



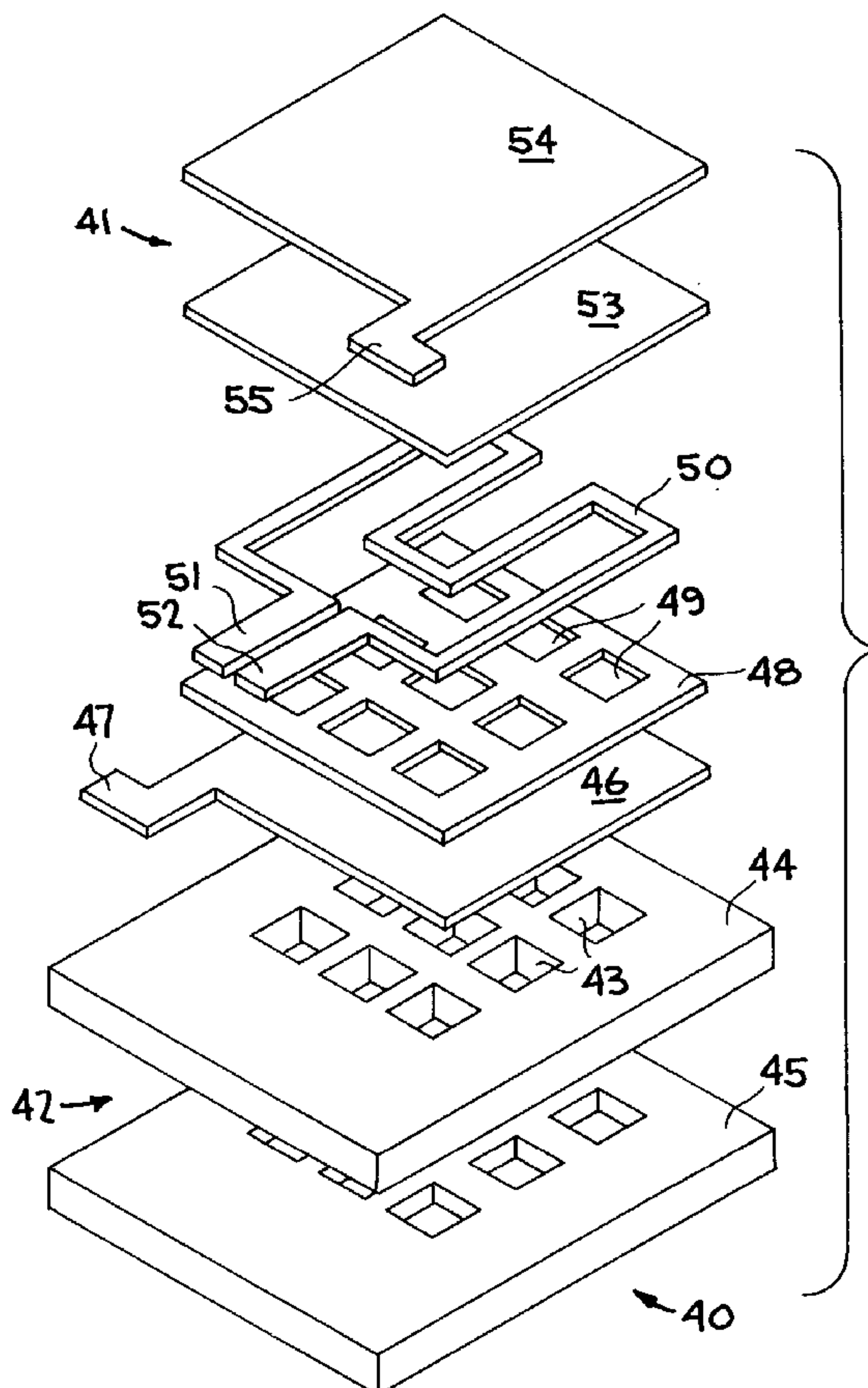
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(19) **United States**(12) **Patent Application Publication**
Jankowski et al.(10) **Pub. No.: US 2003/0039874 A1**(43) **Pub. Date: Feb. 27, 2003**(54) **MEMS-BASED THIN-FILM FUEL CELLS**(75) Inventors: **Alan F. Jankowski**, Livermore, CA
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filed on Feb. 1, 1999.**Publication Classification**(51) Int. Cl.⁷ **H01M 8/04; H01M 8/12;**
H01M 8/10; H01M 8/02(52) **U.S. Cl. 429/26; 429/32; 429/38**(57) **ABSTRACT**

A micro-electro-mechanical systems (MEMS) based thin-film fuel cells for electrical power applications. The MEMS-based fuel cell may be of a solid oxide type (SOFC) having a thickness of 0.5-50 μm at a temperature below 600° C. and a thickness of 0.5-7.5 μm at a temperature over 600° C., or a solid polymer type (SPFC), or a proton exchange membrane type (PEMFC), each operating below 600° C. and having a thickness of 0.5-50 μm , and each fuel cell basically consists of an anode and a cathode separated by an electrolyte layer. The electrolyte layer can consist of either a solid oxide or solid polymer material, or proton exchange membrane electrolyte materials may be used. Additionally catalyst layers can also separate the electrodes (cathode and anode) from the electrolyte. Gas manifolds are utilized to transport the fuel and oxidant to each cell and provide a path for exhaust gases. The electrical current generated from each cell is drawn away with an interconnect and support structure integrated with the gas manifold. The fuel cells utilize integrated resistive heaters for efficient heating of the materials. By combining MEMS technology with thin-film deposition technology, thin-film fuel cells having microflow channels and full-integrated circuitry can be produced that will lower the operating temperature and will yield an order of magnitude greater power density than the currently known fuel cells.



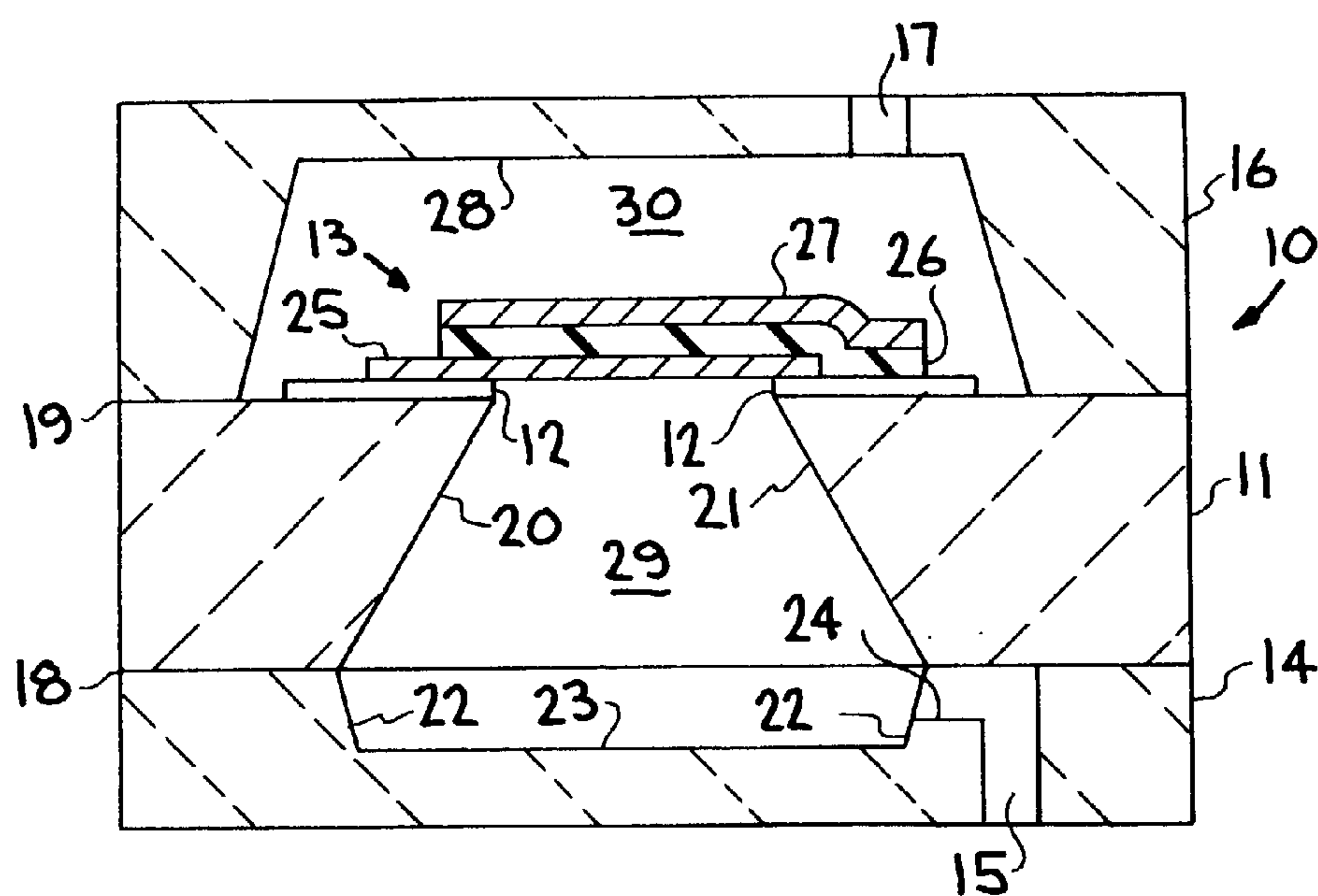


FIG. 1

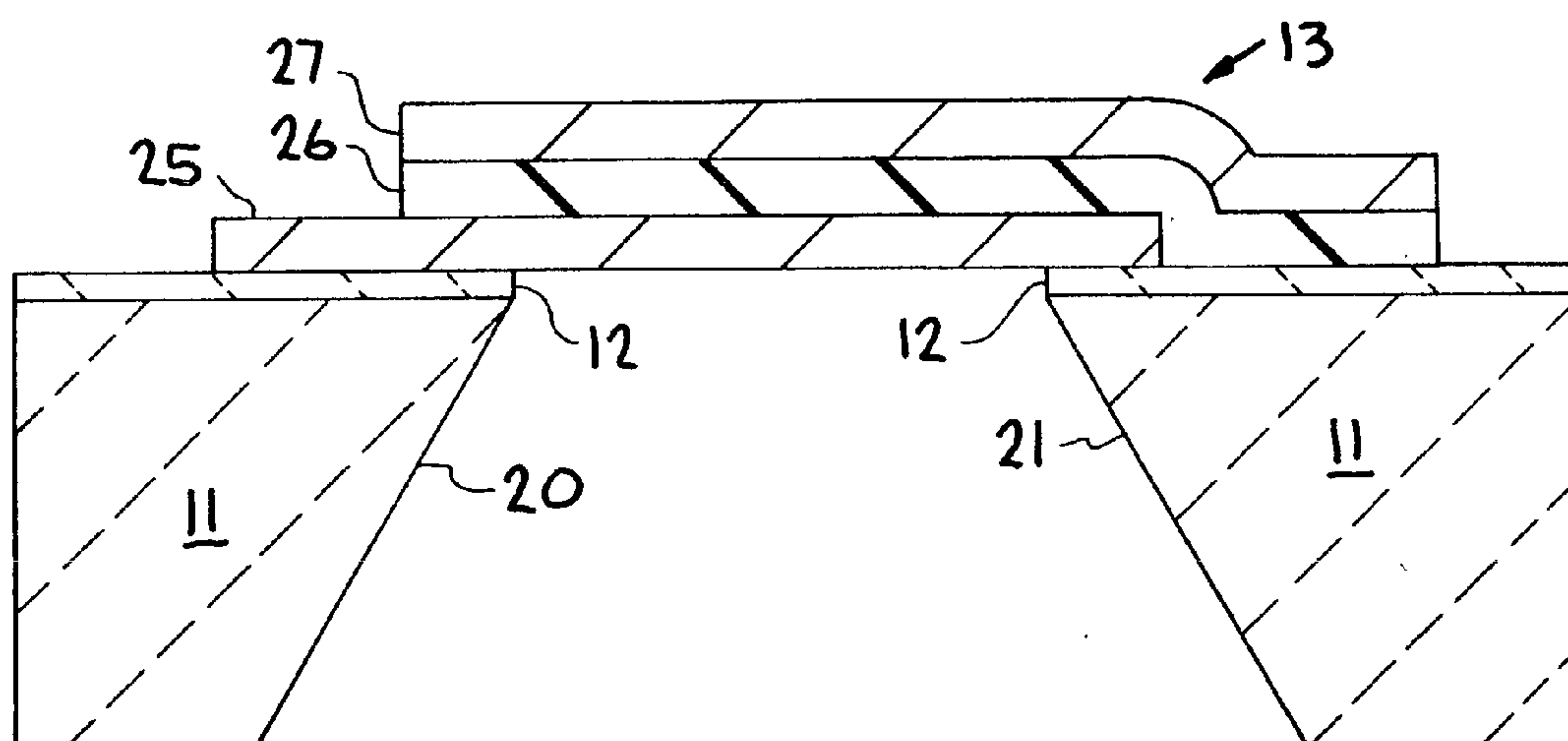
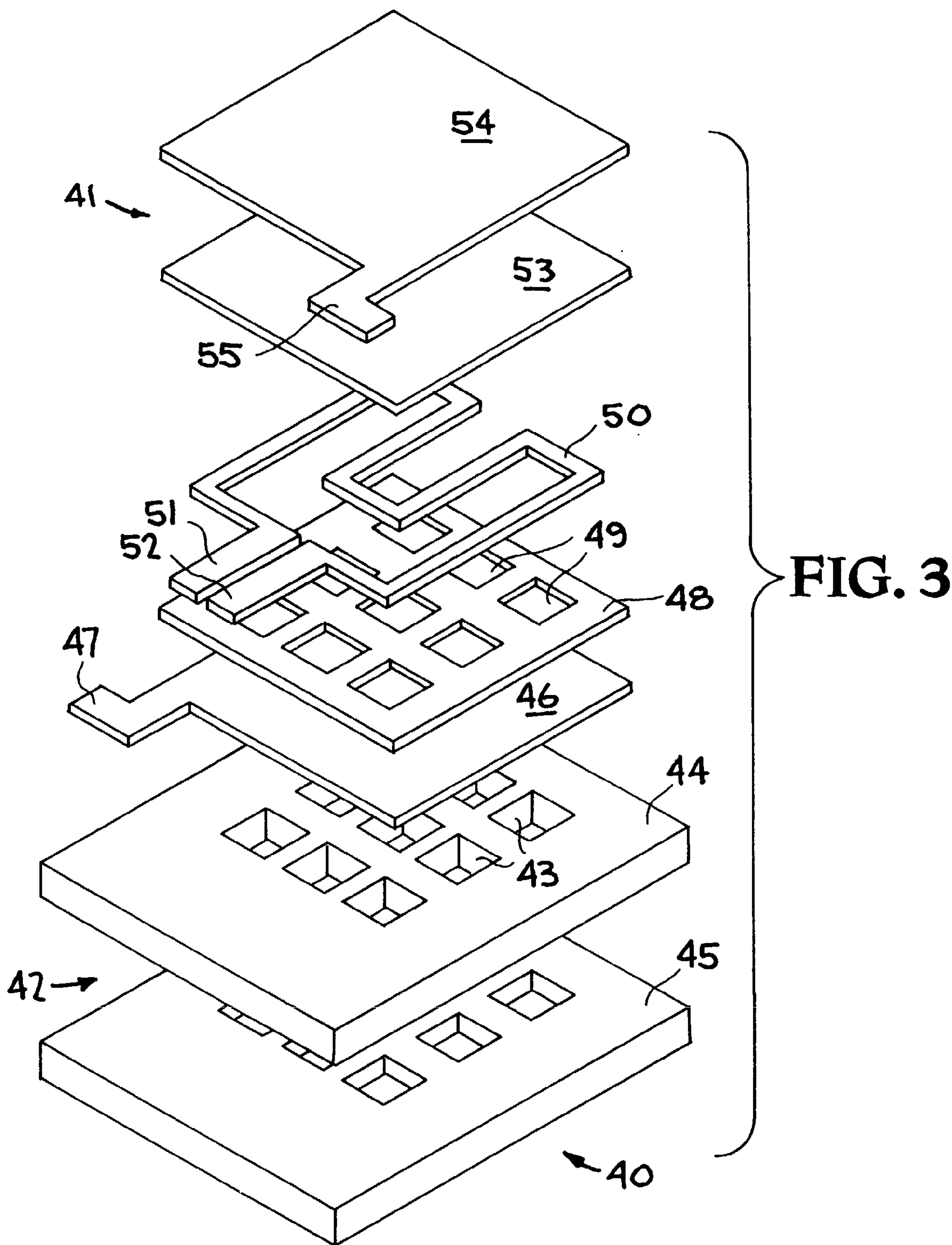
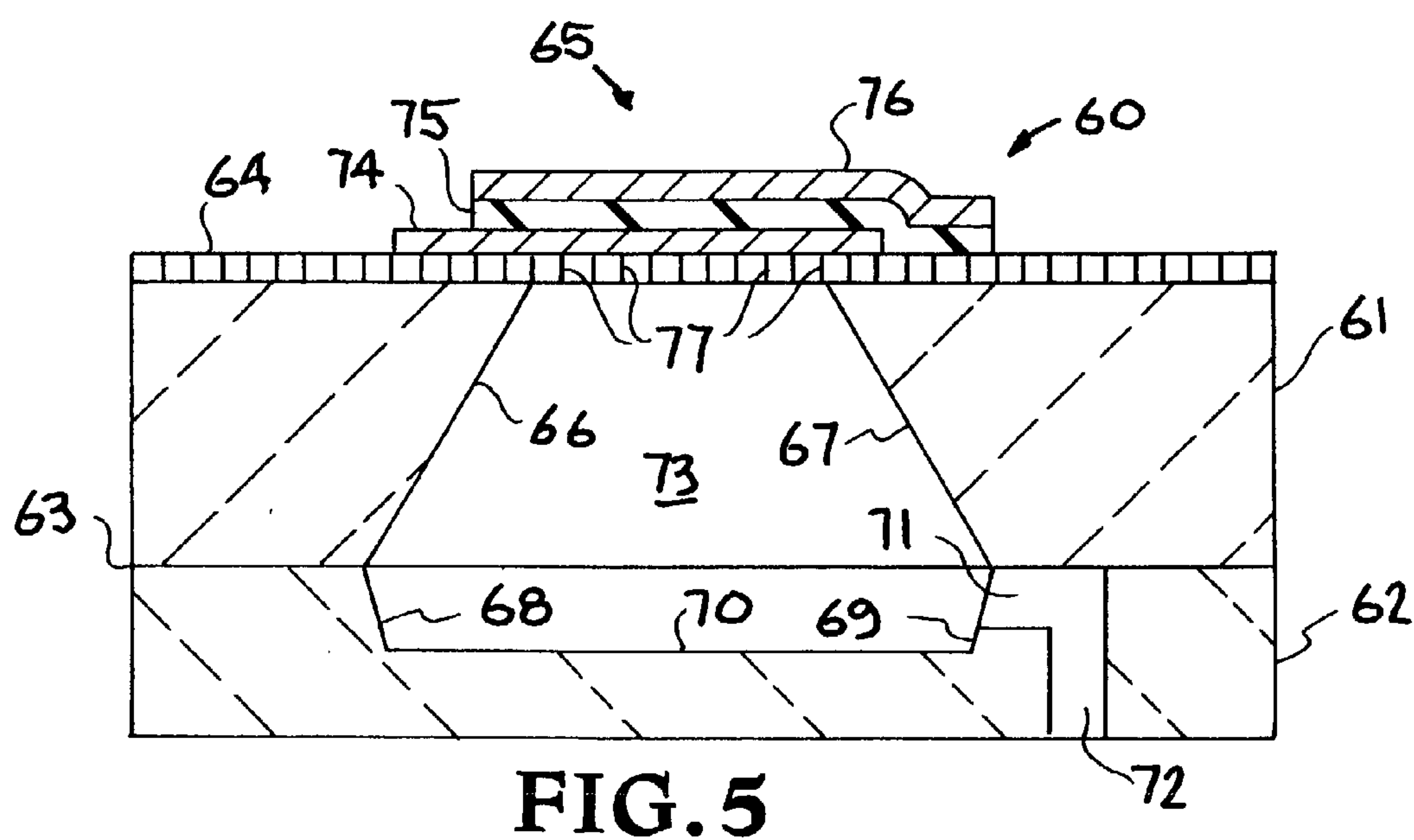
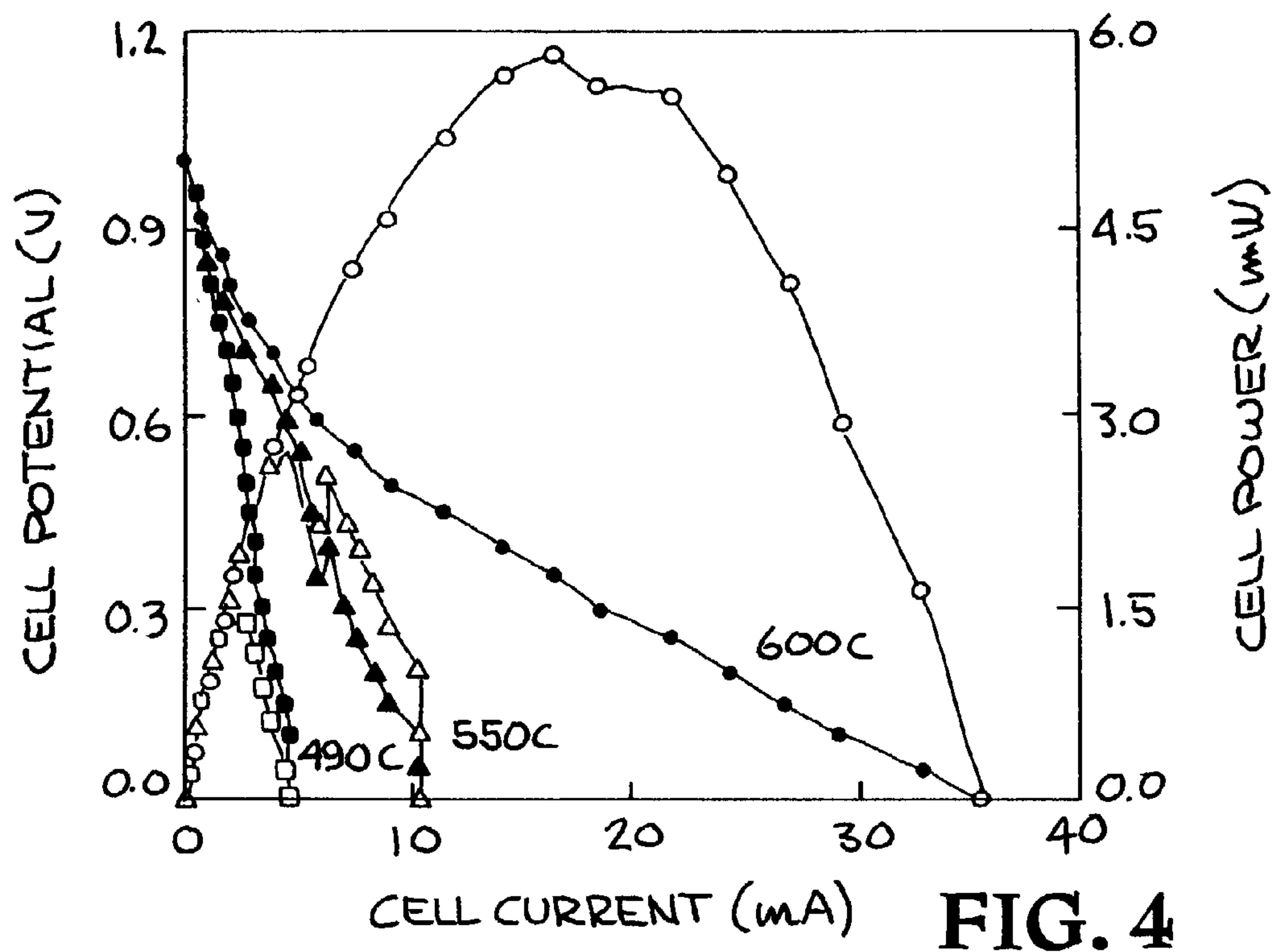


FIG. 2





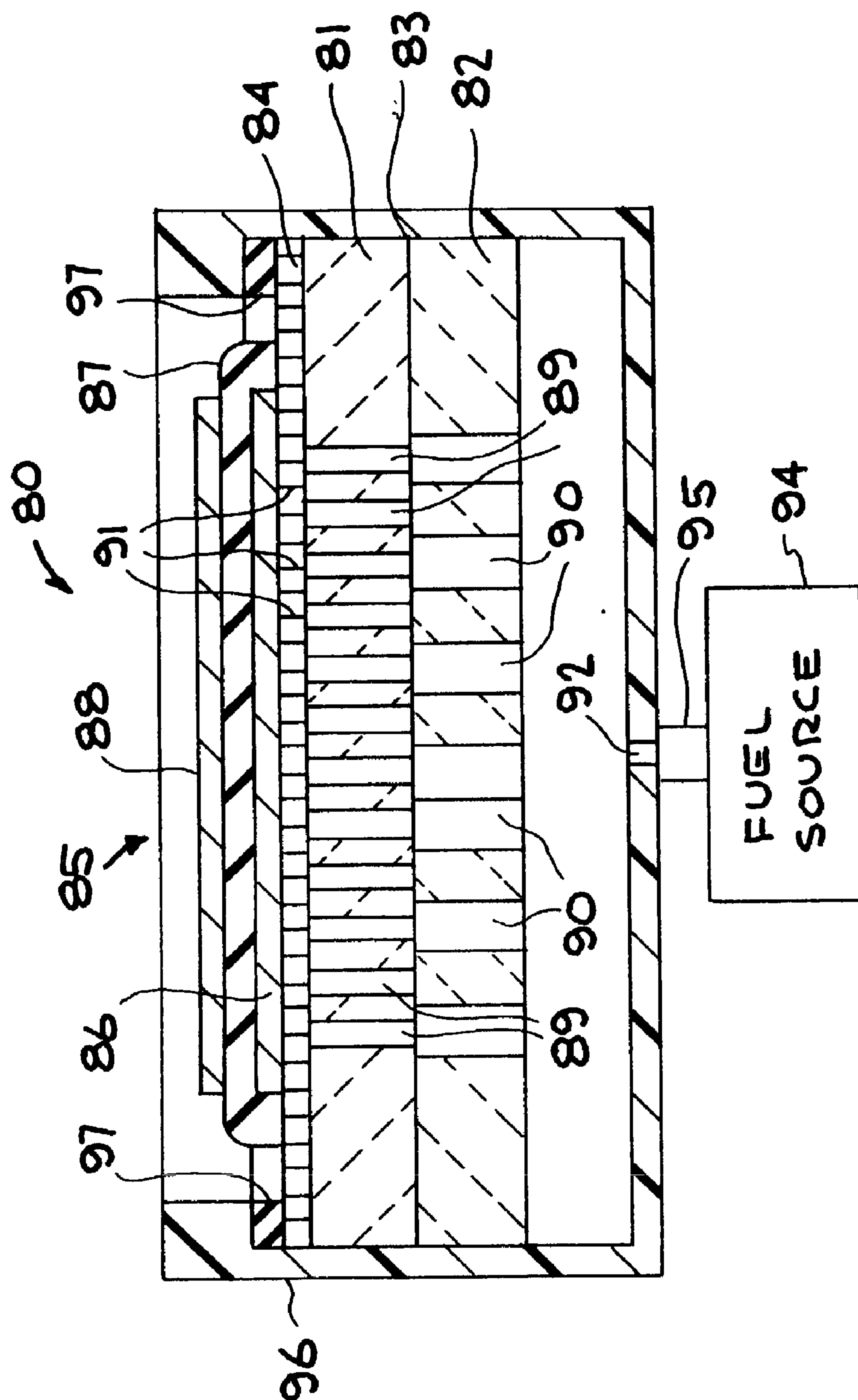


FIG. 6

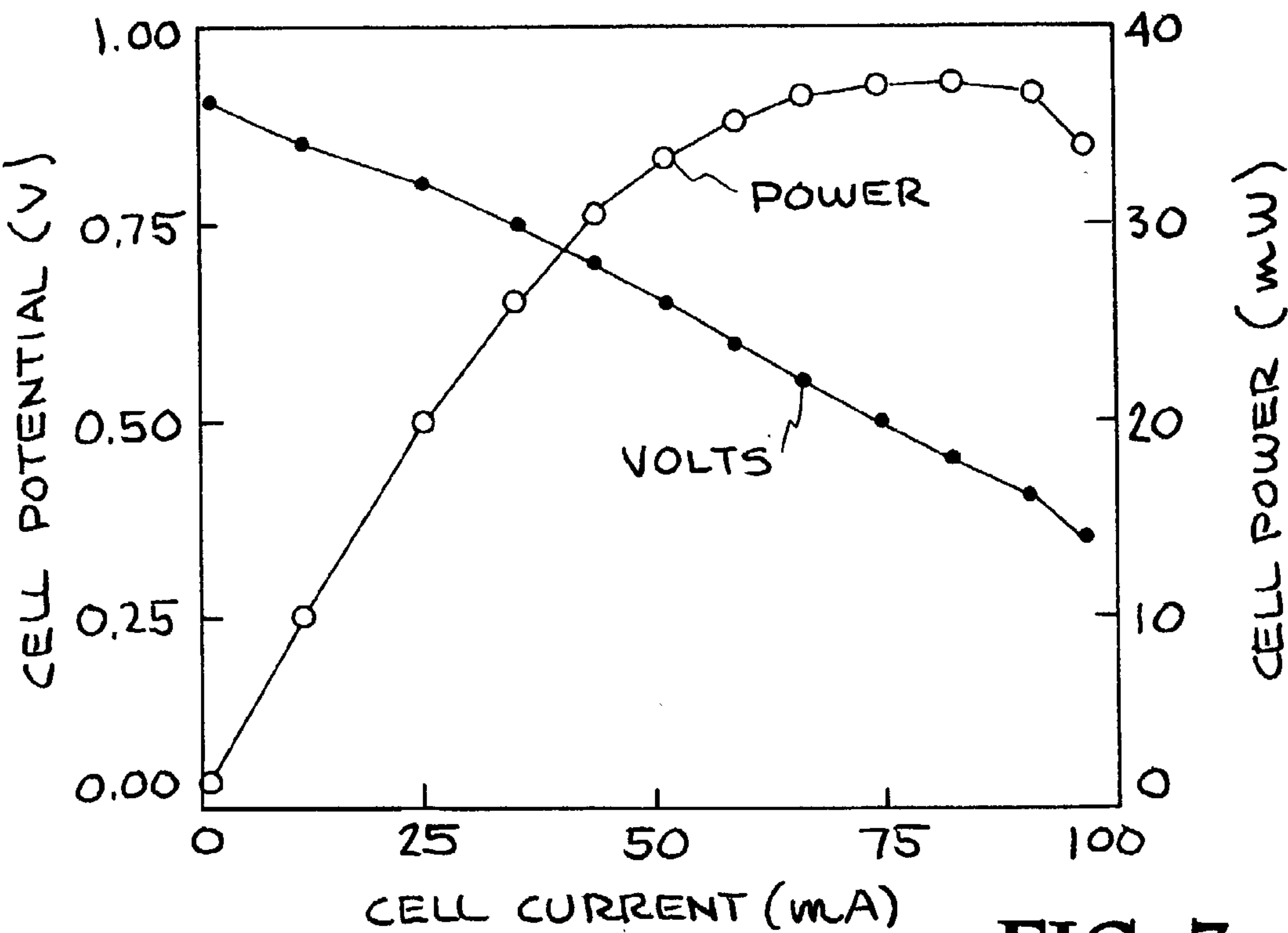


FIG. 7

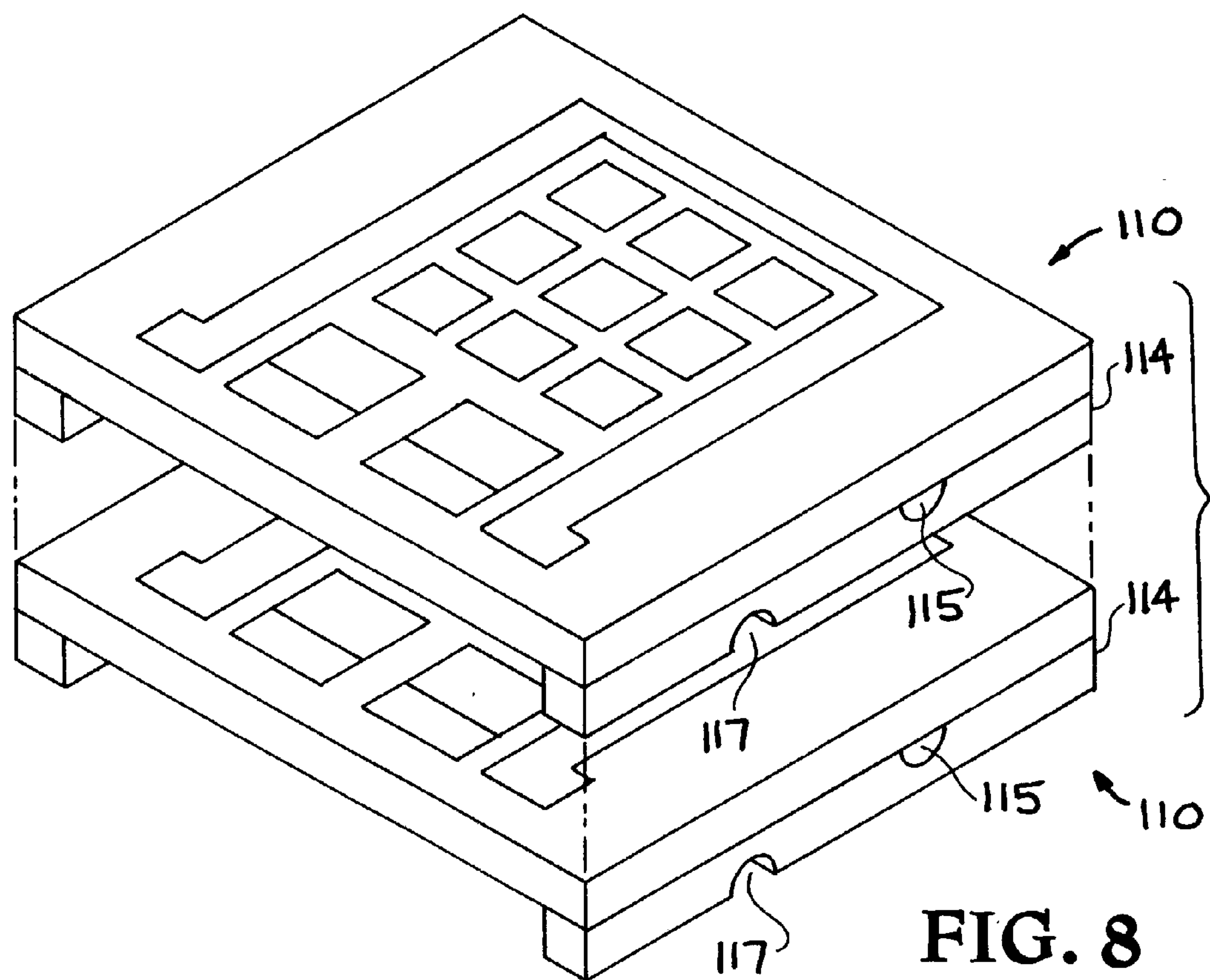


FIG. 8

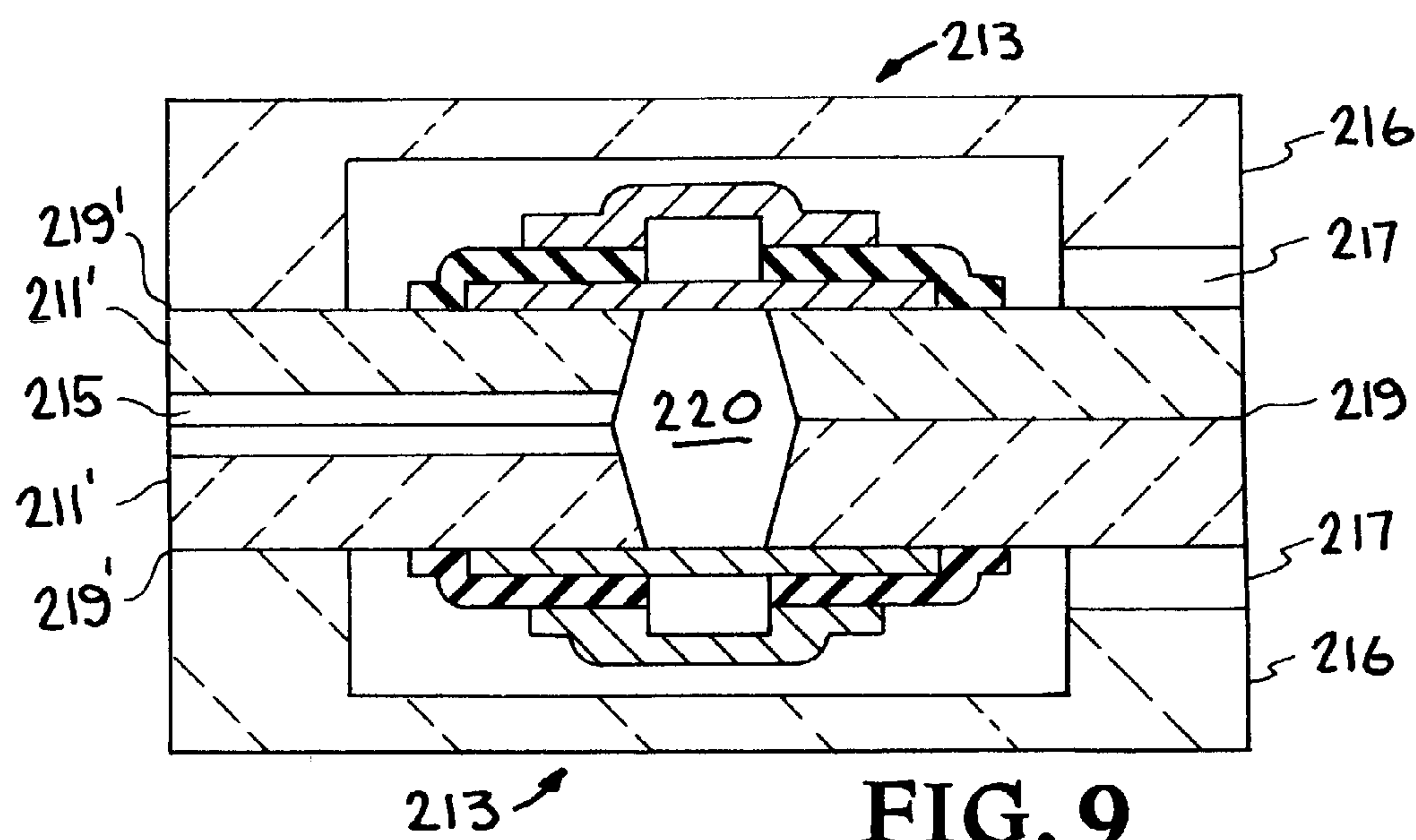


FIG. 9

MEMS-BASED THIN-FILM FUEL CELLS

RELATED APPLICATION

[0001] This application is a Continuation-In-Part of U.S. application Ser. No. 09/241,159 filed Feb. 1, 1999, and claims priority thereto.

[0002] The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to fuel cells, particularly to small, compact fuel cells, and more particularly to a miniature power source composed of a stack of fuel cells fabricated by combining MEMS and thin film deposition technologies to produce fuel cells with microflow channels, fully-integrated control circuitry, and integrated resistive heaters.

[0004] Portable power sources of various types have been under development for many years. A serious need exists for portable power sources with significantly higher power density, longer operating lifetime, and lower cost. Present rechargeable and primary portable power sources have excessive weight, size, and cost with limited mission duration. As an example, batteries covering power range from 1-200 Watts have specific energies ranging from 50-250 Whr/Kg, which represents two to three hours of operation for a variety of commercial and military applications. An alternative power source is the fuel cell which would potentially provide higher performance power sources for portable power applications if the stack structure, packaging, and cell operation were made compatible with scaling down of size and weight.

[0005] Fuel cells typically consist of electrolyte materials based on either polymer (proton exchange type) or solid oxide materials, which are sandwiched between electrodes. The fuel cell operates when fuel (usually hydrogen) is delivered to one electrode, and oxygen to the other. By heating the electrode-electrolyte structure, the fuel and oxidant diffuse to the electrode-electrolyte interfaces where an electrochemical reaction occurs, thereby releasing free electrons and ions which conduct across the electrolyte. Typical fuel cells are made from bulk electrode-electrolyte materials which are stacked and manifolded using stainless steel or other packaging which is difficult to miniaturize. These systems are bulky, requiring labor intensive manual assembly, packaging and testing, and in the case of solid oxide materials, typically operate at high temperatures ($>600^{\circ}\text{C}$). If the electrode-electrolyte stack can be made very thin and deposited using thin film deposition techniques, the temperature of operation will be significantly lower, and the cost of integration, packaging and manufacturing can be reduced.

[0006] Previous efforts at Lawrence Livermore National Laboratory, for example, have demonstrated the synthesis of a thin-film solid-oxide based electrolyte fuel cell. See A. F. Jankowski et al., Mat Res. Soc. Symp. Proc., Vol. 496, pp 155-158, 1998 Material Research Society; and U.S. Pat. No. 5,753,385, issued May 19, 1998 to A. F. Jankowski. In one example, the thin film solid oxide fuel cell (TF-SOFC) stack

was formed using physical vapor deposition (PVD) techniques. The host substrate used was a silicon wafer covered by a thin layer of silicon nitride. A layer of nickel was first deposited, followed by a layer of yttria-stabilized zirconia (YSZ). The conditions during the deposition were adjusted in order to achieve smooth, dense, continuous films, thus, avoiding pinhole formation which could result in direct mixing of the fuel and oxidant as well as electrical shorting through the electrolyte layer. This enables the electrolyte layer to be on the order of about $0.5\text{-}10\text{ }\mu\text{m}$ thick rather than typical thicknesses on the order of $>10\text{ }\mu\text{m}$ for bulk solid oxide fuel cells. For solid polymer and proton exchange membrane electrolytes, the thickness may be in the range of $0.5\text{-}50\text{ }\mu\text{m}$. By thinning the electrolyte layer, the diffusive path for the oxygen ion is shorter and the solid oxide fuel cell operates at much lower temperatures. A silver electrode layer is deposited on top of the YSZ layer. The deposition conditions of this film are adjusted to create a porous structure so that oxygen can readily diffuse to the electrolyte interface.

[0007] The present invention combines an example of thin-film deposition technology, referenced above, with micro-electro-mechanical systems (MEMS) technology to produce a thin-film miniature fuel cell with microflow channels and full-integrated control circuitry, along with integrated resistive heaters for effectively heating the fuel cell such that it will yield an order of magnitude greater power density than any currently known bulk fuel cell. Using this combined technology, thin-film fuel cell stacks can be produced to provide a small, compact miniature power source. The miniature fuel cells of this invention may be either oxygen-ion based, solid oxide or proton exchange membrane (e.g., solid polymer) electrolyte materials, and may also utilize catalyst layers between the electrodes and the electrolyte. The solid oxide electrolyte may have a thickness of $0.5\text{-}7.5\text{ }\mu\text{m}$ and operate at temperatures above and below 600°C .

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a small, compact fuel cell power source.

[0009] A further object of the invention is to provide thin-film fuel cells for electrical power applications.

[0010] A further object of the invention is to provide MEMS-based thin-film fuel cells.

[0011] Another object of the invention is to provide an MEMS-based thin-film fuel cells having microflow channels and integrated resistive heaters and control circuitry.

[0012] Another object of the invention is to provide a MEMS-based thin-film fuel cell stack, manifold structure, and fuel reservoir as a miniature portable power source.

[0013] Another object of the invention is to provide a MEMS-based thin-film fuel cell capable of utilizing an electrolyte of either a solid oxide, a solid polymer, or a proton exchange membrane material.

[0014] Another object of the invention is to provide thin-film fuel cell stack with microflow channels, full-integrated control circuitry, and integrated resistive heaters capable of producing a high power density.

[0015] Another object of the invention is to provide a MEMS-based fuel cell which includes electrode catalyst/electrolyte materials which enable the combination of a fuel and oxidant above room temperature to produce continuous electric current.

[0016] Another object of the invention is to provide a MEMS-based fuel cell having in the form of a module which can be directly stacked as a means of scaling the power and voltage.

[0017] Another object of the invention is to provide a MEMS-based fuel cell utilizing an electrolyte composed of solid oxide, solid polymer and proton exchange membrane material, and wherein the solid oxide electrolyte can operate below or above 600° C.

[0018] Other objects and advantages of the present invention will become apparent from the following description and accompanying drawings. Basically the invention involves combining MEMS technology and thin-film deposition technology to produce a miniature thin-film fuel cell or fuel cell stack as a portable power source. The MEMS-based fuel cell of this invention may utilize an electrolyte layer which may consist of either a solid oxide or a proton exchange membrane material, and may utilize catalyst layers between the electrodes and the electrolyte. The fuel cell includes microflow channels and manifolding micromachined into the host structure/substrate, and may contain a rechargeable microbattery for startup control, and utilize integrated resistive heaters for efficient heating of the stack materials, and may utilize integrated microvalves, resistive heaters, or other means to control the flow of fuel to the fuel cell stack. Furthermore, the fuel cell may exploit the various fuel cell electrode/electrolyte/catalyst materials systems as they are developed such that either direct hydrogen fuel is used, or other gaseous or liquid hydrocarbon fuels, including methanol or propanol, can be used. Additionally, other structures or materials may be readily integrated with a MEMS-based fuel cell which enable reforming of fuel such that a variety of fuels having high percentage concentrations of hydrogen may be used. The MEMS-based fuel cell may incorporate a fuel reservoir as part of a package approach, or as a modular cartridge which can be easily replaced or refilled. Such a fuel reservoir may simply be a volume containing a liquid if liquid fuels are used, or a volume containing a metal hydride or other material which is capable of storing hydrogen within it. In this case, some form of valve may be placed in the micro-flow channels as a means of controlling the flow of fuel to the stack. Additionally, heating elements may be used to control the flow of hydrogen from the reservoir. The MEMS-based fuel cell modules may be directly stacked on top of each other as a means of scaling voltage and power, or connect fuel cell modules in series on a planar level to do the same. Power transforming circuitry may be utilized to provide the appropriate output voltage and power requirements.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The accompanying drawings, which are incorporated into and form a part of the disclosure, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

[0020] FIG. 1 is a cross-sectioned view of an embodiment of a miniature MEMS-based thin-film fuel cell of the invention.

[0021] FIG. 2 is an enlarged cross-section of an upper section of the FIG. 1 embodiment.

[0022] FIG. 3 is an exploded view of another embodiment of the miniature thin-film fuel cell of the invention.

[0023] FIG. 4 graphically illustrates results of initial testing of the miniature fuel cell.

[0024] FIG. 5 is a cross-sectional view of another embodiment of the thin-film fuel cell made in accordance with the present invention.

[0025] FIG. 6 is a cross-sectional view of another embodiment of the fuel cell using a multiple channel fuel manifold arrangement.

[0026] FIG. 7 graphically illustrates cell potential and cell power relative to cell current.

[0027] FIG. 8 is a view which illustrates the approach for stacking the MEMS-based fuel cell modules for power and voltage scaling.

[0028] FIG. 9 is a cross-sectional view of another embodiment of the fuel cell enabling the cells to be inverted and bonded in order to deliver fuel to two cells from one common inlet.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The present invention is a MEMS-based thin-film fuel cell or stack of fuel cells of either a solid oxide fuel cell (SOFC) (operating at temperatures above and below 600° C.), a solid polymer fuel cell (SPFC) or a proton exchange membrane fuel cell (PEMFC), (each operating at temperature below 600° C.) utilizing electrode/catalyst/electrolyte or electrode/electrolyte materials which enable the combination of a fuel and oxidant at elevated temperatures to produce continuous electric current. Fuel manifolds and microflow channels are formed in the host structure/substrate by MEMS-based technology and the electrode/electrolyte/electrode, with or without catalyst layers are formed along with resistive heaters and integrated control circuitry by thin-film deposition technology and microfabrication approaches in combination with MEMS fabrication techniques. Thus, the invention provides a miniature power source composed of fuel cells which can yield zero emissions (when operated on hydrogen and air). The electrical current generated from each cell is drawn away with an interconnect and support structure integrated with the gas manifold. In the present invention, the strengths of microelectronics, fabrication, micromachining approaches, and microelectro-mechanical systems technology are combined with thin-film deposition techniques for the purpose of producing a MEMS-based, thin-film miniature fuel cell. The MEMS-based fuel cell is materials flexible, therefore can utilize either solid oxide, solid polymer or proton exchange membrane electrolyte materials system.

[0030] A fuel cell stack has been fabricated which utilizes thin film electrodes, catalysts, and ion conducting layers deposited by physical vapor deposition techniques. The stack has been patterned with electrical connections using standard microfabrication techniques and subsequently formed into free-standing or supported membranes by micromachining away the silicon substrate. Manifold structures have further been fabricated through silicon micromachining techniques.

[0031] Stand-alone, single thin-film solid oxide fuel cells (TFSOFCs) have been synthesized through multilayer and thin film vacuum deposition technology, see A. F. Jankowski et al., referenced above. The present invention provides the ability to design and build a single MEMS-based fuel cell module suitable for assembly into a fuel cell stack. Development of a usable substrate platform for cell stacking is seen in microelectronic processing of, for example, silicon wafers. The Si wafers are patterned using photolithography and etch processing to yield select areas of thin nitride windows that served as the substrate for deposition of the anode-electrolyte-cathode trilayer. Additional approaches can utilize a host structure/substrate having controlled porosity on which the fuel cell electrode/catalyst/electrolyte layers are deposited. This host structure having controlled porosity is then bonded on top of, mechanically sealed to, or formed within the silicon (or other material) substrate through which the flow channels have been etched. A solid oxide fuel cell (SOFC) trilayer example, similar to that shown in **FIGS. 1 and 2**, has been fabricated based on yttria-stabilized zirconia (YSZ) beginning with deposition of a nickel (Ni) layer and concluding with a silver (Ag) layer. Following deposition of the basic trilayer structure, the nitride window, if present, can be removed by plasma etching or other selective etching techniques. Creation of a multiple cell stack may be pursued, for example, using the Ni—YSZ—Ag trilayers or other solid oxide based trilayers. In this invention the Si-based substrates are used to build the individual TFSOFCs, for example, and use this platform to provide integration of the circuitry, resistive heaters, and required fuel and oxidant manifolding through microflow channel and MEMS fabrication technology. The patterned circuitry provides for controlled power output from each cell as well as a controlled heating of individual fuel cell elements. The MEMS processes allows individual control of gas flow to each cell through use of microvalves as well as control and regulate gas pressure or fuel flow throughout the device. Provision capabilities exist for incorporation of materials for the electrode, catalyst and electrolyte interface that optimize performance at lower temperature by reducing resistive losses along with alternative materials that are suitable for high-temperature internal fuel reforming. The substrate platform enables modular cell assembly providing a capability for servicing and cell upgrade, as well as scaling of voltage.

[0032] Referring now to the embodiment of **FIGS. 1 and 2**, **FIG. 1** illustrates a fuel cell generally indicated at **10** a host structure or substrate **11** having a nitride layer or other porous membrane **12** on which is deposited electrode-electrolyte-electrode layers (with or without catalyst layers) **13**, a substrate **14** having a fuel inlet **15**, and a substrate **16** having an oxidant (oxygen) inlet **17**. Additionally, if the fuel inlet **15** in substrate **14** and the oxidant inlet **17** in substrate **16** enter from the sides, then the fuel cell modules **10** can be directly stacked on top of each other with fuel and oxidant being supplied through the respective inlets for each module from a common reservoir. In this stacking embodiment, the electrodes for each module are connected in series so as to add the voltage produced by each individual module. The substrates **14** and **16** are bonded or mechanically sealed to host structure **11** as indicated at **18** and **19**. As pointed out above, if a nitride layer is used, the central area of the nitride layer **12** is removed following deposition of the electrode-electrolyte-electrode layers **13**. The host structure or sub-

strate **11** is provided with a plurality of openings, channels, pores or windows having tapered or straight sides **20** and **21** which approximately align with tapered or straight sides **22** of a cutaway section **23** of substrate **14** which includes a section **24** which communicates with fuel inlet **15**. The electrode-electrolyte-electrode layers **13**, as seen in **FIG. 2**, is composed of an electrode (anode or cathode depending on type of electrolyte) **25**, an electrolyte layer **26** and an electrode (anode or cathode depending on type of electrolyte) **27**, with the bottom electrode providing a continuous coverage of the plurality of open channels, or pores **20** and the electrolyte **26** providing a continuous electrically insulating barrier between the electrodes **25** and **27**. The top electrode **27** may step down over the edge of the bottom electrode **25** in order to draw the electrical current off of the substrate **11** to an external circuit. The electrode-electrolyte-electrode layers **13** may be composed of a Ni anode, a YSZ electrolyte and a Ag cathode, or other materials which are typical of the solid oxide and solid polymer or proton exchange membrane, fuel cell construction, such as Carbon bottom electrode, Pt catalyst, Nafion electrolyte, and Pt catalyst/electrode. The substrate **16** is provided with a cutaway section **28** which is in communication with oxidant inlet **17**. Thus the opening **20** in substrate **11** and the cutaway section **23** of substrate **14** form a fuel channel **29** in contact with electrode **25**, while the cutaway section **28** of substrate **16** forms an oxidant (oxygen) channel **30** in contact with electrode **27**. As described above, if the fuel inlet **15** and oxidant inlet **17** enter from the sides of the fuel cell module **10**, or in a manner which does not block the inlets, the individual cells **10** can be directly stacked on one another. Furthermore, if the location of the fuel and oxidant inlet channels are offset such that they are easily accessible then fuel can be delivered to the plurality of inlets from a common fuel or oxidant reservoir. Not illustrated in the **FIGS. 1-2** embodiment is a heater for the electrolyte layer **26**, but, for example, a resistive heater as shown in **FIG. 3** may be incorporated into the trilayer **13**. The substrates **11**, **14** and **16** may be composed of silicon, glass, ceramic, plastic, or any material which has sufficient mechanical strength, can withstand the temperature of operation, and can be micromachined or cast to form manifold channels to deliver fuel and oxidant from an external reservoir. The micromachining methods include those known in the general art and include etching, laser drilling, diamond turning, injection molding, and hot embossing.

[0033] As has been shown in **FIG. 1**, the incorporation of manifold structure within the host substrate through micromachining techniques enables a complete fuel cell device to be realized which can be readily attached to fuel and oxidant sources. **FIG. 3** illustrates an exploded view a complete fuel cell stack including the resistive heater, not shown in the **FIGS. 1-2** embodiment. In the approach of **FIG. 3**, the fuel cell generally indicated at **40**, includes a membrane-electrode assembly created by thin-film deposition techniques, or a combination of laminate, thin film and thick film assembly techniques and generally indicated at **41**, and a micromachined substrate-manifold assembly or system generally indicated at **42**. Integrated circuit type microfabrication processes are used to pattern the electrode contacts, as well as to form a resistive heater element within the fuel cell stack structure. The components of the membrane-electrode assembly **41** is subsequently formed into a free standing membrane by selective etching of openings or windows **43**

in a substrate **44** on which the components are deposited as in the **FIG. 2** embodiment, the substrate **44** being an upper component of the manifold assembly **42**. In an alternative embodiment, the components of the membrane-electrode assembly **41** is subsequently formed on a porous thick film membrane or host structure which is positioned over the openings or windows **43** in a substrate **44** on which the components are formed, the substrate **44** being an upper component of the manifold assembly **42**. Manifold channels are micromachined in another substrate **45**, the lower components of the manifold assembly **42**, which is subsequently bonded to the substrate **44**. The membrane electrode assembly **41** includes an electrode (anode) **46** having a contact pad **47**, a heater isolation member **48** having openings or window **49** which align with openings or windows **43** of substrate **44**, a resistive heater **50** having contact pads **51** and **52** and constructed so as not to cover the openings **49** in member **48**, an electrolyte **53**, and an electrode (cathode) **54** having a contact pad **55**. For example, the electrode/electrolyte/electrode (components **46**, **53** and **54**) may be composed of nickel (Ni)-yttria stabilized zirconia (YSZ)-silver (Ag), the resistive heater **50** composed of platinum, and the heater isolation member **48** composed of silicon dioxide or other material which provides electrical isolation from the electrodes with openings **49** being 2 mm×2 mm, and with the substrates **44** and **45** composed preferably of silicon but may be composed of glass, ceramic, plastic, or other material having the qualities described above, with windows **43** being 2 mm×2 mm.

[0034] This approach provides an effective means to efficiently form fuel cell stacks and electrode structures monolithically, and distribute fuel to the entire stack without the need for bulky complex manifolding. Furthermore, since the stack is now only a small percentage of the mass of the entire structure, appropriate thermal design of the fuel cell device, package, and resistive heating elements will allow efficient, low power heating of the stacks.

[0035] A completely fabricated fuel cell module with an integrated heating element, with the fuel cell stack free standing membranes has been tested. The silicon substrate was selectively etched with potassium hydroxide using patterned silicon nitride as the mask to form the window therein. Manifold channels were etched in a silicon substrate utilizing similar techniques. These components were ultimately bonded together, such as illustrated in **FIG. 1**, to form a fuel cell module having inlet and outlet channels with approximately 50 μ m by 200 μ m openings for fuel delivery.

[0036] Initial testing of fuel cell structures consisted of a manifolded tube that can be sealed to the backside of the fuel cell stack to deliver hydrogen gas diluted to 4% or less concentration. The oxidant source was a 20% oxygen gas air mixture delivered to the top side of the structure. Contact wires were attached to the anode and cathode electrode pads, from a parameter analyzer that was utilized to monitor the potential voltage drop across the stack and subsequent current output as a function of temperature. Initial results of this testing are illustrated in **FIG. 4**. While not yet optimal, these results exhibit the expected overpotential for this electrolyte materials system with no output current, along with increasing current output as temperature increases.

[0037] Alternate solid oxide electrolyte materials and proton exchange membrane materials are being tested with

improvements as described in greater detail with respect to **FIGS. 5 and 6**. As an example, test results for a PEMFC are shown.

[0038] **FIGS. 5 and 6** illustrate embodiments of a non-stacked MEMS-based miniature fuel cells, described as being either a solid oxide fuel cell (SOFC), a solid polymer fuel cell (SPFC) or a proton exchange membrane fuel cell (PEMFC), and where air is the oxidant thereby eliminating the oxygen channel and upper substrate **16** of the **FIG. 1** embodiment unless stacking of cells is utilized, in which case the embodiment of **FIG. 1** including the upper substrate **16** have pores or channel inlets formed to allow the flow of air to the top electrode would be required. The MEMS-based miniature fuel cell of **FIG. 5** utilizes electrode/catalyst/electrolyte materials which enable the combination of a fuel and oxidant at elevated temperatures to produce continuous electric current. As pointed out above, the basis of each fuel cell is an anode and cathode separated by an electrolyte layer which can consist, in these embodiments, of either a solid oxide or a solid polymer material, or proton exchange membrane electrolyte materials. Additional layers of catalyst materials can also separate the electrode (cathode or anode) from the electrolyte. In these embodiments micro-machined manifolds can be utilized to transport the fuel and oxidant, to each cell and a provide a path for exhaust gases. The electrical current generated from each cell is drawn away with an interconnect and support structure integrated with the gas manifold.

[0039] The MEMS-based fuel cell of **FIG. 5** consists of three main features. The first two are the substrate host structure on which the fuel cell stack (electrode/electrolyte/electrode) is formed, and in which the manifold structures are formed to deliver the fuel and oxidant to the stack. The substrate can be made of silicon, glass, ceramic, plastic, or any material having the above-described qualities. By utilizing micromachining techniques, the substrate host structure and manifolding for the fuel cell can be made light weight. Furthermore, the manifold structures can be manufactured in a variety of methods using MEMS techniques, including micromachining, injection molding, laser drilling, hot embossing, or diamond machining. As illustrated in **FIG. 5**, the substrate host structure has two parts, one being a substrate host structure **61** with a plurality of channels or pores through it **73** which transport the gas fuel to the fuel cell stack **65**. As described previously, the substrate host structure **61** can be a micromachined substrate formed using the aforementioned techniques, or it can be a porous substrate with pores suitable to allow gas to pass through, as well as complete which can have the fuel cell stack materials deposited on the top side. The second part is a manifold substrate **62** with channels formed in it to transport fuel from one common reservoir, distributing the fuel over the entire area of the channels or pores **73** which deliver fuel to the stack layers. These two parts can be fabricated separately using the techniques cited above, then bonded or mechanically sealed together to form the structure of **FIG. 5**. A variety of bonding techniques, as used in the art are available, including use of adhesive films or eutectics, or mechanical sealing and packaging techniques so long as they are robust enough through the temperature range of operation, which is in the 50-500° C. range, for example, depending on the electrolyte material used.

[0040] Referring now to **FIG. 5**, the fuel cell stack generally indicated at **60** comprises a micromachined host structure or substrate **61**, a micromachined substrate **62** bonded to substrate **61** at **63**, a porous thick-film **64** located on the top surface of substrate **61**, and an electrode/electrolyte/electrode assembly or fuel cell stack **65** deposited on the porous thick film or member **64**. The substrate **61** has a single or plurality of openings, pores or windows defined by tapered or straight surfaces **66** and **67** which approximately align with tapered or straight surfaces **68** and **69** of a cutaway section **70** in substrate **62** which is connected by a cutaway **71** to a fuel inlet **72**, with the single or plurality of openings, pores or windows formed by tapered or straight surfaces **66** and **67** and cutaway section **70** forming a micromachined manifold or pore **73**. The electrode/electrolyte/electrode assembly or fuel cell stack **65** consists of a thin-film electrode **74**, a thin or thick film electrolyte/catalyst **75**, and a thin-film electrode **76**. The porous film **64** includes numerous pores **77**. While not shown the fuel cell stack **65** would include a resistive heater as in **FIG. 3** integrated within the porous thick film **64** or fuel cell stack **65**.

[0041] By way of example, the substrates **61** and **62** are composed of silicon; the porous thick-film **64** is composed of alumina, plastic or porous silicon with a thickness of 10 microns to 200 microns and with pores **77** having a diameter of 200 Å to 5 microns and the film **64** having mechanical strength to support the fuel cell stack **65**; the electrode **74** being composed of copper, nickel, carbon, palladium, or platinum with a thickness of 1000 Å to 2 microns; and the electrolyte/catalyst **75** being composed Ni/YSZ, Pt/Nafion, or Pt/C/Nafion with a thickness of 1 micron to 50 microns and the electrode **76** being composed of oxygen catalyzing conducting material, such as Ag, Pt, lanthanum strontium manganate (LSM), or carbon with a thickness of 1000 Å to 2 microns. The micromachined pore or manifold **73** may have a cross-sectional area of 10 μm by 10 μm to 10 mm by 10 mm, with the fuel inlet **72** having a diameter of 25 μm to 1 mm. While the above description specifies examples of fuel cell stack materials known to those familiar with the art, additional combinations can readily be substituted as dictated by performance and compatibility with a MEMS fabrication approach.

[0042] The host substrate or structure on which the fuel cell stack is formed has the requirement of having many channels or pores which will enable the fuel, whether it be in gas or liquid form, to transport to the electrode structure. This host structure can be created by selective etching of channels in a silicon substrate, for example, which would result in a free standing fuel cell membrane. This host structure could also be created by etching or molding of the channel features in a variety of other materials as described previously, and can be ceramic, glass, or plastic. This host structure could also be made from a thick film porous material which is bonded on top of the manifold substrate or the channel host structure, as illustrated in **FIG. 6**. The requirements of the thick film porous structure are that it have enough mechanical strength that it will support the fuel cell stack that can be created on it when positioned over manifold channels or pores of suitable size (0.1-10 mm diameter). Additionally, the pore size must be large enough to provide flow of fuel from the bottom manifolds to the fuel cell stack, but the pores must be small enough that the thin-films which are deposited on top to form the electrode

will not deposit down into the pores too deep, so as to completely seal the pores. This issue is less important if a fuel cell membrane electrode assembly in laminate form were bonded, attached or mechanically sealed over the host structure rather than deposited directly onto it. Several materials exist in sheet form which already have the desired porosity characteristics. These include glass, plastics, ceramics, or anodized alumina. In the case of the anodized alumina, sheets can be formed which are approximately 50 μm thick which have pore sizes on the order of 0.2 μm, with a small fraction of the structure having pores which are only 0.2 μm diameter. This would allow thin-film deposition on the top side without depositing down into and sealing into the pores, and can be accomplished using a variety of deposition techniques, including sol-gel, or spin cast approaches. Similar structures can be achieved using two porous ceramic materials, or two porous plastic thick films, each having different pore sizes. Again, these materials are readily available from commercial suppliers, or fabricated using techniques reported in the open literature.

[0043] As shown in **FIG. 6**, the fuel cell assembly or device, generally indicated at **80** basically comprises a substrate/host structure **81**, a manifold substrate **82** bonded to substrate **81** at **83**, a porous thick-film layer **84** located on or within substrate **81**, and a thin-film fuel cell stack generally indicated at **85** located on layer **84**. The fuel cell stack **85** includes an electrode **86**, an electrolyte **87**, an electrode **88**, and a heater element, not shown, but which may be constructed as in the **FIG. 3** embodiment. Alternatively, the heater element may be formed on top of the substrate/host structure **81** or within the porous thick film layer **84**, so long as it is electrically isolated from the electrodes **86** or **88**. The substrate/host structure **81** includes a number of vertical channels or pores **89** which are in open communication with manifold channels **90** in substrate **82**. The porous thick-film layer **84** includes numerous pores **91** which are in open communication with channels **89** of substrate **81**. If the porous thick film layer **84** is mechanically strong enough and allows sufficient flow of fuel through to the fuel cell stack **80**, it can be directly bonded or mechanically sealed to the manifold substrate **82** with pores **91** in open communication with manifold channels **90**. The substrate **82** includes an opening or passageway forming a fuel inlet not shown in the **FIG. 6**, but similar to the fuel inlet **72** of **FIG. 5**, in open communication with the plurality of manifold channels **90**, which is adapted to be connected to a fuel source **94** via connector **95**. Note that the substrate/host structure **81** is etched such that the porous thick film **84** aligns with the pores **89** of the host structure **81** enabling fuel to flow to the fuel cell stack **80** and preventing fuel from flow elsewhere. Additionally shown in **FIG. 6** is a package **96** and seals **97** which enable the manifold substrate **82**, host structure/substrate **81** and porous thick film layer **84** supporting fuel cell stack **80** to be assembled and mechanically sealed. If the substrate **82** is positioned such that the pores **90** are in open communication with the bottom portion of the package **96**, the package **96** may include an opening or passageway forming a fuel inlet **92** which is adapted to be connected to a fuel source **94** via connector **95**.

[0044] The third main feature of the MEMS-based miniature fuel cell is the thin film fuel cell stack itself. The series of thin film materials, as illustrated in **FIG. 5**, for example, are an electrode, a catalyst, an electrolyte, a catalyst, and an electrode. Depending on the particular electrolyte the cata-

lyst layers may not be necessary. The thin film fuel cell stack can be formed by a variety of thin-film deposition techniques including sputter or evaporative techniques, sol-gel, spin cast, dip coating approaches. The individual layer thicknesses may vary from 0.5-50 μm . The operating temperatures may be from room temperature to about 600° C. or higher for solid oxide electrolytes. The stack structure may also be formed using a sheet of the electrolyte material which is then sandwiched between the electrode/catalyst layers forming a membrane electrode assembly component or laminate and attached, bonded or mechanically sealed on a MEMS manifold host structures. The requirements of the electrodes are that they have low resistance, continuous conductivity, and are porous enough for the fuel and oxidant to diffuse through to the catalyst/electrolyte interface where the electrochemical reaction occurs, and allow the byproduct of the reaction to diffuse out of the electrode structure. Electrode materials can be made porous through the techniques, including rf-sputtering, electron beam deposition, or sol-gel processes. The electrodes can also be made porous using photolithographic techniques to etch pores into the metal film. Additionally, the porous electrodes could be created using a porous metallic sheet which could also be used as the porous manifold host structure. The catalyst and electrolyte layers are dense continuous films deposited by the techniques described previously. The electrolyte can be either solid oxide, solid polymer, or proton exchange type materials.

[0045] FIG. 7 graphically illustrates cell potential (V) and cell power (mW) relative to cell current (mA).

[0046] FIG. 8 illustrates an embodiment wherein individual cells can be directly stacked on one another. In FIG. 1, the fuel inlet 15 and the oxidant inlet 17 enter from the sides of the fuel cell module 10, or in a manner in which the inlets 15 and 17 remain in open communication with respective flow channels 29 and 30, the individual cells 10 can be directly stacked on one another, as shown in FIG. 8, with the cells indicated a 110, the fuel inlets indicated at 115, and the oxidant inlets indicated at 117. Further, if the location of the fuel and oxidant inlet channels of the cells are offset, as shown in FIG. 8, such that they are easily accessible then fuel can be delivered to the plurality of inlets from a common fuel or oxidant reservoir. Additionally, substrates 14 and 16 of FIG. 1 can be the same substrate, as indicated at 114 in FIG. 8, having appropriate inlets 115 and 117 for fuel and oxidant formed in top and bottom areas of the substrate 114 which have open communication to the appropriate flow channels in order to deliver the fuel to the required electrodes 25 and oxidant to the electrode 27, as seen in FIG. 1. In the case of the oxidant inlet 117, the oxidant or air flow is enabled by forming a channel or pore using micromachining techniques as previously described, or using a material having adequate porosity and mechanical strength which enable ambient flow of air to the electrode. In this stacking embodiment, the electrodes for each module are connected in series so as to add the voltage produced by each individual module. This stacking approach is relevant to all embodiments as described in FIGS. 2, 3, 5 and 6.

[0047] An additional embodiment for stacking of MEMS-based fuel cells is illustrated in FIG. 9. In this embodiment, the substrate/host structure 211' having fuel cell electrode/electrolyte stack 213 and single or plurality of openings, channels or pores 220 is now bonded or mechanically sealed

as indicated at 219 to a similar substrate/host structure 211 which is positioned upside down as illustrated in FIG. 9 such that a symmetrical structure is formed and a single fuel inlet 215 can now deliver fuel to double the effective fuel cell stack area. The fuel inlet 215 is formed using a cutaway section in communication with the flow channel openings, channels or pores 220. The flow channels and cutaway sections are formed using one or more of the various micromachining techniques as previously described. If additional stacking or packaging is required, another substrate structure 216, similar to the substrate 16 of FIG. 1, is positioned over each fuel cell electrode/electrolyte stack 213 and bonded or mechanically sealed as indicated at 219' to the substrate/host structure 211 and 211' similar to that shown in FIG. 1. This embodiment, as illustrated in FIG. 8, enables each of the fuel cell stacks to have a cavity and oxygen inlet structure 217 formed in said substrate 216 as shown using micromachining techniques. This additionally enables direct stacking of fuel cell modules as previously described and illustrated in FIG. 8.

[0048] An integrated resistive heating element can be utilized to efficiently heat the fuel cell stack without heating the entire host structure and package. The resistive heating element is attached to a rechargeable microbattery located within the package, and is used to turn-on the fuel cell by uniformly heating the fuel cell stack. Once the fuel cell is powered on, the resistive heater draws its power from the operating fuel cell. The resistive heater can be located within the fuel cell stack but will require electrical isolation. The heating element can also be located within the porous host structure and be designed such that the heat is conducted to the fuel cell stack structure, and insulated from the manifold substrate and exterior packaging.

[0049] It has thus been shown that the present invention advances the state of the fuel cell art by miniature MEMS-based thin-film fuel cells that will yield an order of magnitude greater power density than any fuel cell currently available. Further the fuel cells of this invention are small and compact and thus offers improved performance over rechargeable batteries as a miniature power source. Since the fuel cell electrolyte layer can be made thinner, e.g. 0.5-10 μm thick as compared to 1 mil, then the operating temperature of room temperature to about 600° C. (for example, ~25°-550° C.) can be reduced by hundreds of degrees from the conventional operation temperatures of >600° C. for the case of solid oxide electrolytes which can operate at about 675° C., for example. The electrolyte material may be a solid oxide, such as YSZ, ceria and ceria-based compounds, or a solid polymer, or a proton exchange membrane. For example, solid polymer or proton exchange membrane electrolytes operate at a temperature range of 23-120° C., and with a thickness ranging from 0.5-50 μm . Solid oxide electrolytes operate at a temperature below 600° C. with a preferred thickness of about 0.5-7.5 μm , but can have a thickness of 0.5-50 μm . Also, the solid oxide electrolyte may operate at a temperature above 600° C. (675° C.) with a thickness of 0.5-7.5 μm . Also, the MEMS-based fuel cells have microflow channels and manifolding micromachined into the host structure/substrate, utilize an integrated thin-film resistive heater for efficient heating of the fuel cell stack, and contain a rechargeable microbattery connected to the heater for startup control. The fuel may be hydrogen (liquid or gaseous) or hydrocarbon fuels, including methanol and propanol.

[0050] While particular embodiments have been illustrated and described along with specific materials and parameters, to exemplify and explain the principles of the invention, such are not intended to be limiting. Modifications may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.

What is claimed is:

1. A fuel cell, including:
 - a fuel cell stack having an electrolyte composed of material selected from the group consisting of solid oxide, solid polymer, and proton exchange membrane materials,
 - means for supplying fuel and an oxidant to opposite sides of said fuel cell stack, and means for heating said fuel cell stack,
 - said means for heating includes a resistive heater,
 - said fuel cell stack including at least a pair of electrodes, and an electrolyte separating said electrodes,
 - said electrolyte having a thickness of about 0.5-50 μm ,
 - said means for supplying fuel and oxidant including at least one substrate having a manifold formed therein,
 - said manifold directing fuel to one side of said fuel cell stack.
2. The fuel cell of claim 1, wherein said means for supplying fuel and oxidant additionally includes a second substrate having a manifold formed therein for directing an oxidant to an opposite side of said fuel cell stack.
3. The fuel cell of claim 1, wherein said fuel cell stack includes a catalyst adjacent the electrolyte.
4. The fuel cell of claim 1, wherein said resistive heater is located in said fuel cell stack.
5. The fuel cell of claim 1, wherein said pair of electrodes of said fuel cell stack includes a first electrode composed of hydrogen catalyzing conducting material selected from nickel, copper, carbon, platinum, and palladium, and a second electrode composed of oxygen catalyzing conducting material selected from silver, carbon, platinum, lanthanum strontium manganate (LSM).
6. The fuel cell of claim 1, wherein said pair of electrodes comprises a first electrode composed of Ni, and a second electrode composed of Ag and wherein said electrolyte is composed of YSZ.
7. The fuel cell of claim 1, wherein said at least one substrate is composed of material selected from the group consisting of silicon, glass, ceramic, and plastic.
8. The fuel cell of claim 1, wherein said means for supplying fuel includes a second substrate bonded to said at least one substrate, said second substrate having at least a fuel inlet extending thereinto and in open communication with said manifold in said at least one substrate.
9. The fuel cell of claim 8, wherein said second substrate additionally includes a cutaway section in a surface located adjacent said at least one substrate and which is in open communication with said manifold and with said fuel inlet.
10. The fuel cell of claim 8, wherein said second substrate additionally includes a plurality of channels in open communication with said manifold and said fuel inlet.
11. The fuel cell of claim 1, additionally including a porous member located intermediate said fuel cell stack and said manifold in said at least one substrate.
12. The fuel cell of claim 1, wherein said manifold of said at least one substrate is composed a plurality of channels.
13. The fuel cell of claim 12, wherein said means for supplying fuel includes a second substrate bonded to said at least one substrate, said second substrate having a fuel inlet and a plurality of channels in open communication with said manifold in said at least one substrate.
14. The fuel cell of claim 1, wherein said electrolyte is composed of solid polymer or proton exchange membrane material, operating at a temperature range of about 23-120° C., and having a thickness in the range of 0.5-50 μm .
15. The fuel cell of claim 1, wherein said electrolyte is composed of solid oxide materials operating at one of a temperature below 600° C. with a thickness of 0.5-7.5 μm or 0.5-50 μm , or at a temperature above 600° C. with a thickness of 0.5-7.5 μm .
16. A miniature thin-film fuel cell, comprising:
 - a fuel cell stack including a pair of electrodes and an electrolyte layer, selected from the group consisting of solid oxides, solid polymers, and proton exchange membrane materials,
 - a resistive heater for heating said fuel cell stack,
 - a first substrate having an opening therein located adjacent said fuel cell stack,
 - a second substrate having at least a fuel inlet therein secured to said first substrate and,
 - a resistive heating means located in said fuel cell stack for at least said electrolyte,
 - said electrolyte having a thickness of 0.5 to 50 μm .
17. The fuel cell of claim 16, additionally including a third substrate secured to said first substrate and having an oxidant inlet and a manifold therein adjacent said fuel cell stack.
18. The fuel cell of claim 16, wherein said first substrate additionally includes a plurality of channels forming said opening.
19. The fuel cell of claim 18, wherein said second substrate additionally includes a plurality of channels in open communication with said fuel inlet and said plurality of channels in said first substrate.
20. The fuel cell of claim 16, additionally including a porous member intermediate said first substrate and said fuel cell stack.
21. The fuel cell of claim 1, additionally including a porous electrode formed by photolithographically patterning and etching a continuous metal electrode layer.
22. The fuel cell of claim 16, additionally including a porous electrode formed by photolithographically patterning and etching a continuous metal electrode layer.
23. The fuel cell of claim 16, additionally including a porous electrode formed by deposition onto a porous member.
24. The fuel cell of claim 21, additionally including a catalyst and electrolyte layers deposited onto a porous electrode structure.
25. The fuel cell of claim 22, additionally including a catalyst and electrolyte layers deposited onto a porous electrode structure.

26. The fuel cell of claim 1, in which a membrane electrode assembly laminate structure is attached, bonded or mechanically sealed to a micromachined manifold host structure.

27. The fuel cell of claim 16, in which a membrane electrode assembly laminate structure is attached, bonded or mechanically sealed to a micromachined manifold host structure.

28. The fuel cell of claim 17, in which the fuel cell modules can be directly stacked on top of each other to scale voltage and power.

29. The fuel cell of claim 28, additionally including a plurality of fuel inlets to deliver fuel from a common reservoir.

30. The fuel cell of claim 16, wherein said electrolyte is composed of solid polymer material or proton exchange membrane material having a thickness of 0.5-50 μm , and wherein said fuel cell operates at a temperature below 600° C.

31. The fuel cell of claim 30, wherein said operating temperature is about 23°-120° C.

32. The fuel cell of claim 16, wherein said electrolyte is a solid oxide material having a thickness of 0.5-50 μm , and wherein said fuel cell operates at a temperature above 600° C. and below 600° C.

33. The fuel cell of claim 32, wherein the operating temperature is below 600° C., and wherein said electrolyte has a thickness of 0.5-50 μm .

34. The fuel cell of claim 33, wherein the electrolyte has a thickness of less than 10 μm .

35. The fuel cell of claim 34, wherein the electrolyte has a thickness of 0.5-7.5 μm .

36. The fuel cell of claim 32, wherein said electrolyte has a thickness of about 0.5-7.5 μm , and wherein the operating temperature is above 600° C.

37. The fuel cell of claim 36, wherein said operating temperature is 675° C.

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