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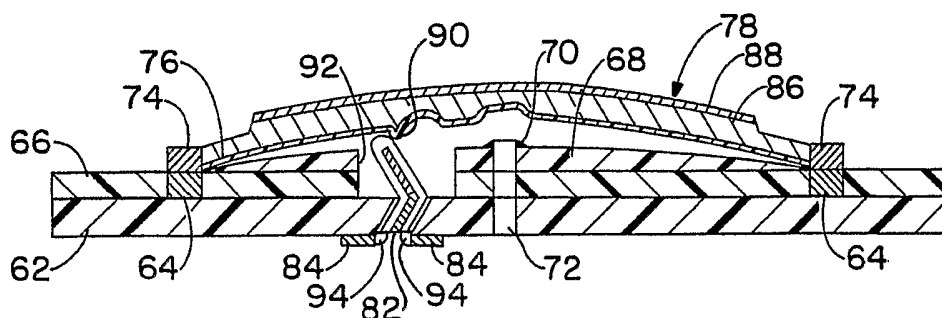
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(54) Title: FLUID REGULATING MICROVALVE ASSEMBLY FOR FLUID CONSUMING CELLS



(57) Abstract: A fluid regulating microvalve assembly for use to control fluid flow to a fluid consuming electrode, such as an oxygen reduction electrode, in an electrochemical cell. The microvalve assembly includes a stationary valve body comprising a polymer, elastomer or rubber having an aperture and a microactuator movable from a first position where the microvalve body aperture is closed to fluid flow to at least a second position where fluid is able to pass through the microvalve body aperture. The fluid regulating microvalve assembly can utilize cell potential or a separate source to open and close the microvalve. The fluid regulating microvalve assembly can be located outside the cell housing or inside the cell housing, for example between one or more fluid inlet apertures and the fluid consuming electrode. The invention includes a method of making a multilayer microvalve assembly, particularly one for use in a fluid depolarized battery, using a printing process to deposit at least one of the layers.

FLUID REGULATING MICROVALVE ASSEMBLY FOR FLUID CONSUMING CELLS

FIELD OF THE INVENTION

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The present invention relates to fluid regulating microvalve assemblies adapted to control the rate of flow of one or more fluids, particularly a gas, between an interior and an exterior of a cell housing of a cell, such as a fuel cell or battery that is preferably air-depolarized or air-assisted, as well as fuel cells and batteries containing the fluid regulating microvalve assemblies. Methods for preparing fluid regulating microvalve assemblies and cells containing the microvalve assemblies are disclosed.

BACKGROUND OF THE INVENTION

Electrochemical battery cells that use a fluid, such as oxygen or other gas(es), from outside the cell as an active material to produce electrical energy, such as air-depolarized, air-assisted and fuel cell battery cells, can be used to power a variety of electronic devices. For example, air containing oxygen enters into an air-depolarized or air-assisted cell, where it can be used as, or can recharge, the positive electrode active material. The oxygen reduction electrode promotes the reaction of the oxygen with the cell electrolyte and, ultimately the oxidation of the negative electrode active material with the oxygen. The material in the oxygen reduction electrode that promotes the reaction of oxygen with the electrolyte is often referred to as a catalyst. However, some materials used in oxygen reduction electrodes are not true catalysts because they can be at least partially reduced, particularly during periods of relatively high rate discharge.

One type of air-depolarized cell is a zinc/air cell. This type of cell uses zinc as the negative electrode active material and has an aqueous alkaline (e.g., KOH) electrolyte. Manganese oxides that can be used in zinc/air cell air electrodes are capable of electrochemical reduction in concert with oxidation of the negative electrode active material, particularly when the rate of diffusion of oxygen into the air electrode is insufficient. These manganese oxides can then be reoxidized by the oxygen during periods of lower rate discharge or rest.

Air-assisted cells are hybrid cells that contain consumable positive and negative electrode active materials as well as an oxygen reduction electrode. The positive electrode can sustain a high discharge rate for a significant period of time, but through the oxygen reduction electrode, oxygen can partially recharge the positive electrode during periods of

lower or no discharge, so oxygen can be used for a substantial portion of the total cell discharge capacity. This means the amount of positive electrode active material put into the cell can be reduced and the amount of negative electrode active material can be increased to increase the total cell capacity. Examples of air-assisted cells are disclosed in
5 U.S. Patent No. 6,383,674 and U.S. Patent No. 5,079,106.

An advantage of air-depolarized, air-assisted and fuel cells is their high energy density, since at least a portion of the active material of at least one of the electrodes comes from or is regenerated by a fluid (e.g., a gas) from outside the cell.

A disadvantage of these cells is that the maximum discharge rates they are capable
10 of can be limited by the rate at which oxygen can enter the oxygen reduction electrode. In the past, efforts have been made to increase the rate of oxygen entry into the oxygen reduction electrode and/or control the rate of entry of undesirable gases, such as carbon dioxide, that can cause wasteful reactions, as well as the rate of water entry or loss (depending on the relative water vapor partial pressures outside and inside the cell), that
15 can fill void space in the cell intended to accommodate the increased volume of discharge reaction products or dry the cell out, respectively. Examples of these approaches can be found in U.S. Patent Numbers 6,558,828; 6,492,046; 5,795,667; 5,733,676; U.S. Patent Publication No. 2002/0150814; and International Patent Publication No. WO 02/35641. However, changing the diffusion rate of one of these gases generally affects the others as
20 well. Even when efforts have been made to balance the need for a high rate of oxygen diffusion and low rates of CO₂ and water diffusion, there has been only limited success.

At higher discharge rates, it is more important to get sufficient oxygen into the oxygen reduction electrode, but during periods of lower discharge rates and periods of time when the cell is not in use, the importance of minimizing CO₂ and water diffusion
25 increases. To provide an increase in air flow into the cell only during periods of high rate discharge, fans have been used to force air into cells (e.g., U.S. Patent No. 6,500,575), but fans and controls for them can add cost and complexity to manufacturing, and fans, even micro fans, can take up valuable volume within individual cells, multiple cell battery packs and devices.

Another approach that has been proposed is to use microvalves to control the
30 amount of air entering the cells (e.g., U.S. Patent No. 6,641,947 and U.S. Patent Publication No. 2003/0186099), but external means, such as fans and/or relatively complicated electronics can be required to operate the microvalves.

Yet another approach has been to use a water impermeable membrane between an oxygen reduction electrode and the outside environment having flaps that can open and close as a result of a differential in air pressure, e.g., resulting from a consumption of oxygen when the battery is discharging (e.g., U.S. Patent Publication No. 2003/0049508).

5 However, the pressure differential may be small and can be affected by the atmospheric conditions outside the battery.

Additional approaches utilizing microvalves to control the amount of gas entering a cell are set forth in U.S. Patent Numbers 5,304,431; 5,449,569; 5,541,016; and 5,837,394; incorporated herein by reference, wherein the microvalves are formed utilizing
10 a silicon or semiconductor substrate and etching, deposition and micromachining processes.

Microactuators are further described in U.S. Patent Numbers 4,969,938; 5,069,419; 5,271,597; and publications such as "Fluister: semiconductor microactuator" described in Instruments and Apparatus News (IAN), October 1993, p. 47, and Electronic Design,
15 November 1, 1993, p.3.

SUMMARY OF THE INVENTION

In view of the above, it is an object of the present invention to provide a low cost, reliable fluid regulating microvalve assembly that is relatively inexpensive and
20 straightforward to produce.

A further object is to provide a fluid regulating microvalve assembly that is relatively small in size and takes up little volume in a cell in which the microvalve assembly is incorporated, thereby maximizing volume for energy producing components.

Another object of the invention is to provide a cell, particularly a fuel cell or
25 battery with a fluid consuming positive electrode, preferably an oxygen reduction electrode and a fluid regulating microvalve assembly that allows high rate discharge of the cell with relatively low or even no capacity loss during periods of low rate or no discharge.

Yet another object of the invention is to provide a multi-layer microvalve assembly that can have a complex configuration and be efficiently and economically produced at
30 high speeds, preferably utilizing a printing process during at least one step utilized to form the microvalve assembly.

Accordingly, one aspect of the invention is a microvalve assembly for an electrochemical cell, comprising a stationary microvalve body comprising a polymer, elastomer or rubber and an aperture located between a first surface and a second surface;

and a movable microactuator connected to the microvalve body and capable of moving between a first position where fluid cannot pass through the microvalve body aperture and a second position which allows fluid to pass through the microvalve body aperture, and wherein the microactuator is thermally actuated.

5 Another aspect of the invention is an electrochemical cell, comprising a housing including one or more fluid inlet apertures, a negative electrode, a fluid consuming positive electrode, and a microvalve assembly operatively connected to the one or more fluid inlet apertures for controlling passage of fluid to the fluid consuming positive electrode, wherein the microvalve assembly comprises (a) a stationary microvalve body
10 comprising a polymer, elastomer or rubber and an aperture located between a first surface and a second surface; and (b) a movable microactuator connected to the microvalve body and capable of moving between a first position where fluid cannot pass through the microvalve body aperture and a second position which allows fluid to pass through the microvalve body aperture.

15 Yet another aspect of the invention is a method for preparing a microvalve assembly, comprising the steps of forming a microvalve body having one or more layers; forming a microactuator having one or more layers; and operatively joining the microvalve body to the microactuator, wherein the microvalve body comprises an aperture that extends through the body from a first surface to a second surface, wherein the forming
20 of the one or more microvalve body or microactuator layers, or both, includes utilizing a printing process, and wherein the microactuator is operatively connected to the microvalve body and capable of moving between a first position where fluid cannot pass through the microvalve body aperture and a second position which allows fluid to pass through the microvalve body aperture.

25 These and other features, advantages and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims and appended drawings.

Unless otherwise specified, as used herein, the following terms are defined as follows:

30 fluid - a substance that can flow such as a liquid or a gas;

 fluid consuming electrode - an electrode that uses a fluid from outside the cell housing as an active material; and

 thermally actuated microactuator - a microactuator whose motion is caused by a change in temperature in a portion of the microactuator.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood and other features and advantages will become apparent by reading the detailed description of the invention, taken together with the drawings, wherein:

FIG. 1 is a cross sectional side view of a cell including a fluid regulating microvalve assembly.

FIG. 2 is a cross sectional side view of a second cell including a fluid regulating microvalve assembly.

FIG. 3 is a cross sectional side view of one embodiment of a fluid regulating microvalve assembly.

FIG. 4A is a cross sectional side view of an embodiment of a fluid regulating microvalve assembly incorporating one alternative of a latching device wherein the microvalve assembly is in a closed position.

FIG. 4B is the cross sectional side view of FIG. 4A, wherein the microvalve assembly is in an open position with the latch arm engaged with the microactuator.

FIG. 5 is a schematic of one embodiment of a circuit plan including a battery, control unit, microactuator and switch.

FIG. 6 is a cross sectional side view of an embodiment of a fluid regulating microvalve assembly including two portions in position to be connected.

FIG. 7 is a cross sectional side view of an embodiment of a fluid regulating microvalve assembly including two portions in position to be connected, further incorporating a latching device.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the invention, a fluid regulating microvalve assembly is operatively connected to a cell that uses a fluid, such as oxygen or other gas or gases, from an exterior of the cell, such as the surrounding atmosphere, as an active material for an electrode present in the interior of the cell. The fluid regulating microvalve assembly controls the flow rate of fluid between the exterior and interior of the cell and ultimately the flow rate to a fluid consuming electrode, such as an oxygen reduction electrode. The cell can be a fuel cell such as a methanol or hydrogen fueled oxygen cell, an air-depolarized cell, or an air-assisted cell as known in the art. Other possible cell types include, but are not limited to, chlorine or bromine depolarized cells. Also, the microvalve

assemblies of the present invention can be used in "reserve" cells where the fluid admitted into a predetermined area of the cell by the microvalve assembly is stored in a separate reservoir until required. The fluid can be a salt containing electrolyte or solvent which will dissolve salts in the body of the cell which in combination with the salts form the electrolyte necessary for the cell operation. Similarly, cells designed to operate under water, including saltwater or seawater, can incorporate a microvalve of the present invention allowing the cell to be relatively light in weight until placed in the water whereby the microvalve assembly selectively admits the water into the cell to be used therein.

10 The fluid regulating microvalve assembly is configured to selectively supply the fluid in sufficient amounts from the exterior of the cell so that the cell can discharge at a high rate or power level, and also minimize or prevent the fluid from entering the interior of the cell when the cell is not being discharged or being discharged at an extremely low rate.

15 The fluid regulating microvalve assembly of the invention is described hereinbelow with respect to air-depolarized cells, preferably utilizing an oxygen reduction electrode, but it is to be understood that the microvalve assemblies can also be utilized with other types of fluid consuming electrodes, such as fuel cells that can utilize one or more fluids other than oxygen, or from outside the cell housing as active materials for one or all of the electrodes of the cell. The fluid regulating microvalve assemblies can be
20 utilized with fluids such as seawater, particularly for an underwater application. Examples of seawater batteries are described in U.S. Patent No. 3,007,993 and in U.S. Patent No. 3,943,004.

25 One embodiment of an air-depolarized electrochemical cell including a fluid regulating microvalve assembly is a button cell, as shown in FIG. 1. The cell includes a housing with a container 11 and a cover 2 and has one or more fluid inlet apertures 9 which preferably are the only fluid communication port(s) between the interior and the exterior of the cell housing. At least one fluid regulating microvalve assembly 10 is operatively connected to the one or more apertures 9 such that, when microvalve 10 is in a
30 closed position, fluid communication from the ambient atmosphere to an oxygen reduction positive electrode located in the interior of the cell is prevented. Likewise, when microvalve assembly 10 is in an open position, fluid communication from the exterior to the oxygen reduction positive electrode in the cell is permitted. The cover 2 is made from an electrically conductive metal. The metal can include a steel or stainless steel

substrate. The exterior surface can have a layer including a metal, such as nickel or tin, that is resistant to corrosion, and the interior surface can have a layer including one or more metals, such as copper, tin, zinc and alloys thereof, with a relatively high hydrogen over potential, to minimize hydrogen gas generation. The substrate metal can be plated and/or clad on one or both surfaces. For example, the cover 2 can be formed from a triclاد material with a stainless steel substrate, a nickel layer on the external surface, and a copper layer on the internal surface, and the formed cup can optionally be plated or otherwise coated after forming with another metal, such as tin. The container 11 can be made from an electrically conductive metal such as steel or stainless steel, which may be plated with tin on one or both surfaces.

The housing also includes a gasket 3 between the adjacent side walls of the cover 2 and container 11 to provide a compression seal therebetween and to electrically insulate the cover 2 from the container 11. The gasket 3 can be made from any suitable thermoplastic material that provides the desired sealing properties. Material selection is based in part on the electrolyte composition. Suitable materials for alkaline zinc-air cells include nylons, propylenes, sulfonated polyethylenes, and impact modified polystyrenes.

The cell contains a negative electrode 1 that is adjacent to and in electrical contact with the cover 2, which can be the negative terminal of the cell. The negative electrode includes an active material mixture comprising an electrochemically active material, such as zinc, and an electrolyte, preferably an aqueous electrolyte with a solute such as KOH. The zinc is preferably a low gassing zinc alloy, as described in U.S. Patent No. 6,602,629, incorporated herein by reference, particularly when the cell contains no added mercury. Alternatively the zinc can be a low expansion zinc, as disclosed in U.S. Patent No. 5,464,709, incorporated herein by reference, such as an alloy of zinc alloyed with bismuth, indium and aluminum, as disclosed in U.S. Patent Publication No. 2005/0106461-A1, incorporated herein by reference. The negative electrode mixture can be a gelled mixture, using an acrylic acid polymer in the 100% acid form (e.g., CARBOPOL® 940 or 934, available from Noveon, Inc., Cleveland, Ohio, USA) as a gelling agent. The mixture can also include various organic and inorganic compounds as additives, such as additives that can reduce hydrogen gas generation in the cell. Examples of such additives include zinc oxide, indium hydroxide, and a polyethylene glycol compound (e.g., a methoxyethylene glycol such as CARBOWAX® 550, available from Dow Chemical, Midland, Michigan, USA).

The cell also contains an oxygen reduction positive electrode 7, which can be referred to as an air electrode. In one embodiment as shown in FIG. 1, the positive electrode 7 is isolated from the container 11 such that electrical output is passed through the microvalve assembly 10 connected in series to the positive electrode 7. In another embodiment, the positive electrode 7 is in electrical contact with the container 11, which can be the positive terminal of the cell. The positive electrode 7 is a porous layer containing a reversibly reducible material that promotes the reaction of oxygen from outside the cell with the electrolyte so the zinc in the negative electrode 1 can be oxidized. In addition, the porous layer of the positive electrode 7 can also contain carbon or graphite and a binder such as polytetrafluoroethylene. Positive electrode 7 can further include an electrically conductive metal (e.g., nickel) screen or mesh current collector located in the portion of the positive electrode 7 adjacent to the negative electrode 1. The positive electrode can also include a gas (e.g., oxygen) permeable, electrolyte impermeable membrane 5 on the surface of the porous layer facing the apertures 9. The membrane 5 can be a polymeric film, such as a polytetrafluoroethylene film.

At least one, preferably two layers of separator 8 are disposed between the negative electrode 1 and the positive electrode 7. The separator 8 is a thin microporous membrane that is ion-permeable and electrically nonconductive. It is capable of holding at least some electrolyte within the pores of the separator 8. The separator 8 is disposed between adjacent surfaces of the electrodes 1, 7 to electrically insulate them from each other. The separator layers can be the same or different materials. Suitable materials include polypropylene separators. For example, if two layers are used, the layer immediately adjacent to the positive electrode 7 can be a hydrophobic polypropylene membrane, and the other layer can be a water-wettable nonwoven polypropylene.

Located on the side of the positive electrode 7 opposite the separator 8 can be a porous gas diffusion pad, to allow distribution of air entering the cell across the bottom surface of the positive electrode 7. This pad can be made from any suitable material, such as a sheet of polytetrafluoroethylene film.

Below the gas diffusion pad, between it and the inside surface of the bottom of the container 11 can be a spacer 6 with one or more cavities therein to accommodate the microvalve assembly/assemblies 10. The spacer 6 cooperates with the container 11 and microvalve assembly 10 so the only path for gas communication between the exterior and interior of the cell is through apertures 9 and microvalve assemblies 10.

A second gasket 4 can be disposed on the inside of container 11 to electrically isolate positive electrode 7, if desired, such that electrical output is passed through microvalve assembly 10 as shown in FIG. 1. In other embodiments, microvalve assembly 10 is controlled utilizing a control circuit, and gasket 4 is absent or otherwise situated such that positive electrode 7 is in electrical contact with container 11. Materials suitable for gasket 4 include those types of materials listed above as suitable for gasket 3.

Figure 2 illustrates a further embodiment of the present invention, wherein fluid regulating microvalve assembly 15 is disposed in a cylindrical cell housing. While a cylindrical cell is shown, it is understood by one of ordinary skill in the art that other shapes and/or sizes of cells can be utilized. For example, the cell can be a prismatic cell, having a housing with a generally rectangular or square shape. The cell in Figure 2 has a housing that includes a can 26 with a closed bottom and a top end, as well as a cell cover 12 and a gasket 18 disposed in the top end of the can 26. The can 26 is in electrical contact with a positive electrode 24, located within an annular chamber, and the cover 12 is in electrical contact with the negative electrode mixture 23 through the microvalve assembly 15 as shown in FIG. 2. The negative electrode 23 is located in a cavity within the annular positive electrode chamber. A separator 21 is located between positive electrode 24 and negative electrode 23.

The top end of the can 26 cooperates with the cell cover 12 and gasket 18, as well as a sealing member 20, a structural bracing member 17 and a contact member 13 to close the top of the cell, except for one or more passageways for fluid from outside the cell to reach the positive electrode chamber. The fluid passageway includes at least one fluid inlet aperture 16 in the cell cover 12 and at least one opening in the bracing member 17, and the sealing member 20 is either porous or contains at least one hole 19. At least one microvalve assembly 15 is in fluid communication with the passageway(s) to selectively control fluid flow to the positive electrode 24, closing the fluid passageway(s) when the microvalve assembly 15 is in the closed position. When the microvalve assembly 15 is closed, the active ingredients of the cell are effectively sealed from the ambient atmosphere, and when the microvalve assembly is open, fluid communication from the ambient atmosphere to the desired active portions of the cell is permitted. In one embodiment, the microvalve assembly 15 is electrically connected to the negative electrode 23 and positive electrode 24 of the cell, directly or optionally through a control circuit.

The can 26 has a bead or reduced diameter step near the top end to support gasket 18 and cell cover 12. Gasket 18 is compressed between can 26 and cover 12 to form a seal, and a compression seal is also formed between the sealing member 20 and both the can 26 and the contact member 13. The gasket 18 also electrically insulates the negative cell cover 12 from the positive can 26.

The negative electrode 23 includes a current collector 25, which is in electrical contact with contact member 13, and contact member 13 is in electrical contact with cell cover 12, either directly or through microvalve assembly 15. Bracing member 17 holds contact member 13 in a centered position, and when electrical contact between the contact member 13 and the cell cover 12 is through the microvalve assembly 15, insulating cap 14 provides electrical insulation between the contact member 13 and cell cover 12.

In one embodiment, the negative electrode 23 includes zinc as an electrochemically active material and an electrolyte. Positive electrode 24 preferably is porous and electrically conductive and includes a catalyst, such as manganese dioxide, and optionally a binder.

A decorative label 22 surrounds the outside of the can 26 except on the end where the positive terminal cover 27 covers the end of the can 26.

In general, components of the cell shown in Figure 2 can be made from materials of similar compositions to the corresponding components of the button cell described above.

It is to be understood that additional cell parts, arrangements, or the like may also be employed without departing from the teachings of the present invention. For example, the locations of the positive and negative electrodes can be reversed; this requires corresponding relocation of the air inlets and microvalve assemblies. Moreover, two or more cells in one or more housings may utilize the same microvalve assembly or more than one microvalve assembly can be connected to a single cell. The microvalve assembly can be located outside or within the cell housing. The fluid regulating microvalve assembly can be designed to be operated prior to integration into the electrochemical cell, or otherwise be designed to begin functioning after incorporation into the cell. In one embodiment, the cell is provided with seal over a fluid inlet aperture. In another embodiment the seal is removed manually. In a further embodiment, the microvalve assembly is provided with a seal thereon, that is broken, perforated or split on initial activation of the electrical device.

As described hereinabove, in an air-depolarized cell the fluid regulating microvalve assembly is operatively connected to the surface of the oxygen reduction electrode that is accessible to fluid (air) from outside of the cell, i.e., the air side, and thus is able to control fluid access to the oxygen reduction electrode. The fluid regulating microvalve assembly can be disposed in any suitable location in relation to the cell housing, i.e., operatively connected to, on, or within, as long as the assembly is on the air side of the oxygen reduction electrode. For example, a fluid regulating microvalve assembly can be connected to or positioned adjacent to the inside surface of that portion of the housing in which one or more air entry ports are located, or connected to or adjacent to the oxygen reduction electrode, connected to another cell component such as an internal seal member, bracing member or gas permeable sheet, on the air side of the oxygen reduction electrode, or integrated into the case of a battery containing the cell(s).

A printing device is utilized in one embodiment to form one or more layers or components of the fluid regulating microvalve assembly. While the terms "printing" and "depositing" are utilized throughout the specification to describe the microvalve assembly and methods of the present invention, it is to be understood in the broadest aspect of the invention that at least one layer of the microvalve assembly is printed on one or more other layers. The one or more other layers of the microvalve assembly can be printed or formed using one or more different processes, and combinations thereof. The printing device can produce one or more layers in numerous configurations at a relatively high speed on a substrate. Thus, fluid regulating microvalve assemblies of various shapes and sizes can be mass produced in high volume. The substrate can form a portion of the microvalve assembly, such as a microvalve body, or be removed from the printed layers of the microvalve assembly once the printing operation has been performed. In the latter case, the printed layers can form the microvalve assembly alone, or be used in conjunction with one or more other components or layers, such as a housing, to form a microvalve assembly. Any suitable printing process can be used. Examples of printing processes include indirect (offset) processes, in which ink is applied to a printing plate to form an image to be printed, transferred to a rubber "blanket", and then transferred to the substrate, and direct processes, in which an image is transferred directly from an image carrier to the substrate. Lithography is an example of an offset process, and examples of direct processes include gravure, flexography, screen printing, letterpress printing, and photolithography. Printing processes such as ink jet and laser jet processes can be adapted to making a microvalve assembly. Preferred printing processes include ink jet printing

and laser jet printing. Commercially available printing devices and services can be used. Contract manufacturing and design services can be obtained from companies such as First Index of Spokane, WA and Whippany, NJ as well as from Conductive Technologies, Inc. of York, PA and Connection Technologies of Detroit MI. Ink jet printers or printer
5 services are available from REA Elektronik GmbH Cleveland, OH, and Muehtal, Germany as well as from Aesthetic Finishers of Piqua, OH. Etching services are available from Northwest Etch Technology of Tacoma, WA, and Fotofabrication of Chicago, IL. Laser cutting and other services are available from Magni-fab Division of Wooster, OH, Schoonover Industries of Ashland, OH and Marian, Inc. of Indianapolis, IN. Miniature
10 spring or spring-like devices are available from Moyer Spring Co., Angola, IN, or Maverick Spring Makers Limited of Brantford, Ontario, Canada.

In addition to the printing device, additional devices and processes can be utilized in combination to produce the microvalve assembly. For example, devices can be utilized to create apertures or vents in one or more layers of the microvalve assembly; to remove a
15 portion of a layer or coating of the microvalve assembly such as by a process, but not limited to, cutting, melting, washing, dissolving, or the like; and to join portions of the microvalve assembly. Accordingly, additional devices that can be used to prepare a microvalve assembly, individually or in combination, include, but are not limited to, die cutting devices, drilling devices, chemical and photochemical etching processes, and
20 devices such as lasers, laminating devices, machining or micromachining devices, or the like. Devices and processes can be utilized that wash away or melt out a portion of one or more (a) temporary layers such as a filler plug, or (b) permanent layers of the microvalve assembly to create a desired form such as, but not limited to, a cavity or fluid transport channel, or a free space to allow movement of one or more parts. One or more layers can
25 be printed which do not adhere to parts of the substrate or subsequent layers so they function as parting layers allowing movement of adjacent parts. Examples of various materials and techniques are set forth in U.S. Patent Application No. 2003/0201175, U.S. Patent No. 5,246,730, and U.S. Patent No. 4,830,922, herein fully incorporated by reference.

30 Fluid regulating microvalve assemblies generally comprise a stationary microvalve body having one or more fluid apertures and a microactuator, which is movable from a closed position to an open position, thereby allowing fluid to flow through the microvalve body one or more apertures. In one embodiment, construction of a fluid regulating microvalve assembly is accomplished using a printing process to build layers of the

microvalve assembly on a substrate. Many different types of substrates can be utilized, including, but not limited to, metals, metal oxides, glass, polymers, rubbers or elastomers, and combinations thereof.

Non-limiting examples of metals and metal oxide substrates comprise silica,
5 silicon, aluminum, iron, nickel, tin, zinc, copper, titanium and combinations and alloys thereof, such as brasses, bronzes, stainless steels and shape memory alloys.

Non-limiting examples of polymers comprise polyester, polycarbonate, polystyrene, polyolefins such as polyethylene or polypropylene, polyethylene terephthalate, polyamide, polyoxides such as polyethylene oxide, polyacrylamide,
10 polyurethane, polyalkene, polyacrylate, polymethacrylate, polyvinyl ether, polyvinyl thioether, polyvinyl alcohol, polyvinyl ketone, halogenated polymers such as polytetrafluoroethylene (TEFLON® from DuPont) or polyvinyl halides such as polyvinyl chloride, polyvinyl nitrite, polyvinyl ester, polyarylene, polysulfonate, polysiloxane, polysulfide, polythioester, polysulfone, polyacetal, or copolymers or combinations thereof.

Non-limiting examples of substrate rubbers or elastomers comprise or are derived
15 from one or more same or different conjugated dienes having from 4 to about 12 carbon atoms with specific examples including butadiene, isoprene, pentadiene, hexadiene, octadiene, and the like. Rubbers of the substrate include copolymers of the above-noted conjugated diene monomers with one or more vinyl substituted aromatic monomers
20 containing from 8 to 12 carbon atoms such as styrene, alpha-methyl styrene, t-butyl styrene, or a vinyl compound such as acrylonitrile, vinylpyridine, acrylic acid, methacrylic acid, alkyl acrylate, and alkyl methacrylate. Still further rubbers include copolymers of olefins with a non-conjugated diene (EPDM rubbers) such as ethylene propylene cyclopentadiene terpolymers, ethylene-propylene-5-ethylidene-2-norbornene terpolymers,
25 and ethylene propylene 1,4-hexadiene terpolymers. Further examples of suitable rubbers include polybutadiene, synthetic polyisoprene, natural rubber, styrene-butadiene rubber, EPDM rubber, nitrile rubber, halogenated rubber, neoprene, silicone elastomers, ethylene acrylic elastomers, ethylene vinyl acetate copolymers, epichlorohydrin elastomers, and the like, or combinations thereof.

30 The polymers, rubbers, or elastomers, and combinations thereof, whether utilized in the substrate layer, or in one or more other layers of the present invention, independently, can include one or more of various additives, fillers, lubricants, stabilizers, processing aids, antidegradants, waxes, fibers that are synthetic or natural or both, mineral

fibers, glass, clay, silica, compatibilizers, flame retardants, dispersing agents, colorants, and the like, which are utilized in conventional amounts as known to the art and to the literature. Examples of natural fibers include, but are not limited to, cotton and cellulose fibers. Examples of synthetic fibers include, but are not limited to, fiberglass, polyester, polyamide both nylon and aramid, polyethylene, polypropylene, and carbon fibers.

The substrate is rigid or flexible in character. In a preferred embodiment, the substrate is a rigid sheet or film. In a preferred embodiment, the substrate has a thickness of generally from about 0.01 to about 0.375 millimeters, and preferably from about 0.05 to about 0.25 millimeters. In one embodiment, the substrate forms at least a portion of the microvalve body of the fluid regulating microvalve assembly and remains in a stationary position when the microvalve assembly microactuator is actuated between a closed position and an open position. The substrate may be porous or non-porous to fluids, with non-porous substrates being preferred to more accurately control the amount of fluid that passes through the fluid regulating microvalve assembly.

A fluid regulating microvalve assembly is fabricated in one embodiment as follows. One embodiment of the particular microvalve assembly is illustrated in FIG. 3. A desired substrate 62 is provided, preferably having a thickness sufficient to bear the contemplated fluid pressure. The substrate 62 is perforated or cut to produce an aperture 72 through which fluid will flow. When the substrate 62 utilized is of a larger area than the desired area for the microvalve assembly, the substrate may be perforated or cut to the size of the desired microvalve assembly to be produced.

The length, width and height dimensions of the microvalve assembly are limited by the dimensions and desired placement in a cell, battery, or case design. Independently, the length and width generally range from about 2 to about 25 millimeters, and preferably from about 5 to about 10 millimeters. The size of one aperture 72 ranges generally from about 0.1 to 10 millimeters, and preferably from about 0.4 to about 2 millimeters. In one embodiment, a preferred microvalve assembly is 5 millimeters in length by 5 millimeters in width having a 1 millimeter diameter aperture. It is contemplated that numerous fluid regulating microvalve assemblies can be prepared on a single substrate being formed in rows and columns with appropriate spacing between each microvalve assembly. The microvalve assemblies can be mass produced and separated for incorporation into a cell or housing.

One or more layers are then deposited upon the substrate 62 in desired areas thereof. Such layers can be part of the microvalve body or microactuator and can be

conductive or non-conductive as desired. A first layer is deposited onto the substrate 62. The first layer deposited onto the substrate 62 can be a conductive layer 64, deposited in two lines, each of which form an electrical lead, so that one end of each lead is adjacent an edge of the microvalve assembly. In a preferred embodiment, the conductive layer 64 is
5 formed of two electrical lead lines which extend in a direction parallel to the length or width of substrate 62.

An insulating layer 66 is then printed onto the assembly, over at least a portion of the conductive layer 64. The insulating layer 66 generally comprises a dielectric coating sheet or film, or the like, which is electrically non-conductive and will not decompose,
10 become conductive or unintentionally adhere to a subsequent layer when exposed to heating of the later applied resistive layer, as described below. Such insulating coatings are known to those skilled in the art and include, but are not limited to, urethanes, acrylates, polysulfones, polysiloxanes, halogenated polymers, and polyesters, or combinations thereof. In one embodiment, one or more insulating layers 66 deposited on
15 the substrate 62 or another layer, or combinations thereof, can be formed from non-conductive or dielectric polymers, rubbers, or elastomers as described for the substrate 62 hereinabove. In FIG. 3, three insulating sublayers are shown, but any appropriate number of layers can be used to create the desired form. If more than one insulating layer is used, each layer can be the same or a different material. In some embodiments, insulating layer
20 66 is chosen to provide effective parting layer characteristics.

In a preferred embodiment as shown in FIG. 3, the insulating layer 66 covers substantially all of the substrate 62 of the microvalve assembly and the conductive layer 64 except for one or more areas near one or more ends or edges of the substrate 62. Printing of one or more insulating layers, such as 66, 68, and 70 as illustrated in FIG. 3,
25 can be accomplished in one or more passes in order to build up the insulating layers 66, 68, 70 on the substrate 62, such as in the area where the aperture will be or any other desired area. In a preferred embodiment as illustrated in FIG. 3, microvalve body insulating layer 66 has a further insulating layer 68 printed on a portion thereof, generally between the lead lines of conductive layer 64. The upper surface of insulating layer 68 is
30 curved in order to cause resistive layer 78 to expand away from insulating layer 68 during heating and expansion of the resistive layer 78. The microvalve body also includes an additional insulating layer formed as a boss 70 on insulating layer 68. Boss 70 is generally a raised rim surrounding aperture 72 that serves to provide a gasket having desired sealing characteristics. A laser or chemical etching process then is utilized to remove the portions

of the insulating layer above the conductive lines of the first layer or any insulating layer material above aperture 72 in substrate 62, and combinations thereof.

Afterwards, conductive material, which can be of the same type or a different type than utilized in the first layer, is deposited in the areas removed by the laser to provide rigid electrical contacts 74 protruding up through the insulating layer. The composition of the conductive material of protruding electrical contact 74 is not critical, but preferably the material is of appropriate resistivity, is rigid, has adequate cohesive strength, and is readily adhered to by the resistive layers 78 described below. It is important, however, that the conductive material, if a liquid, be able to dry upon being printed or coated on the substrate or other layer, leaving a conductive coating thereon. Examples of conductive materials include, but are not limited to, metals and solvated polymer solutions containing conductive particles such as aluminum, carbon, silver, gold, copper, platinum, or combinations thereof. The conductive solids content of the solvated polymer generally ranges from about 40 to about 90 percent by weight, based on the total weight of the solvent, polymer, and conductive solids in the mixture. The amount of conductive particles required to be present in the mixture to provide the desired electrical conductivity may vary depending on the identity of the conductive particle due to differences among the particles with respect to density, conductivity, etc. The same or different coatings may be utilized in the same or different layers of the microvalve assembly. The conductive material may be comprised of a variety of film forming polymers which are compatible with the conductive particles and mixed therewith and which will adhere to the substrate or other layer upon drying or removal of the solvent. Examples of film forming polymers which may be utilized to form a conductive material include, but are not limited to, polymers such as polyesters and polyacrylates. One of ordinary skill in the art can readily ascertain the identity of acceptable polymers for use in the conductive material layer(s). Alternatively, direct metal deposition by electrochemical or vapor deposition means could be employed alone, or in combination with the above polymer matrix films to form either conductive layer 64 or conductive protruding electrical contact 74, and combinations thereof.

An aperture or apertures 72 are left uncoated or created after forming the one or more insulating layers 66, 68, and 70 immediately above and matching the aperture or apertures 72 in the substrate 62, to extend through both the substrate and the insulating layers. A plug of material is then placed in each aperture 72 which can be washed or melted out after the next layer or layers have been deposited. Examples of suitable

materials include waxes and low molecular weight polymers that can be at least partially removed. The plug is utilized to prevent subsequent material applied to the microvalve assembly from obstructing or partially obstructing aperture 72. A parting layer 76 is next printed on desired areas of the insulating film 68, 70 so that the resistive layer 78 will not
5 adhere to the insulating film. The resistive material layer 78 is deposited upon a predetermined portion of an upper surface of the microvalve assembly, generally on the parting layer 76. The resistive material layer 78 is conductive and has a coefficient of thermal expansion (CTE) greater than that of preferably all of the insulating layers 66, 68, 70. The resistive material layer 78 is deposited at least in an area which makes electrical
10 contact with the two electrical contacts 74 protruding upward through the insulating layer 66 and also covers the aperture 72 in the insulating layers 66, 68 and 70. A segment of a circuit is formed running from the first lead through the resistive material layer 78 to the second lead. The resistive material layer 78 is secured to the microvalve assembly in at least one location. The plug of material is removed from aperture 72 after the resistive
15 material layer 78 is formed. Upon the application of a potential to the resistive material layer 78 through the electrical leads 74 or contacts 64 of the conductive layers, the resistive material layer 78 heats and distorts away from the insulating layers 68, 70, creating a passage between the resistive material layer 78 and insulating layer 68, 70 having parting layer 76 thereon to the aperture or apertures 72 in the insulating layer and
20 substrate through which fluid can pass. The substrate 62 insulating layers 66, 68 and 70, and parting layer 76 of the microvalve body remain stationary while the microactuator comprising resistive material layer 78 moves from a first position to a second position, thereby opening the microvalve of the microvalve assembly thereby permitting fluid flow through aperture 72. Examples of resistive materials include, but are not limited to,
25 materials described for the conductive layers 64 and 74 hereinabove, and preferably are high thermal expansion conductive polymer matrix materials including conductive particles, and high thermal expansion metals such as aluminum, certain brasses, bronzes and magnesium.

The microvalve assembly optionally contains a cover layer (not shown in FIG. 3)
30 which is preferably non-conductive and is formed having a cavity to accommodate the distorting resistive material layer 78. The cover layer preferably includes at least one aperture to allow for flow of fluid into or out of the passage between the resistive material layer 72 and insulating layers 68, 70 when the resistive microactuator is in the second (open) position. Alternatively, cover layers are generally not utilized when space is

available for the microvalve microactuator comprising the resistive material layer 78 to deform away from the microvalve aperture 72 to allow flow of fluid.

The above described fluid regulating microvalve assembly is optionally detached from the substrate 62 and assembled into a cell as desired to control flow of fluid. That said, if the substrate 62 is removed, insulating layer 66 is generally considered the base of the microvalve body of the microvalve assembly.

In an alternative embodiment, the resistive material layer can be a multi-layer material, as described below for the embodiment shown in FIGS. 4A and 4B.

The fluid regulating microvalve assembly optionally includes a latch. FIGS. 4A and 4B show an embodiment of a microvalve assembly with a latch in a closed position and an open position, respectively. A control unit, which can include a microchip or imbedded microcircuit, as shown in FIG. 5, can be added to keep the microvalve open without expenditure of parasitic power. The control unit can be connected electrically through two additional conductive contact lines included in the conductive layer of the microvalve assembly, extending across at least part of the substrate to provide electrical connections to the latching mechanism. The control unit can be used to provide power to the latching mechanism only when power is required from the cell or battery for a powered appliance.

The latching mechanism includes a multi-layer actuator, or latch arm, made from resistive material that will heat and bend when current passes through it. In FIG. 4A, latch arm 82 is shown in a first position when the microvalve is in the closed position. Upon application of a potential across the latch arm 82, through conductive strips 84 connected to opposite sides of the latch arm 82, the latch arm 82 heats, causing it to bend up and to the left. At the same time, a potential applied across the resistive layer 78 through conductive strips 64, causing the resistive layer 78 to expand and move upward with parting layer 76, beyond the level shown in FIG. 4B, thereby allowing the latch arm 82 to move past a downward projection 90 from the parting layer 76. The potential is then removed from the resistive layer 78, allowing it to cool and move downward slightly, into the position shown in FIG. 4B, where the parting layer 76 and resistive layer 78 are held in this position by the latch arm 82. Once the projection 90 has moved downward, it will retain the latch arm 82 in its second position as shown in FIG. 4B, so the potential across the latch arm 82 can be removed and the latch arm 82 will hold the microvalve in the open position shown in FIG. 4B, providing a passageway through which fluid can pass to the aperture 72 in the substrate 62 and insulating layer 66, 68, 70, even though no current is

flowing through the resistive layer 78 or the latch arm 82. The microvalve is connected to a control unit, and when the control unit senses that power is no longer required from the cell, the control unit allows a potential to be placed across the resistive layer 78 through conductive strips 64 for a sufficient time for the resistive layer 78 and parting layer 76 to move upward slightly so the projection 90 no longer retains the latch arm 82. The latch arm 82 returns to its first position, allowing the parting layer 76 and resistive layer 78 to return to their first position after the potential is removed from the resistive layer 78 and the resistive layer 78 cools. In this manner, power from the cell is consumed only to move the microvalve from the closed position (FIG. 4A) to the open position (FIG. 4B) and vice versa, and the useful life of the cell is extended.

The microvalve assembly in FIGS. 4A and 4B can be made utilizing a process similar to that described above for the microvalve assembly in FIG. 3, except as follows. Two additional conductive strips 84 are deposited on the bottom surface of the substrate 62. A hole is also made in the substrate 62 through which the latch arm 82 can be inserted. The hole can be angled so the latch arm 82 will be at an acute angle to the upper surface of the substrate 62 as shown in FIG. 4A. A portion of insulating sublayers 66 and 68 is removed (alternatively sublayers 66 and 68 are deposited in such a way that they do not completely cover the substrate 62) so there is a cavity 92 in the sublayers 66 and 68 above the latch arm hole in the substrate 62 into which the latch arm 82 can extend. The cavity 92 is large enough to allow the latch arm 82 to move between its first and second positions, and the hole and cavity 92 are located such that, when the latch arm 82 is inserted, each of two opposing surface layers (described below) is near one of the conductive strips 84. The latch arm 82 is inserted through the latch arm hole so its distal end extends into the cavity 92 in sublayers 66 and 68. After the latch arm 82 is inserted through the substrate 62, electrical connections are made between each of the opposing surface layers of the latch arm 82 and the adjacent conductive strips 84. This can be done by applying an electrically conductive material 94, which can be a conductive adhesive that also secures the end of latch arm 82 in position within the latch arm hole. The hole can be filled in around the latch arm 82 with a nonconductive material to help hold the latch arm 82 in place and prevent fluid from flowing through the latch arm hole. A downward protrusion 90 can be added to the parting layer 76.

The latch arm 82 can be a multi-layer component, having high- and low-CTE sublayers, similar to the multi-layer resistive layer 78 shown in FIGS. 4A and 4B and

described below. Preferably it has three sublayers – a high-CTE material sublayer, a low-CTE material sublayer, and a sublayer of nonconductive material therebetween except at its distal end. At the distal end the resistive material layers are in direct contact to provide a complete electrical path through the latch arm between the points of electrical contact with the conductive strips 84 at the opposite end of the latch arm 82.

In an alternative method of making a microvalve with a latch mechanism the latch arm is deposited within the cavity in the insulating layer; e.g. by depositing layers of the latch arm and parting layers, using a printing process for example. This can eliminate the need to make a hole in the substrate for inserting the latch arm, a separate latch arm insertion process and subsequent filling of the hole around the inserted latch arm. After forming a cavity for the latch arm in the substrate, a parting layer is deposited over portions of the substrate and conductive leads so the latch arm will not adhere thereto, except as desired at one end of the latch arm to secure that end to the substrate and make the proper electrical contacts with the conductive leads. Strips of the high-CTE layer, nonconductive layer and low-CTE layer of the latch arm are sequentially deposited to form the latch arm, with one end of the high-CTE layer adhered to one of the conductive strips, the nonconductive layer covering the high-CTE layer except at the opposite end, where the low-CTE layer is adhered to the exposed end of the high-CTE layer. The low-CTE layer also extends beyond the end of the high-CTE layer and is adhered to the other conductive strip to create an electrical path from the one electrical contact strip and through the high-CTE layer and the low-CTE layer to the other electrical contact strip. A second parting layer can then be deposited over the completed latch arm if necessary to prevent the latch arm from adhering to other components of the microvalve assembly with which it may come in contact. In such an embodiment, it may be desirable to provide an angled surface onto which the latch arm is deposited, rather than depositing it directly onto the flat substrate, in order to optimize the placement of the latch arm to move from its first position to an optimal (e.g., vertical) second position.

In the embodiment of a microvalve assembly shown in FIGS. 4A and 4B, the resistive layer 78 includes two sublayers, a low-CTE sublayer 86, disposed adjacent to the parting layer 76, and a high-CTE sublayer 88, disposed above the low-CTE sublayer 86. The low-CTE sublayer 86 is made from material with a low CTE, such as glass, silicon or INVAR® (an iron alloy comprising about 36 weight percent nickel). The high-CTE sublayer 88 can be made from material with a high CTE, such as those described above for

single layer resistive layer. Such a multi-layer structure may produce greater vertical movement to provide a larger fluid passageway. The embodiment shown in FIGS. 4A and 4B also shows the resistive layer 78 being thinner at its edges. This can make the resistive layer 78 more flexible at the edges, so the thin peripheral area acts as a hinge.

5 In alternative embodiments to the microvalve assemblies in FIGS. 3, 4A and 4B, the parting layer 76 can be made from a material that will adhere to the insulating layer 68 and not to the resistive layer 78. In these embodiments, aperture 72 and the latch arm cavity 92 would extend through the parting layer 76 as well, to provide a fluid passageway between the resistive layer 78 and the parting layer 76 to the aperture 72.

10 A further embodiment of fluid regulating microvalve assembly is illustrated in cross section in FIG. 6. The cross-section shows a microvalve assembly in two sections which are in position to be connected, such as through an adhesive or lamination, or the like, to create an assembled microvalve assembly. The microvalve assembly includes a microvalve body comprising substrate 36 which is preferably in the form of a rigid sheet or film, as described hereinabove. Substrate 36 includes aperture 37. End supports 38 are deposited on substrate 36, preferably utilizing a printing process. Boss 48 can be deposited around aperture 37 utilizing the same material as end supports 38. If desired, end supports 38 and boss 48 can be deposited as a continuous layer on the substrate 36 and portions of the material subsequently removed to create the end supports 38 and boss 48. Preferably boss 48 is a different material, selected to provide a good seal with boss 46. Alternatively, a coating could be deposited on the surface of at least one of boss 48 and boss 46 to function as a gasket.

The upper portion of the microvalve assembly comprising a microactuator as illustrated in FIG. 6 is formed on a non-conductive membrane sheet 40, at least utilizing the printing process. In one embodiment, the membrane sheet 40 is formed of material as described for the substrate hereinabove, such as polymer matrix semiconductors, glasses, silicon, polymers, rubbers, or elastomers. Selected areas of the membrane sheet 40 are overprinted in one embodiment with a non-conductive layer 49, preferably adjacent to two opposite ends of the membrane sheet 40 at least in the area above end supports 43, with the same or a different material as membrane sheet 40 in order to create a relatively thin section within supports 43, located radially outward from the location of boss 46. An expansion layer 41, which includes a resistive material, is deposited on membrane sheet 40 preferably by printing. In this embodiment, expansion layer 41 is preferably formed in an annular strip disposed around boss 48, rather than having a planar shape as in the

embodiment shown in FIGS. 4A and 4B. Conductive leads make electric contact between each of contact points 44 and 45 and expansion layer 41, such as illustrated. Upon application of a potential to the contact points 44 and 45, expansion layer 41 heats, expands, and causes deformation of membrane sheet 40. Aperture 39 is preferably placed
5 in membrane sheet 40 to admit fluid to the center of the microvalve. A boss 46 is deposited on the underside of membrane sheet 40 in one embodiment and is sufficient in size and located to cover boss 48 in the lower portion of the microvalve assembly. Boss 46 functions as a sealing plug on lower annular boss 48. End supports 43 are deposited along one or more lower edges of the membrane sheet 40. Boss 46 and end supports 43
10 can be deposited utilizing a printing process. If desired, end supports 43 and boss 46 can be deposited as a continuous layer on the underside of membrane sheet 40 and portions of the material subsequently removed to create the end supports and boss 46.

As stated hereinabove, the upper and lower end supports are connected to form the microvalve assembly. The supports can be connected via lamination or an adhesive such
15 as known in the art. Optionally, a gasket or sealant layer is deposited on boss 48 to optimally seal aperture 37 in conjunction with boss 46. The gasket or sealant layer is preferably formed of an elastomeric compound which will not adhere to the layer, such as boss 46 contacting it during the operation of the microvalve and microactuator. Suitable materials include, but are not limited to, polyethylene terephthalate,
20 polytetrafluoroethylene such as TEFLON® (DuPont), or polymethylsiloxane. In an open position, fluid can flow through the gap in the sides of the microvalve if not sealed by end supports 38 and 43, or through aperture 39 if the microvalve ends are sealed, and ultimately through aperture 37 into the cell or into a battery compartment. If desired different portions of a layer (e.g., end supports 38 and boss 48 on substrate 36, or end
25 supports 43 and boss 46 on membrane sheet 40) can be either the same material, as described above, or they can contain different materials.

The embodiment shown in FIG. 6 can be modified to incorporate a latch mechanism, which can be controlled by a control unit. For example, as shown in FIG. 7, a latch arm 82 is inserted through a hole in the substrate 36, in a manner similar to that
30 described above for the embodiment shown in FIGS. 4A and 4B. A downward projection 90 can be deposited on the underside of the membrane sheet 40 to retain the latch arm 82 in its second position to hold the microvalve in an open position. In this embodiment, conductive strips 84 are deposited on the top surface of the substrate 36, but they could be

located on the bottom surface, as shown in the embodiment in FIGS. 4A and 4B. If the conductive strips 84 are on the top surface of the substrate 36, electrical connections to a control unit could be provided, for example in a manner similar to that described above for making electrical connections between the lead lines of conductive layer 64 and the resistive layer 78 in the microvalve assembly shown in FIGS. 4A and 4B.

Figure 5 is a schematic diagram illustrating one embodiment of a control circuit for microactuator 50 of a microvalve assembly of the present invention. Microactuator 50 is connected to a control unit 54, that can be printed in one embodiment, connected in series with an electrical switch 52. Figure 5 also illustrates load 51, connected in series with switch 52, control unit 54 and battery 53. Control unit 54 responds to voltage and current characteristics of the circuit it is connected to. Control unit 54 can vary the potential supplied to the microactuator 50 in order to regulate or optimize fluid flow through the microvalve assembly.

The fluid regulating microvalve assemblies of the present invention include microactuators that can move in various ways and in combinations of ways from a first position where fluid cannot pass through the microvalve body aperture to at least a second position which allows fluid to pass through the microvalve body aperture. Movements include, but are not limited to, motion towards and away from a portion of the microvalve body particularly an aperture, linear or non-linear movement, movement parallel to a surface such as a microvalve body, and movement which serves to engage or disengage a latch.

In one embodiment the fluid regulating microvalve assembly is electrically connected, preferably in a series circuit, to the cell it is controlling fluid access thereto. In a further embodiment, the fluid regulating microvalve assembly is provided with a separate power source other than the cell or cells it is operatively connected to. Electrical connections between the microvalve assembly electrical contacts and the cell electrodes can be accomplished in any suitable manner that provides a reliable connection. For example, one of the microvalve assembly electrodes can be in direct physical and electrical contact with the positive electrode such as the oxygen reduction electrode. Alternatively, one electrical contact can be in direct contact with an electrically conductive portion of the cell housing that is in electrical contact with the positive electrode. Further, if desired, an electrical lead can be used to provide electrical contact with the positive electrode.

The microvalve assembly electrical contact that is electrically connected to the negative electrode of the cell can be connected with an electrical lead. An electrical lead can have a travel path around or through the positive electrode or oxygen-reduction electrode, as long as the lead is electrically insulated therefrom. In one embodiment, the electrical connector connecting the microvalve assembly to the negative electrode of the cell may be in the form of a wire or thin metal strip with dielectric material insulating any parts of the lead that may otherwise come in electrical contact with the positive electrode, either directly or indirectly through another cell component such as a conductive portion of the cell housing, a positive electrode, current collector, or a positive electrode electrical contact, lead or spring. In a further example, the electrical lead to the negative electrode may be in the form of one or more thin layers of metal printed or otherwise deposited on a portion of one or more other cell component, such as surfaces of gasket, insulators, cans, covers, and the like. Layers of the dielectric material may be coated over or beneath, or a combination thereof, the metal layers to provide the necessary insulation from the positive electrode.

The potential applied to the fluid regulating microvalve assembly to operate the microactuator can originate within the cell. For example, the potential applied to the microvalve assembly can be the cell potential, as described above. The cell potential can also be changed. If a higher voltage is needed to produce a desired microvalve assembly microactuator movement, the cell potential can be adjusted upward. Adjusting the cell potential can allow for the use of different types of materials for the microactuator. Increasing the cell potential can be accomplished, for example, with a controlled circuit, to regulate or step up the cell voltage and thus more strongly induce movement of the microactuator to operate the microvalve assembly.

The control circuit can also be utilized to control other cell features or components. For example, the control circuit can be utilized to monitor the need for oxygen and then apply a potential across the microvalve assembly to open or close the microactuator. For example, the control circuit can include an oxygen sensor to monitor the oxygen level in the cell. The control circuit can also be utilized to monitor the cell voltage or monitor the potential of the positive electrode against a separate reference electrode. The control circuit can be printed utilizing the printing process of the present invention or another process. The control circuit can be applied to a cell or battery component or be included on a separate substrate or wafer or chip, or any other suitable arrangement can be utilized.

The control circuit can have components including, but not limited to, fuses, inductors, capacitors, resistors, and transistors. The control circuit can be designed to fail on contact with a corrosive fluid or shut down upon excessive current demand.

5 The fluid regulating microvalve assemblies of the present invention can be incorporated into cells in various ways, depending on the type and design of the microvalve assembly and the cell. In one embodiment as described hereinabove, the fluid regulating microvalve assembly is contained within the cell housing. However, it is to be understood, that other embodiments of the invention are contemplated in which the microvalve assembly, control circuit, or combinations thereof, can be disposed outside the
10 cell, such as between the external surface of the cell housing and a battery jacket or case. The minimal volume requirements for the fluid regulating microvalve assembly make such embodiments possible in batteries with little space available between the cell and jacket or case.

As disclosed above, a preferred embodiment of an electrochemical cell using a
15 microvalve assembly according to the invention is an air-depolarized cell. Another preferred embodiment is an air-assisted cell. Yet another preferred embodiment is a fuel cell. A preferred cell shape is a button shape. Another preferred cell shape is a cylindrical shape. Yet another preferred cell shape is a prismatic shape.

An electrochemical cell according to the invention can be part of a battery
20 comprising one or more cells. In one preferred embodiment more than one battery cell can share a single microvalve assembly, and in another preferred embodiment each cell can have a separate microvalve assembly. In other preferred embodiments, microvalve assemblies can be located within or on the battery housing, or they can be mounted on a portion of an appliance in which the battery is installed. Similarly, in one preferred
25 embodiment more than one cell can share the same control unit, and in another preferred embodiment each cell can have a separate control unit. In other preferred embodiments, control units can be located within on or on the battery housing, or at least portions of the control units can be mounted on a portion of an appliance in which the battery is installed.

It will be understood by those who practice the invention and those skilled in the
30 art that various modifications and improvements may be made to the invention without departing from the spirit of the disclosed concept. The scope of protection afforded is to be determined by the claims and by the breadth of interpretation allowed by law.

WHAT IS CLAIMED IS:

1. A microvalve assembly for an electrochemical cell, comprising:

a stationary microvalve body comprising a polymer, elastomer or rubber and an
5 aperture located between a first surface and a second surface; and

a movable microactuator connected to the microvalve body and capable of moving
between a first position where fluid cannot pass through the microvalve body aperture and
a second position which allows fluid to pass through the microvalve body aperture, and
wherein the microactuator is thermally actuated.

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2. The microvalve assembly according to claim 1, wherein the microvalve body
includes a substrate and at least one printed layer.

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3. The microvalve assembly according to claim 2, wherein an insulating layer is
printed on at least a portion of the substrate.

4. The microvalve assembly according to claim 3, wherein the insulating layer has a
curved upper surface, and wherein a parting layer is present on the insulating layer curved
upper surface.

20

5. The microvalve assembly according to claim 4, wherein the insulating layer of the
microvalve body includes a boss deposited as a rim around the valve body aperture.

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6. The microvalve assembly according to claim 1, wherein the microactuator
comprises at least one printed layer.

7. The microvalve assembly according to claim 1, wherein the microactuator
comprises a resistive material layer.

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8. The microvalve assembly according to claim 7, wherein the resistive material layer
comprises metal or a polymer containing conductive particles.

9. The microvalve assembly according to claim 1, wherein the microvalve assembly
includes a segment of a circuit extending from a first lead located on the microvalve body

to a resistive material layer of the movable microactuator to a second lead of the microvalve body.

10. The microvalve assembly according to claim 9, wherein the resistive material layer
5 heats and distorts away from the microvalve body aperture to the second position when a potential is applied between the first lead and the second lead.

11. The microvalve assembly according to claim 1, wherein the microvalve assembly
10 includes a latch operatively connected to the microvalve body.

12. The microvalve assembly according to claim 1, wherein the microvalve assembly
includes an integrated control unit capable of controlling the movement of the
microactuator between the first position and the second position.

13. The microvalve assembly according to claim 1, wherein the movable microactuator
15 is operatively connected to the microvalve body through one or more printed supports, and
wherein the movable microactuator comprises a membrane sheet and a resistive material
layer printed on the membrane sheet.

14. The microvalve assembly according to claim 13, wherein the microactuator
20 includes a boss connected to a bottom side of the membrane sheet that seals the
microvalve body aperture in the first position to prevent fluid flow through the microvalve
body aperture.

15. The microvalve assembly according to claim 13, wherein the movable
25 microactuator includes a segment of a circuit extending from a first lead to the resistive
material layer to a second lead, and wherein a potential applied between the first lead and
the second lead causes distortion of the microactuator and movement from the first
position to the second position.

16. An electrochemical cell, comprising:
30 a housing comprising one or more fluid inlet apertures, a negative electrode, a fluid
consuming positive electrode, and a microvalve assembly operatively connected to the one
or more fluid inlet apertures for controlling passage of fluid to the fluid consuming

positive electrode, wherein the microvalve assembly comprises (a) a stationary microvalve body comprising a polymer, elastomer or rubber and an aperture located between a first surface and a second surface; and (b) a movable microactuator connected to the microvalve body and capable of moving between a first position where fluid cannot pass
5 through the microvalve body aperture and a second position which allows fluid to pass through the microvalve body aperture.

17. The electrochemical cell according to claim 16, wherein the microactuator moves away from the microvalve body in moving from the first to the second position, and the
10 microactuator moves toward the microvalve body in moving from the second to the first position.

18. The electrochemical cell according to claim 16, wherein at least one of the microvalve body and the microactuator comprises a printed layer.

15

19. The electrochemical cell according to claim 16, wherein the fluid consuming positive electrode is an oxygen reduction electrode, and wherein the microactuator is thermally actuated.

20. The electrochemical cell according to claim 16, wherein the microvalve assembly includes a control unit that is adapted to monitor a fluid level within the housing and is able to apply a potential across the microvalve assembly.

21. The electrochemical cell according to claim 19, wherein the microvalve assembly
25 is disposed within the cell housing or outside of the cell housing.

22. The electrochemical cell according to claim 21, wherein the cell can be disposed within an appliance on which the microvalve assembly is mounted.

23. The electrochemical cell according to claim 21, wherein the cell can be disposed within an appliance on which at least a portion of a control circuit for monitoring a fluid
30 level within the cell housing and applying a potential across the microvalve assembly.

24. The electrochemical cell according to claim 21, wherein the cell is a sole power source of power to operate the microvalve assembly.

25. The electrochemical cell according to claim 16, wherein the microvalve assembly is operatively connected between the one or more fluid entry apertures and the fluid consuming positive electrode.

26. The electrochemical cell according to claim 16, wherein the cell is an air depolarized cell, an air-assisted cell, or a fuel cell.

27. The electrochemical cell according to claim 16, wherein the cell is a button cell, a cylindrical cell, or a prismatic cell.

28. The electrochemical cell according to claim 16, wherein the microvalve body includes a substrate and an insulating layer printed on at least a portion of the substrate.

29. The electrochemical cell according to claim 28, wherein the insulating layer has a curved upper surface, and wherein a parting layer is present on the insulating layer curved upper surface.

30. The electrochemical cell according to claim 29, wherein the insulating layer of the microvalve body includes a boss deposited as a rim around the valve body aperture.

31. The electrochemical cell according to claim 16, wherein the microactuator comprises a resistive material layer.

32. The electrochemical cell according to claim 31, wherein the resistive material layer comprises metal or a polymer containing conductive particles.

33. The electrochemical cell according to claim 16, wherein the microvalve assembly includes a segment of a circuit extending from a first lead located on the microvalve body to a resistive material layer of the movable microactuator to a second lead of the microvalve body.

34. The electrochemical cell according to claim 33, wherein the resistive material layer heats and distorts away from the microvalve body aperture to the second position when a potential is applied between the first lead and the second lead.

5 35. The electrochemical cell according to claim 16, wherein the microvalve assembly includes a latch operatively connected to the microvalve body.

36. The electrochemical cell according to claim 16, wherein the microvalve assembly includes an integrated control unit capable of controlling the movement of the
10 microactuator between the first position and the second position.

37. The electrochemical cell according to claim 16, wherein the movable microactuator is operatively connected to the microvalve body through one or more printed supports, and wherein the movable microactuator comprises a membrane sheet and
15 a resistive material layer printed on the membrane sheet.

38. The electrochemical cell according to claim 37, wherein the microactuator includes a boss connected to a bottom side of the membrane sheet that seals the microvalve body aperture in the first position to prevent fluid flow through the microvalve body aperture.
20

39. The electrochemical cell according to claim 37, wherein the movable microactuator includes a segment of a circuit extending from a first lead to the resistive material layer to a second lead, and wherein a potential applied between the first lead and the second lead causes distortion of the microactuator and movement from the first
25 position to the second position.

40. A method for preparing a microvalve assembly, comprising the steps of:
forming a microvalve body having one or more layers;
forming a microactuator having one or more layers; and
30 operatively joining the microvalve body to the microactuator, wherein the microvalve body comprises an aperture that extends through the body from a first surface to a second surface, wherein the forming of the one or more microvalve body or microactuator layers, or both, includes utilizing a printing process, and wherein the microactuator is operatively connected to the microvalve body and capable of moving

between a first position where fluid cannot pass through the microvalve body aperture and a second position which allows fluid to pass through the microvalve body aperture.

41. The method according to claim 40, wherein the microvalve assembly comprises a latch and a control unit, and at least one of the latch and the control unit comprises at least one material deposited by printing.

42. The method according to claim 40, wherein the microvalve body is formed by applying a conductive layer to a substrate, said conductive layer comprising first and second electrical leads.

43. The method according to claim 42, wherein an insulating layer is applied on at least a portion of the substrate and on at least a portion of the conductive layer.

44. The method according to claim 43, wherein material from the insulating layer is removed from over at least a portion of the conductive layer.

45. The method according to claim 44, wherein electrical contact is formed and is connected to the conductive layer, and wherein a parting layer is formed on at least a portion of the insulating layer.

46. The method according to claim 44, wherein a resistive layer is applied to the assembly and is in electrical contact with at least two electrical contacts, wherein a segment of a circuit is formed extending from the first lead to the resistive material to the second lead, and wherein upon application of a potential between the first lead and the second lead, the resistive material layer distorts away from the microvalve body aperture allowing fluid to flow therethrough.

47. The method according to claim 41, wherein the valve body is formed by printing at least one support on a substrate.

48. The method according to claim 41, wherein the microactuator is formed by printing at least one support to a membrane.

49. The method according to claim 48, wherein a resistive material layer is printed on the membrane.

50. The method according to claim 40, wherein the microvalve body and the
5 microactuator are joined by lamination or an adhesive.

51. The method according to claim 49, wherein the microactuator includes a boss that seals the microvalve body aperture in the first position.

10 52. The method according to claim 47, wherein the microvalve body includes two printed end supports and a printed boss formed as a rim around the aperture in the substrate.

53. The method according to claim 40, wherein the microvalve body is formed having
15 a latch.

54. The method according to claim 40, further including the step of connecting the microvalve assembly to a control unit.

20 55. The method according to claim 40, further including the step of assembling the microvalve assembly into an electrochemical cell.

56. The method according to claim 55, further including the step of positioning the
25 microvalve assembly between a fluid inlet aperture of the cell and a fluid consuming electrode of the cell.

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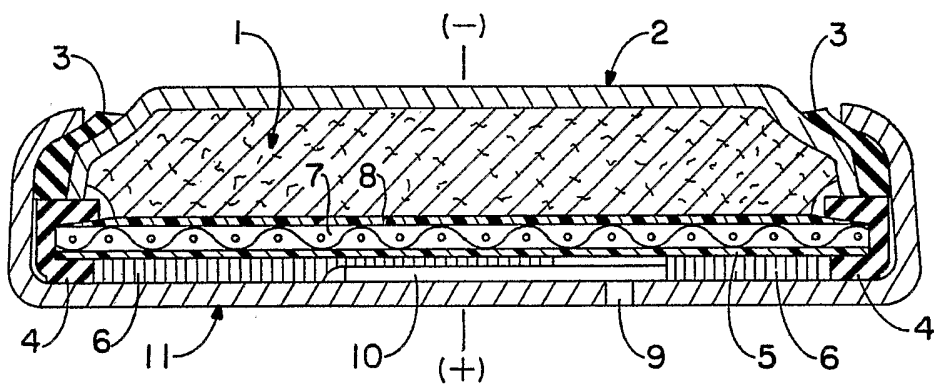


FIG.-1

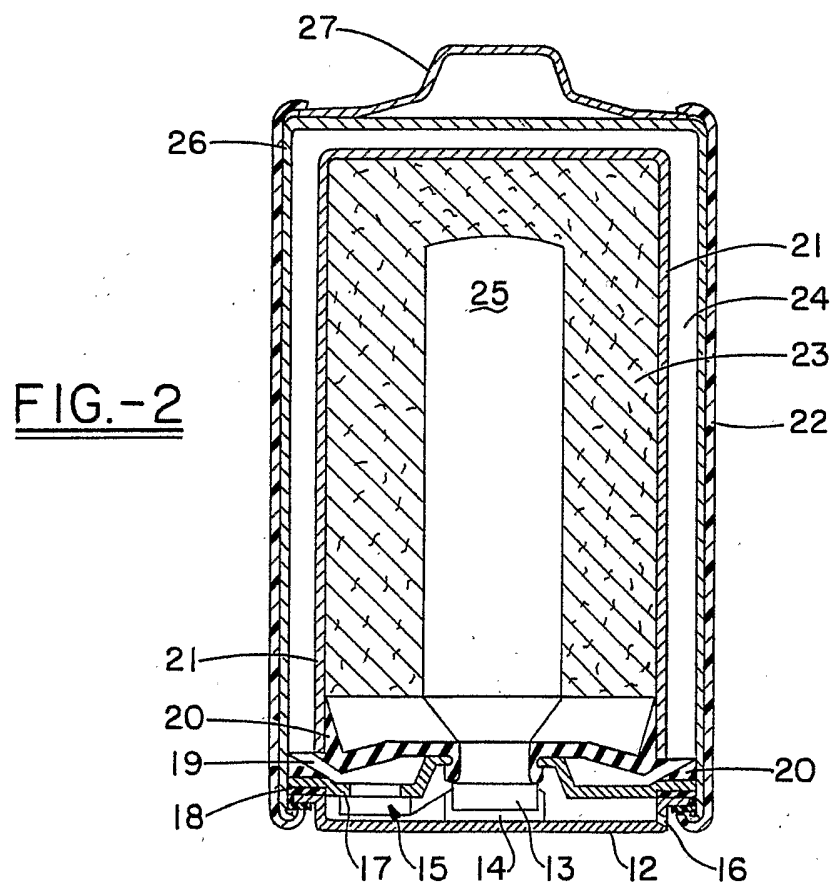


FIG.-2

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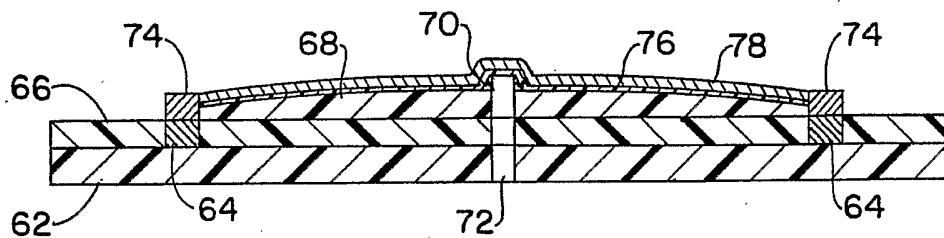


FIG. -3

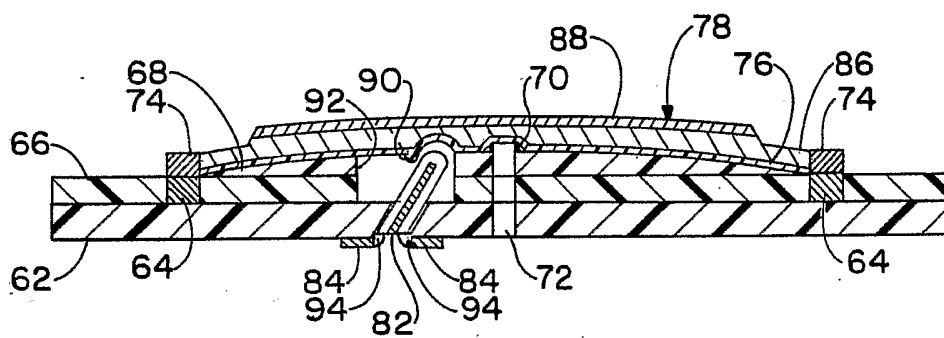


FIG. -4A

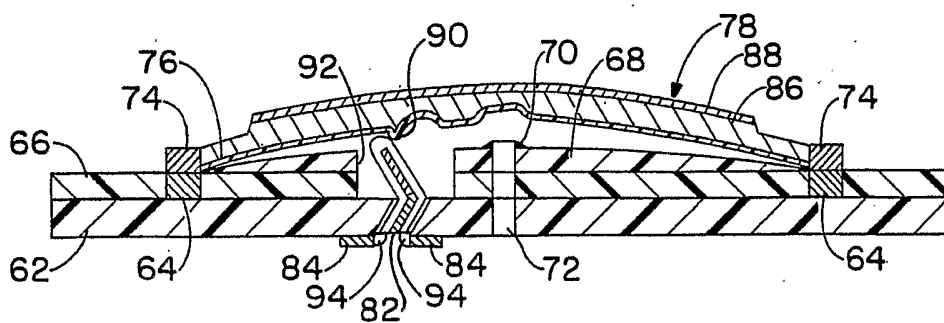
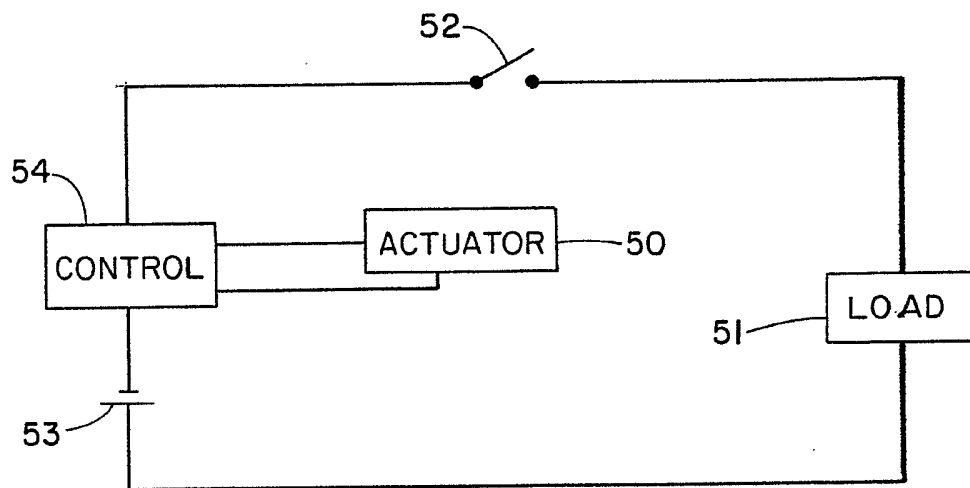
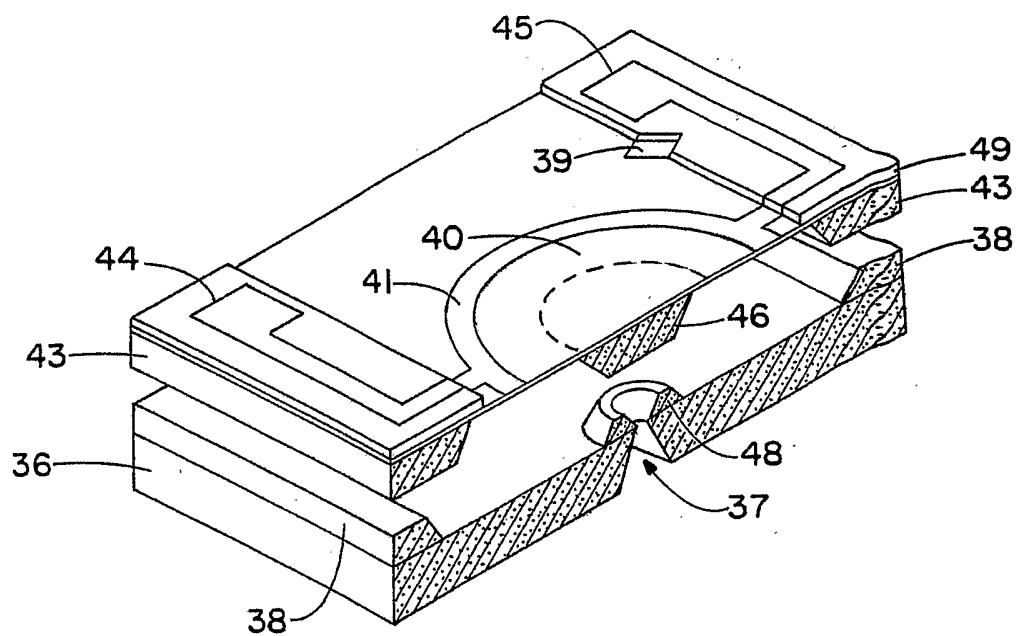
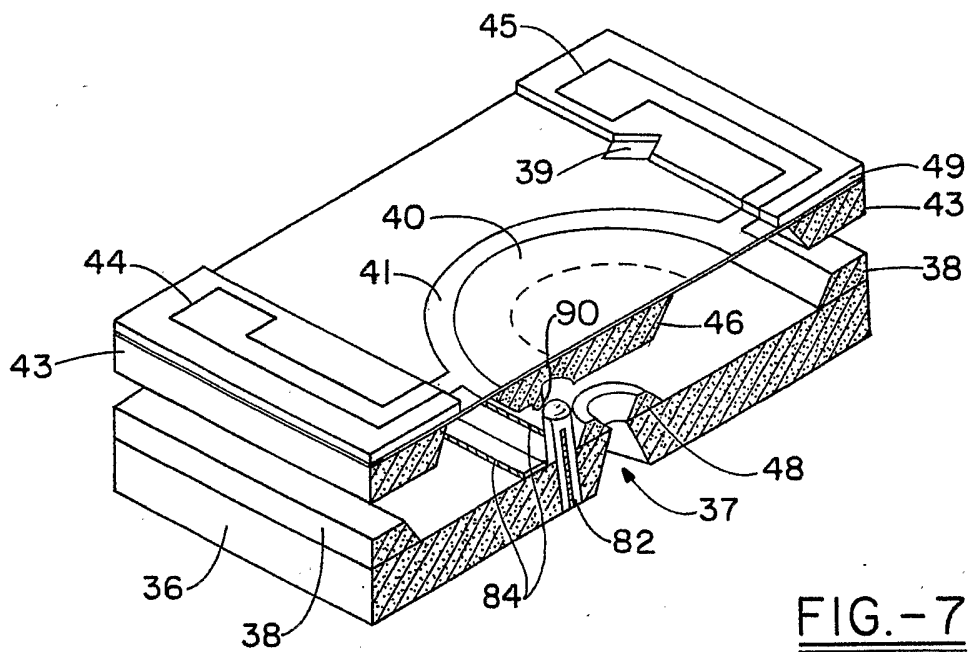


FIG. -4B

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FIG.-5FIG.-6

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/038559

A. CLASSIFICATION OF SUBJECT MATTER

H01M2/12

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)
H01M

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 practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 12 71 794 B (GEORG NEUMANN; LABORATORIUM FUER ELEKTROAKUSTIK G.M.B.H) 4 July 1968 (1968-07-04) claims 1-4; figures 1-3 -----	1-56
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 250 (E-633), 14 July 1988 (1988-07-14) & JP 63 037559 A (YUASA BATTERY CO LTD), 18 February 1988 (1988-02-18) abstract -----	1-56
A	US 3 664 878 A (HELMUT K. AMTHOR) 23 May 1972 (1972-05-23) claims 1-19; figure 4 -----	1-56

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

20 February 2006

Date of mailing of the international search report

28/02/2006

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/038559

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