoroborate ($LiBF_4$, Fluka, Buchs, Switzerland) dissolved in a 1:1 mixture of ethylene glycol dimethyl ether (Aldrich, Milwaukee, Wisconsin) and propylene carbonate (Aldrich, Milwaukee, Wisconsin).

Separator material was a hydrophobic microporous polyolefin membrane (Pall RAI Manufacturing Company, Hauppauge, N.Y.). Nickel mesh was used as current collectors.

For purposes of illustration of the present invention, an embodiment of the solid electrolyte fluid dispensing micropump is shown in FIG. 5.

Pump housing 1 is fabricated of a chemically resistant and electronically conductive material such as 304 or 316 stainless steel. Gas passages 3 or holes are perforated through the pump housing 1. Anode material 2 is pressed into the pump housing 1. Anode material 2 is comprised of an oxidized compound of the general formula A_xO_y such as Ag_2O or a nitride compound of the general formula $A'_\alpha N_\beta$ combined with other constituents which improve electronic and ionic conductivity and which are electrocatalysts. On top of said anode material, solid electrolyte material 4 is pressed or otherwise forms spontaneously when anode and cathode materials are contacted as indicated hereinabove. The composition of said solid electrolyte material is selected based on the cation A or A' which is to be conducted. For example, AgI mixed with Al_2O_3 or Ag_4RbI_5 or Ag-Nasicon could be selected to conduct Ag^{+1} cations, or AgI, an Ag^+ conductor will form spontaneously when Ag_2O is contacted with I_2 to form an electrolytic interface. Cathode material 5 comprised of solid halogen material such as I_2 mixed with poly(2-vinylpyridene), or S mixed with Ag_2S and Ag_4RbI_5, is pressed into the cathode cap 14 which is an electronic conductor such as 304 or 316SS. A spacer 6 comprised of an electrically insulating material separates the cathode material 5 and cathode cap from the pump housing 1. The cathode cap 14 and the spacer 6 are crimped by the pump housing 1 to form a seal. The gas shell 7 is attached to the pump housing 1. The gas chamber 8 is bounded by the gas shell 7 and the pump housing 1. Within said gas chamber is a fluid sack 9 which contains the fluid to be dispersed 10. Said fluid sack is made of a flexible material, such as Barex or ethylene vinyl alcohol film, which has adequate corrosion properties for said fluid. Said fluid sack has an outlet 11 which passes through said gas shell and is sealed thereto. The fluid sack is preferably a polymeric, filmy, material impervious to both the pressurizing gas molecules and the fluid material.

The fluid sack outlet 11 may be very simple or may have a fitting for the attachment of tubing, or may have an attachment suitable for promoting evaporation of the fluid into the surrounding air. Said fluid sack may be sealed from the external environment before the time of activation with a plug 12, clip or other means, or may have a sealed portion which protrudes through said outlet which is cut off or punctured by the user at the time of activation. Contact clip 13 fabricated of an electronic conductor completes the electrical circuit between said anode contact and said cathode contact after activation by the user. At the time of activation, cations migrate from said anode material to said cathode material to form compound AR, $AR_{x/2y}$ or $A'R_{\alpha/3\beta}$ which remain with cathode material 5. Gas is released from anode material 2, passes through gas passages 3, and enters gas chamber 8. As gas enters said gas chamber, the pressure increases, forcing fluid 10 to be dispensed from fluid sack 9. The thickness of said electrolyte and the cross-sectional area of the active electrochemical cell formed by this device are selected so that the desired fluid dispensing rate is achieved. Optionally, an electronic resistor (not shown) may be placed between the contact clip 13 and cathode cap 14 to modulate the current and dispensing rate to a lower level if desired.

FIG. 6 shows a perspective sectional view of an embodiment of the invention which is a variation of what was shown in FIG. 5. Those features similar to features in FIG. 5 are similarly numbered. In this embodiment, contact clip 17 is stationary. The device is activated by the user by pressing on tab 18 which inverts to make contact with cathode 5. Another feature variation is shown in this embodiment; a fluid sack 9 is sealed at the outlet 19. At the time of activation, the user cuts or punctures said outlet so that the fluid 10 contained can be dispensed as the device operates.

FIG. 7 shows a perspective sectional view of an embodiment of the invention which features a battery integrated into the design. Those features similar to features in FIGS. 5 and 6 are similarly numbered. Pump housing 22 is fabricated of a chemically resistant and electronically conductive material. Into said pump housing is pressed anode material 2 comprised of a chemically inert, electronically conductive material such as graphite or carbon fibers mixed with an oxidized compound of the general formula, A_xO_y or $A'_\alpha N_\beta$ such as Cu_2O. A solid electrolyte material 4 is pressed onto the anode material 2.

The composition of said solid electrolyte material is selected based on the cation A or A' which is to be conducted. For example, $Rb_4Cu_{16}I_7Cl_{13}$, CuI mixed with Al_2O_3, or Cu-Nasicon could be selected to conduct Cu^{+1} cations. Cathode material 20, comprised of an electronic conductor such as graphite fiber or copper or reducible material such as I_2 or S mixed with an electronic conductor and ionic conductor, is pressed against solid electrolyte 4. A spacer 27 comprised of an electrical insulator prevents contact between the cathode 20 and the pump housing 22. Said pump housing also encloses a button cell 21, such as a silver oxide or alkaline cell, which are readily available commercial cells.

The negative pole of said button cell contacts the cathode 20. Spacer 28 comprised of an electrical insulator prevents contact between the button cell 21 and the pump housing 22. The cathode cap 14 and the spacer 28 are crimped by the pump housing 22 to form a seal. Optionally, spacer 27 and spacer 28 may be integrated into one part. The contact clip 13 completes the circuit after an electronic insulating pull tab 24 is removed by the user at the time of activation. Fluid to be dispensed 10 is contained between a flexible diaphragm 25 and outer shell 26. The gas chamber 8 into which gas is electrochemically introduced is bounded by the diaphragm 8, the gas shell 7, and the pump housing 22.

FIGS. 8A, 8B and 8C are schematics of general examples of the electrochemical portion of the device, where the cathode includes a reducible material.

The figures include regions Z1, Z2, Z'2, Z3, Z'4, Z4, Z5 interfaces Z1/Z2, Z2/Z'2, Z'2/Z3, Z3/Z'4, Z'4/Z4, Z4/Z5. FIG. 8A represents a pre-discharged cell. FIG. 8B represents a discharging cell. FIG. 8C represents a cell which does not require an electrolyte in addition to the anode and cathode since the reaction product formed serves the function of the electrolyte.

Z1 is the anode current collector and must be an electronic conductor, preferably porous. It may also have a porous inner layer and a nonporous outer layer with a single port or multiple ports to allow escape of released oxygen or nitrogen gas at particular locations. Z1 material must be non-reactive with material Z2 and the oxygen or nitrogen which will be released.

Z2 is the anode and must include the gas releasing compound, either A_xO_y or $A'_\alpha N_\beta$, and must be an ionic conductor or a mixed conductor.

If A_xO_y or $A'_\alpha N_\beta$ are ionically conductive and have low electronic conductivity, then material Z2 may consist entirely of those compounds and may be non-porous; in this case, oxidation will occur at the Z1/Z2 interface, A or A' ions will migrate through layers Z2 and Z3 through the Z2/Z3 and Z3/Z4 interfaces. When this occurs, the thickness of the Z2 layer decreases and it is desirable to have the entire assembly in compression to maintain contact. This may be achieved through utilization of one or more springs.

If A_xO_y or $A'_\alpha N_\beta$ are not ionic conductors, a material which has lower tendency to oxidize relative to A_xO_y or $A'_\alpha N_\beta$ but which is ionically conductive must be added to material Z2, in addition, an electronic conductor must be added, usually, the electronic conductivity will be higher than the ionic conductivity which results in initial oxidation at the Z2/Z3 interface. As oxidation of A_xO_y or $A'_\alpha N_\beta$ occurs, a zone Z' is formed where A_xO_y or $A'_\alpha N_\beta$ has been consumed but includes the ionic and electronic conducting materials which had been added to material Z2. Oxidation continues at the Z2/Z'2 interface as electrons are conducted through Z2 and cations are conducted through Z'2. Oxygen or nitrogen permeates through Z2 and Z1, thus layer Z2 must be porous enough to allow this permeation. Permeation can also be enhanced if necessary by providing small channels in the Z2 material.

Z5 the cathode current collector and is a non-porous electronic conductor which is non reactive with material Z4.

Z4 is the cathode and includes a reducible material. It must either be an anionic conductor, or mixed conductor. Electrons are provided at the Z5/Z4 interface which ultimately reduce the material in Z4 to anions. Usually, electrons are conducted through Z4, initially anions are formed at the Z3/Z4 interface where cations and anions form a reaction product and create a new layer Z'4. Subsequently, anions may be formed at the Z4/Z'4 interface.

Z'4 material must be either conductive to cations so that reaction product forms at the Z4/Z'4 interface, otherwise Z'4 must be conductive to anions so that reaction product forms at the Z3/Z'4 interface.

Z3 is the electrolyte, a layer which is conductive to either cations or anions but which is an electronic insulator. This layer is necessary if both Z2, Z2' (if formed), Z'4, and Z4 are all electronic conductors. If any one of those layers is electronically insulating, then layer Z3 is unnecessary since the insulating layer functions as an electrolyte.

An electrolyte referred to herein above as Ag-Nasicon, Li-Nasicon or other Nasicon material is a metal super ion conductor, and has the general formula $Me_{(1+x)}Zr_2Si_xP_{(3-x)}O_{12}$ wherein Me is a metal such as silver, lithium, sodium, copper and the like. The sodium ion version is referred to as Nasicon, which was the earliest material developed. Other cation conductors are referred to as Li-Nasicon, Ag-Nasicon, etc. These metals are monovalent cations in ionic form. Such electrolytes are solid, ceramic-type materials which are well known cation (positive metal ions) conductors, having been used in sodium-sulfur batteries and similar electrochemical cells in which transport of a metal ion from an anode chamber to cathode chamber was desired. In the above-stated formula, the value of x is equal to or less than 3 and equal to or greater than 0. A typical value for x is 2. The various Nasicon-type materials used in the instant examples had a value for x of about 2.

Although the instant invention is illustrated with a fluid dispensing portion consisting of a flexible membrane or flexible sack, it is to be understood that the invention may include pistons, bellows or other components which may be moved by a pressurized gas to dispense fluids, typically liquids, from a dispenser to the external environment.

CLAIMS

What is claimed is:

1. A solid-state, electrically self-contained, fluid-dispensing micropump comprising:

a galvanic electrochemical cell having an anode compartment, a cathode compartment, solid electrolyte separating said anode and cathode compartments;

a solid anode material of the composition A_xO_y or $A'_\alpha N_\beta$,

wherein A is a cation of a metal selected from the class consisting of silver and copper,

wherein A' is a cation of a metal selected from the class consisting of sodium and lithium,

wherein O is oxygen and N is nitrogen and the value for x is 1 to 3 and y is 1 to 4, α is 1 to 3 and β is 1 to 3;

an electrolyte consisting essentially of an ion transport material selected from the class of materials which transport A cations or A' cations;

a cathode material in intimate contact with said electrolyte, said cathode material consisting essentially of a halogen ionizable to a minus one valence state or a compound consisting of carbon and halogen ionizable to a mixture of carbon and halogen with valence of minus one state or a Group VIB substance ionizable to a minus two valence state;

an electrical conductor connectable between said anode and cathode materials, which upon connection results in oxygen or nitrogen being released from the anode material as the cation present, A or A' migrates through the electrolyte to react with the cathodic material in a reaction which includes the electrons released at the anode;

a fluid containing chamber having a fluid discharge outlet; and

duct means providing gas communication between said anode compartment and said fluid containing chamber.

2. Apparatus as set forth in claim 1, wherein solid anode material includes the compound Ag_2O.

3. Apparatus as set forth in claim 1, wherein said solid anode material includes a compound selected from the class consisting of Li_3N and NaN_3.

4. Apparatus as set forth in claim 1, wherein said solid cathode material includes a compound selected from the class consisting of I_2, S and CF_x where x ranges from 0.8-1.2.

5. Apparatus as set forth in claim 1, wherein said fluid is dispensed to a room, vehicle, or container through evaporation.

6. Apparatus as set forth in claim 1, wherein desired rate of dispensing of a beneficial substance contained in said fluid to be dispensed is achieved by preselecting the cross-sectional area of the active cell, preselecting the thickness of the solid electrolyte or preselecting the concentration of said beneficial substance in said fluid.

7. Apparatus as set forth in claim 1, wherein an electrical circuit is completed through said electrical conductor by a contact clip pressed into place such that said contact clip electrically communicates with both the anode and the cathode.

8. Apparatus as set forth in claim 1, wherein an electrical circuit is completed through said electrical conductor by inverting a contact clip, to make contact between that portion of said electrical conductor communicating with the anode and that portion of the electrical conductor communicating with the cathode.

9. Apparatus as set forth in claim 1, wherein an electrical circuit is shorted by a removable insulating pull tab which electrically isolates two electrical contact points in said electrical conductor.

10. Apparatus as set forth in claim 1, wherein a principal component of the electrolyte is selected from one class consisting of AgI, LiI, NaI, KI, RbI and Ag_4RbI_3.

11. Apparatus as set forth in claim 1, wherein a component of the electrolyte is Ag-Nasicon.

12. Apparatus as set forth in claim 1, wherein the anode and cathode are separated by a microporous membrane.

13. Apparatus as set forth in claim 12, wherein an electrolyte dissolved in a non-aqueous solvent is utilized.

14. Apparatus as set forth in claim 13, wherein a component of said electrolyte is $LiBF_4$.

15. Apparatus as set forth in claim 13, wherein a component of said electrolyte is $AgBF_4$.

16. Apparatus as set forth in claim 13, wherein a component of said non-aqueous solvent is ethylene glycol dimethyl ether.

17. Apparatus as set forth in claim 13, wherein a component of said non-aqueous solvent is propylene carbonate.

18. Apparatus as set forth in claim 1, wherein the anode and cathode are separated by a solid polymer electrolyte.

19. A solid state, battery driven, fluid dispensing micropump where oxygen is electrochemically released from a solid anode material of the general form A_xO_y where A is a cation with an oxidation state of 2y/x as A ions migrate across a suitable solid ion conducting electrolyte, or similarly, oxygen is released from solid anode ions migrate across a suitable solid ion conducting electrolyte, or nitrogen is electrochemically released from a solid anode material of the general form $A'_\alpha N_\beta$ where A' is a cation of oxidation state $3\beta/\alpha$, as A ions migrate across a suitable solid ion conducting electrolyte. And where a solid cathode material, R_2, where R is a halogen, is ionized to R^- or where solid cathode material CR'_x is

ionized to C+XR′ or where solid cathode material R′, where R′ is a group VIB substance, is ionized to R'^{-2} or where the migrating cations are reduced to elemental state at the cathode. And where the released oxygen or nitrogen gas pressurizes a chamber resulting in fluid contained in a flexible bladder within the chamber to be forced through an outlet.

20. Apparatus as set forth in claim 19, wherein solid anode material includes the compound Cu_2O.

21. Apparatus as set forth in claim 19, wherein solid cathode material includes copper or graphite or carbon.

22. Apparatus as set forth in claim 19, wherein a component of the solid electrolyte is CuI.

23. Apparatus as set forth in claim 19, wherein a component of the solid electrolyte is $Rb_4Cu_{16}I_7Cl_{13}$.

24. Apparatus as set forth in claim 19, wherein a component of the solid electrolyte is Cu-Nasicon.

25. A solid-state, electrically self-contained electrochemical cell having a substantially uniform rate of gas production comprising:

a galvanic electrochemical cell having an anode compartment, a cathode compartment, solid electrolyte separating said anode and cathode compartments;

a solid anode material of the composition A_xO_y or $A'_\alpha N_\beta$ wherein O is oxygen and N is nitrogen and the value for x is 1 to 3 and y is 1 to 4, α is 1 to 3 and β is 1 to 3,

solid electrolyte consisting essentially of an ion transport material selected from the class of materials which transport A cations or A′ cations;

a cathode material in intimate contact with said electrolyte, said cathode material consisting essentially of a halogen ionizable to a minus one valence state or a compound consisting of carbon and halogen ionizable to a mixture of carbon and halogen with valence of minus one state or a Group VIB substance ionizable to a minus two valence state; and

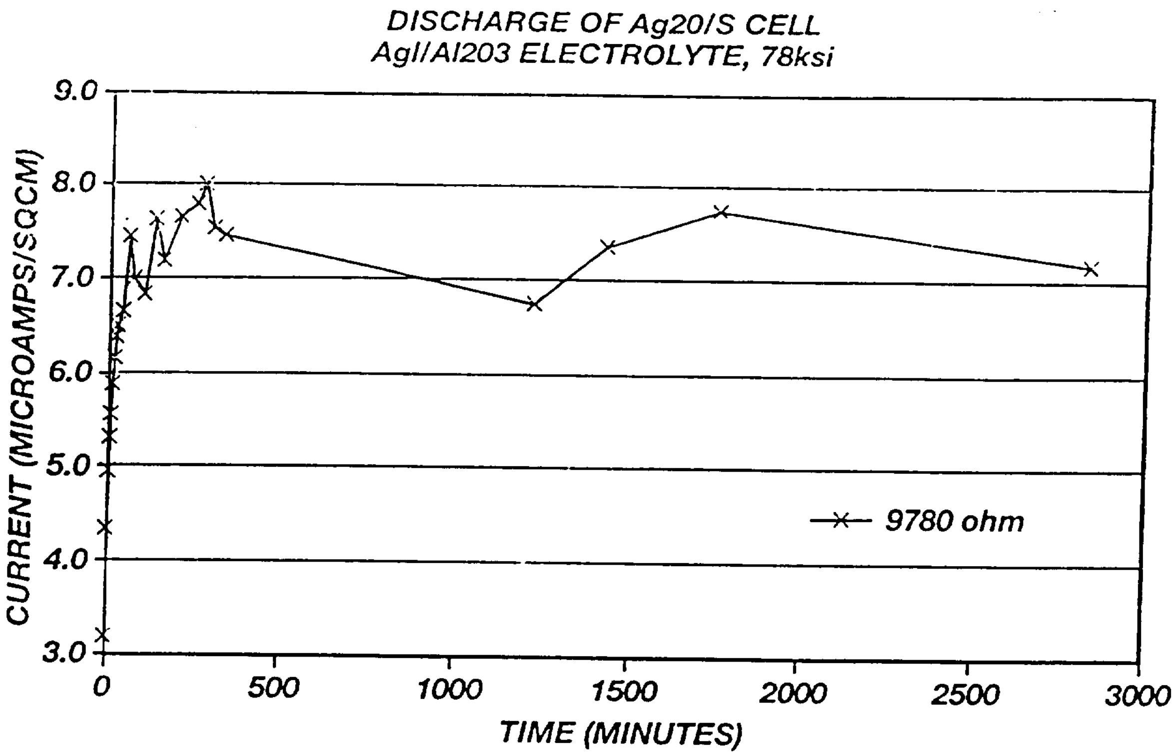
an electrical conductor connectable between said anode and cathode materials, which upon connection results in oxygen or nitrogen being released from the anode material as the cation present, A or A′ migrates through the electrolyte to react with the cathodic material in a reaction which includes the electrons released at the anode.

26. A fluid dispensing micropump comprising:

a miniature, solid-state, self-contained, gas-producing galvanic electrochemical cell;

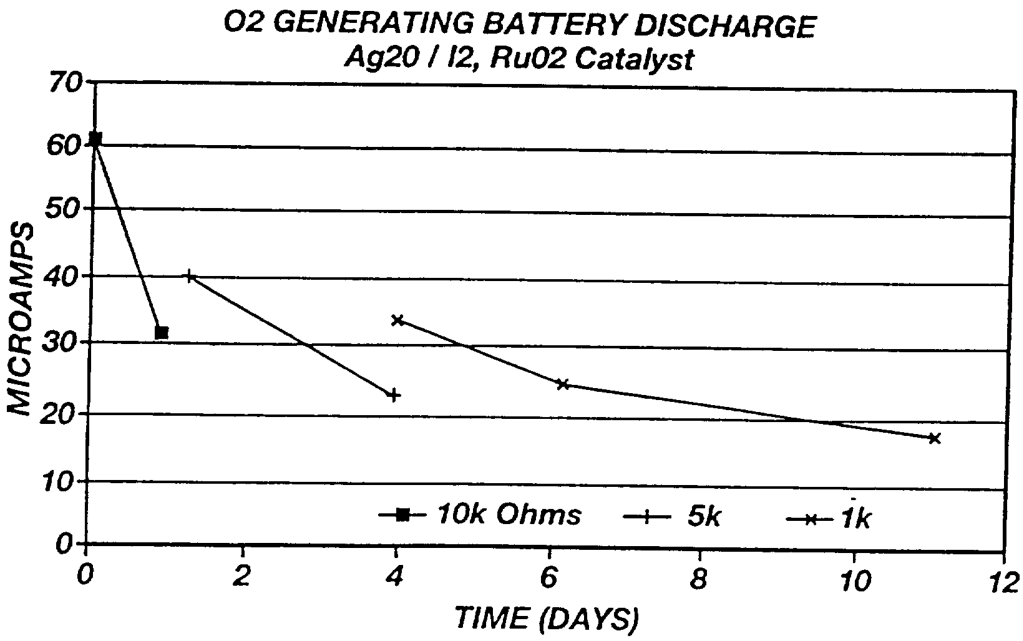
a fluid-containing chamber having a fluid discharge outlet; and

duct means providing gas communication between said cell and said fluid-containing chamber.



DISCHARGE OF Ag20/S CELL
AgI/Al203 ELECTROLYTE, 78ksi
CURRENT (MICROAMPS/SQCM)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
0
500
1000
1500
2000
2500
3000
TIME (MINUTES)
9780 ohm

Fig. 1



O2 GENERATING BATTERY DISCHARGE
Ag20 / I2, Ru02 Catalyst
MICROAMPS
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
TIME (DAYS)
10k Ohms
5k
1k

Fig. 2

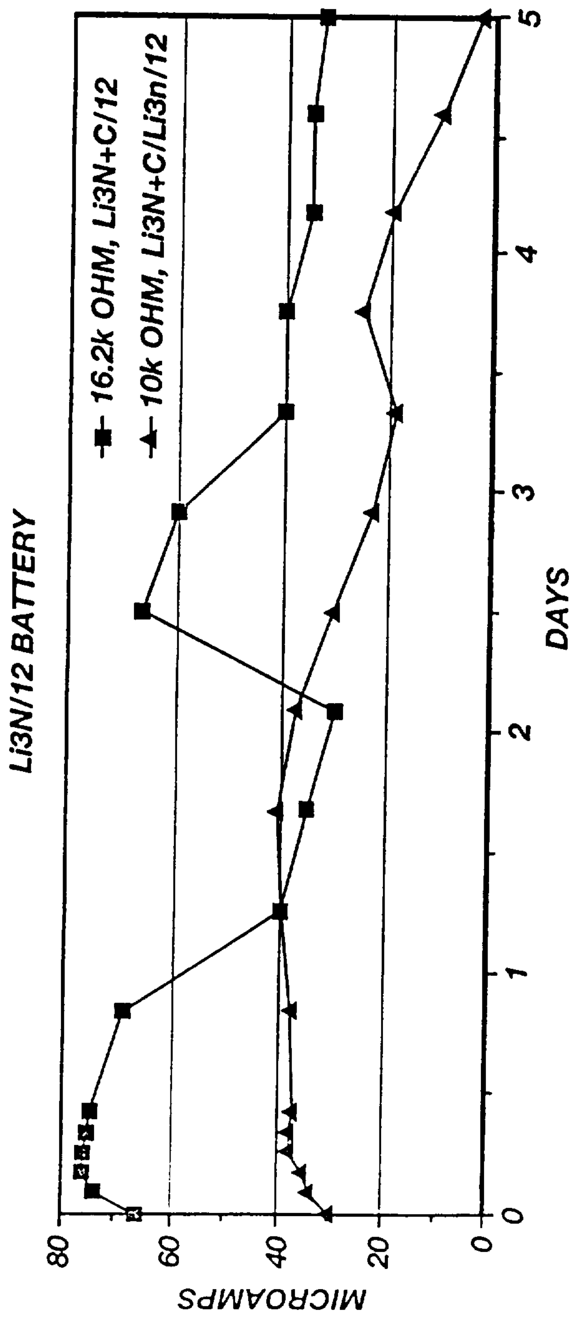
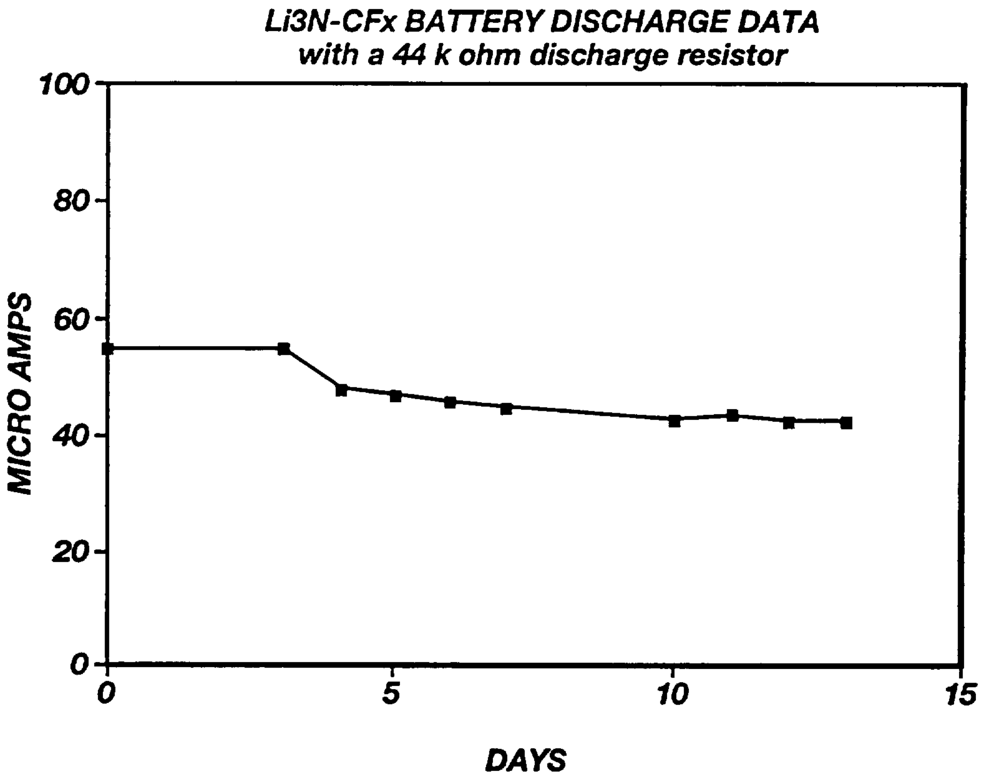

Li3N/12 BATTERY
16.2k OHM, Li3N+C/12
10k OHM, Li3N+C/Li3n/12
MICROAMPS
80
60
40
20
0
DAYS
0
1
2
3
4
5

Fig. 3



Li3N-CFx BATTERY DISCHARGE DATA
with a 44 k ohm discharge resistor
MICRO AMPS
100
80
60
40
20
0
0
5
10
15
DAYS

Fig. 4

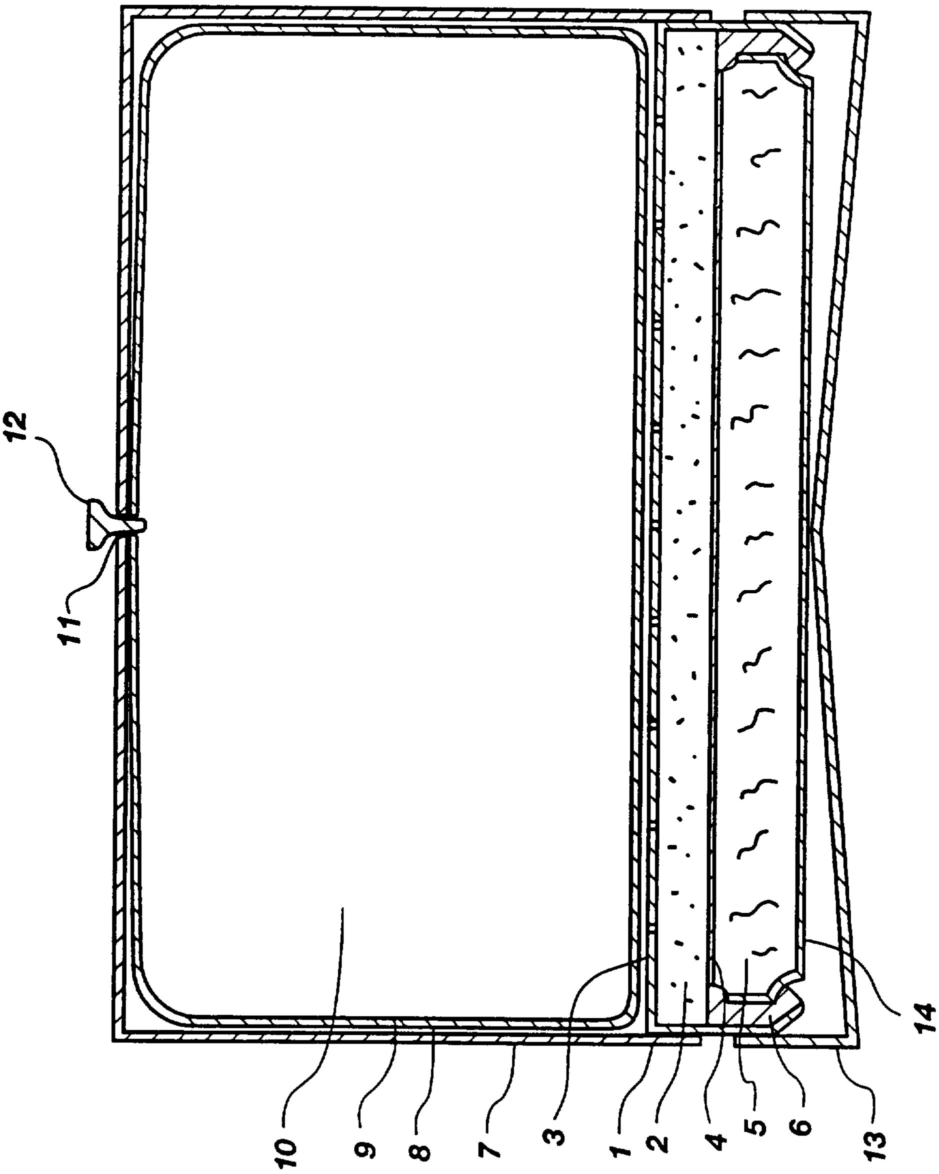


Fig. 5

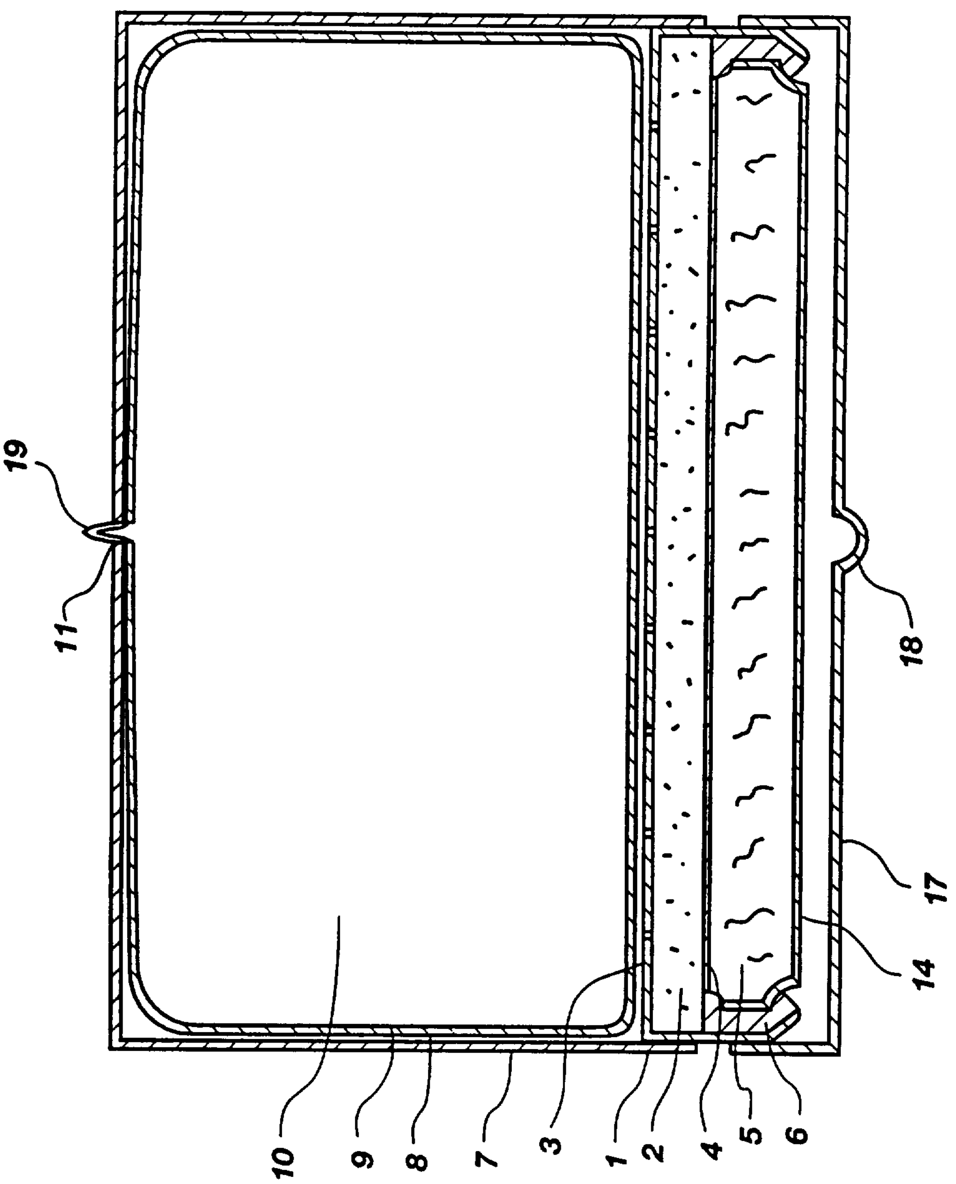


Fig. 6

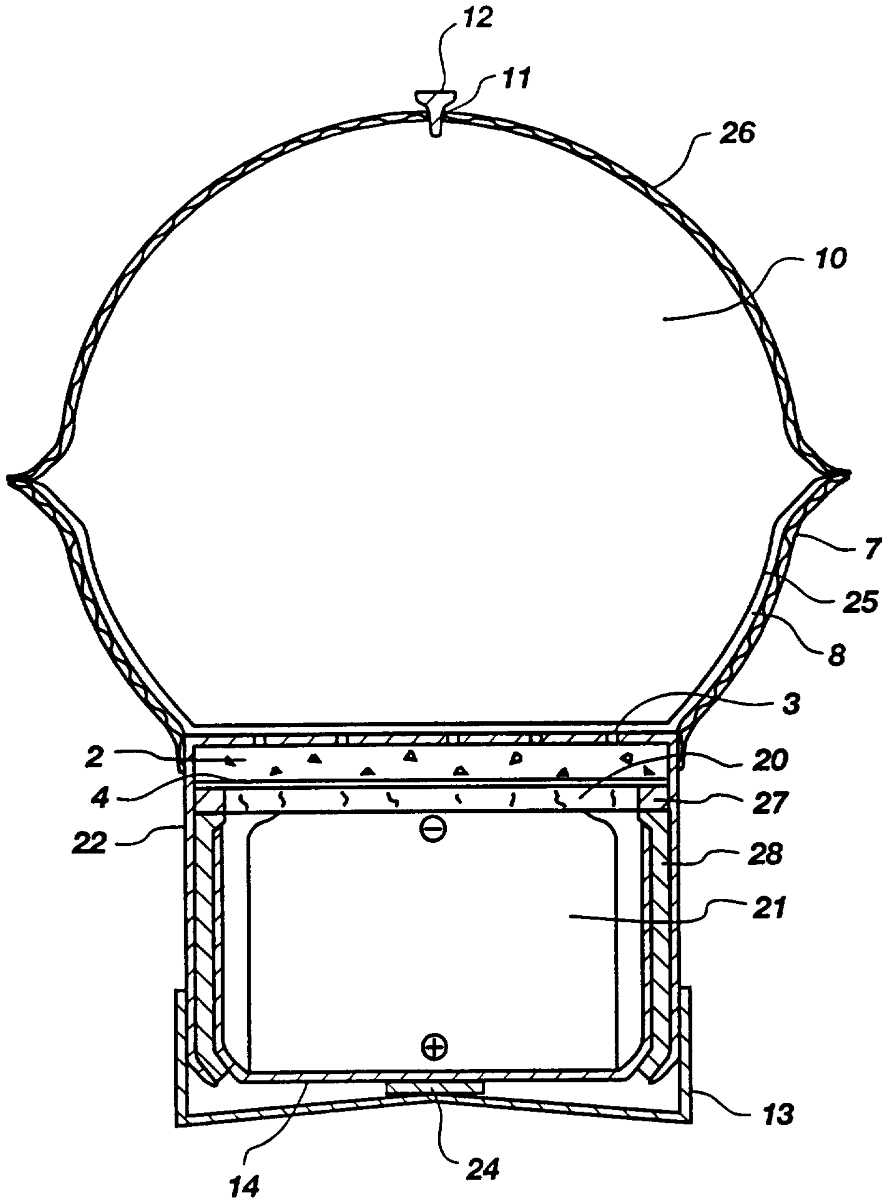


Fig. 7

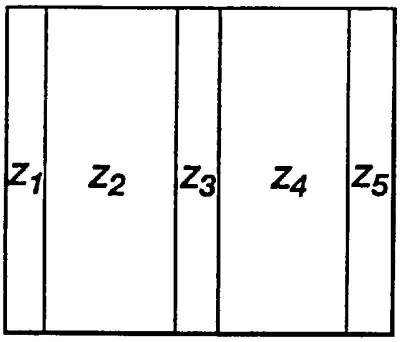


Fig. 8A

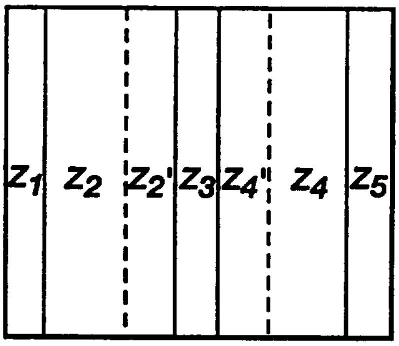


Fig. 8B

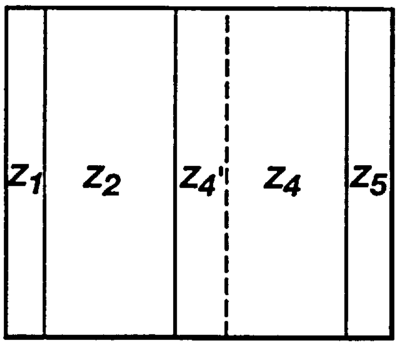


Fig. 8C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/11337

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 4/00; G01N 27/26
US CL :Please See Extra Sheet.
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. : 204/415, 252, 265, 266, 291, 292, 294; 429/12, 27, 30, 33, 40, 46, 219, 220

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

none

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

none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,902,278 (MAGET ET AL) 20 FERUARY 1990, see abstract	1-26
A	US, A, 4,262,062 (ZATSKY) 14 APRIL 1981, see abstract	1-26

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"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)	"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
"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	"&"	document member of the same patent family

Date of the actual completion of the international search 13 OCTOBER 1995	Date of mailing of the international search report 15 DEC 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BRUCE BELL Telephone No. (703) 308-0661

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

204/415, 252, 265, 266, 291, 292, 294; 429/12, 27, 30, 33, 40, 46, 219, 220