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(54) **OXYGEN GETTERS FOR ANODE PROTECTION IN A SOLID-OXIDE FUEL CELL STACK**

(76) Inventors: **Diane M. England**, Bloomfield, NY (US); **Karl J. Haltiner JR.**, Fairport, NY (US); **Sean M. Kelly**, Churchville, NY (US); **Michael T. Faville**, Geneseo, NY (US)

Correspondence Address:
Delphi Technologies, Inc.
Mail Code 480410202
P.O. Box 5052
Troy, MI 48007 (US)

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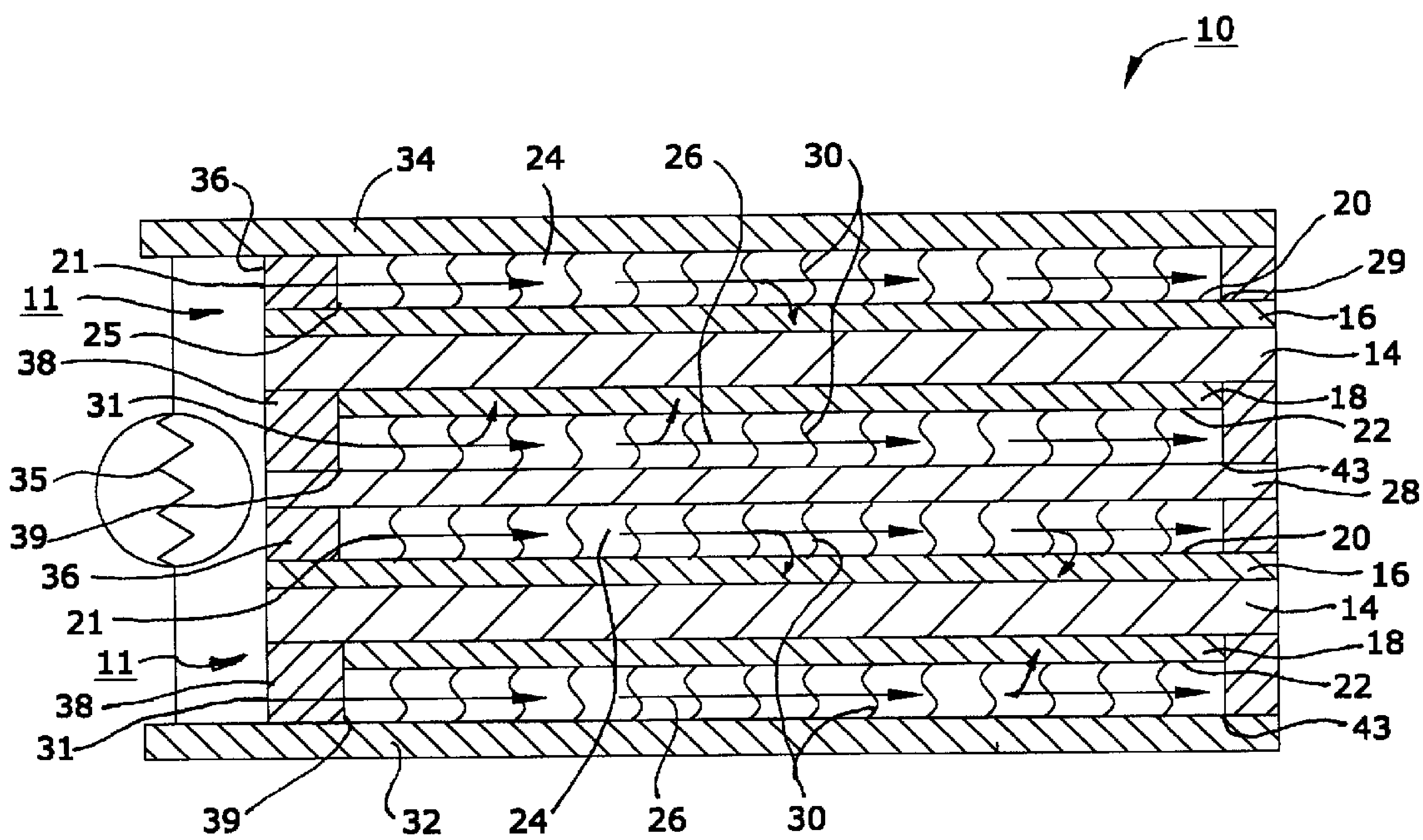
(57) **ABSTRACT**

In a fuel cell assembly, nickel-based anodes are readily oxidized when exposed to oxygen as may happen through atmospheric invasion of the assembly during cool-down following shutdown of the assembly. Repeated anode oxidation and reduction can be destructive of the anodes, leading to cracking and failure. To prevent such oxygen migration, oxygen getter devices containing oxygen-gettering material such as metallic nickel are provided in the fuel passageways leading to and from the anodes. Oxidation of the oxygen-gettering material is readily reversed through reduction by fuel when the assembly is restarted.



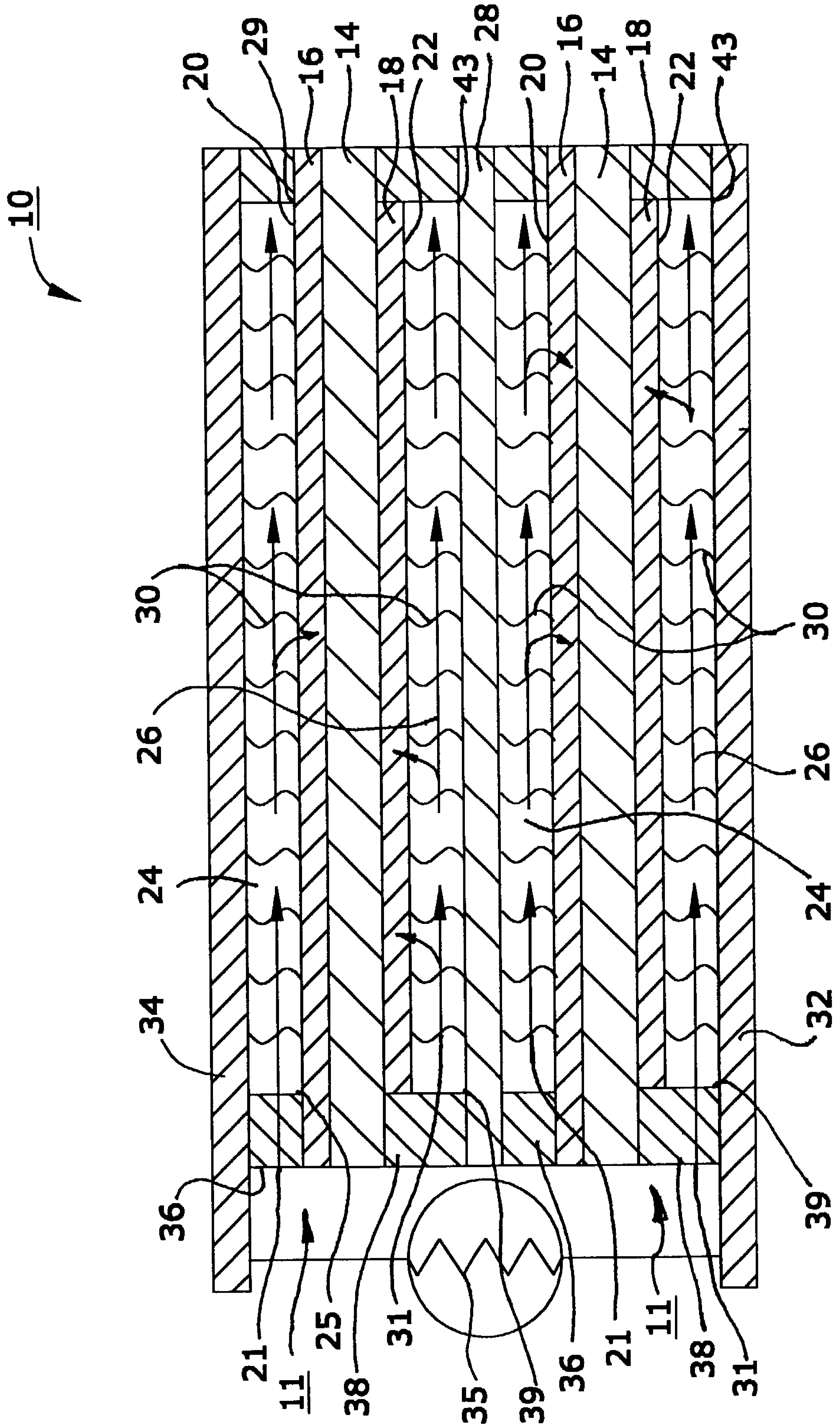

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FIG. 1

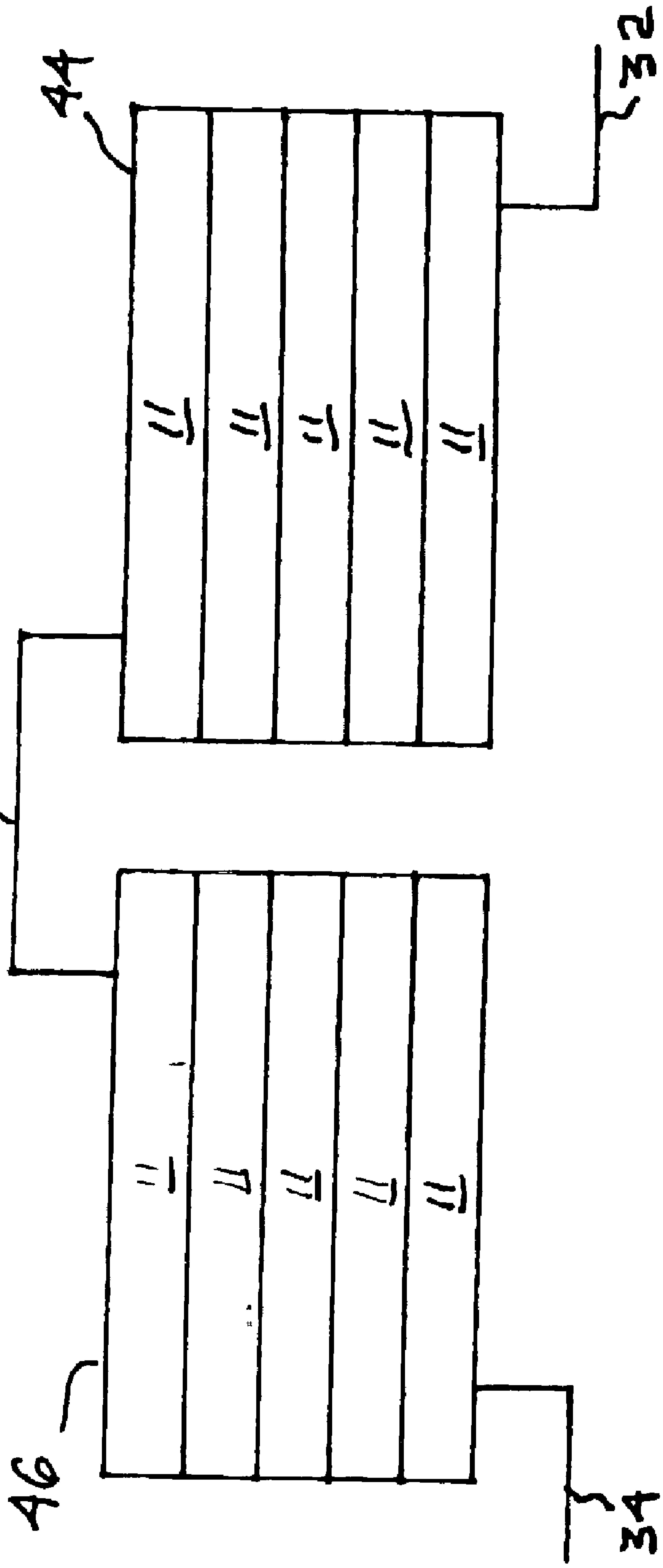

FIG. 2

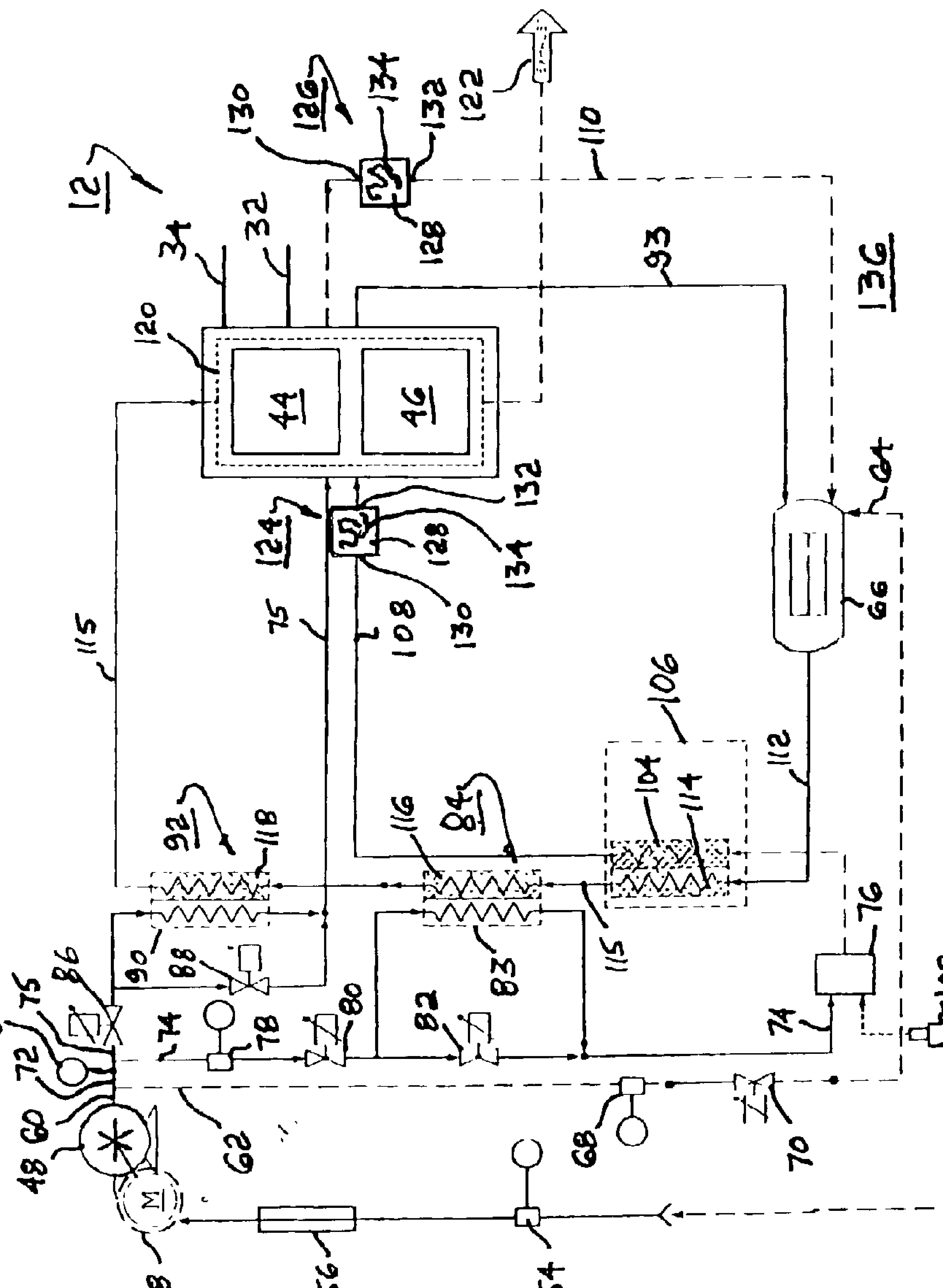
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FIG. 3

OXYGEN GETTERS FOR ANODE PROTECTION IN A SOLID-OXIDE FUEL CELL STACK

TECHNICAL FIELD

[0001] The present invention relates to hydrogen/oxygen fuel cells having a solid-oxide electrolytic layer separating an anode layer from a cathode layer; more particularly, to fuel cell stack assemblies and systems comprising a nickel-based anode; and most particularly, to such fuel cell assemblies and systems wherein the anode is protected from oxidation, especially during cool-down after the assembly has been shut down.

BACKGROUND OF THE INVENTION

[0002] Fuel cells which generate electric current by the electrochemical combination of hydrogen and oxygen are well known. In one form of such a fuel cell, an anodic layer and a cathodic layer are separated by an electrolyte formed of a ceramic solid oxide. Such a fuel cell is known in the art as a "solid oxide fuel cell" (SOFC). Hydrogen, either pure or reformed from hydrocarbons, is flowed along the outer surface of the anode and diffuses into the anode. Oxygen, typically from air, is flowed along the outer surface of the cathode and diffuses into the cathode. Each O_2 molecule is split and reduced to two O^{-2} anions catalytically by the cathode. The oxygen anions transport through the electrolyte and combine at the anode/electrolyte interface with four hydrogen ions to form two molecules of water. The anode and the cathode are connected externally through a load to complete the circuit whereby four electrons are transferred from the anode to the cathode. When hydrogen is derived from "reformed" hydrocarbons, the "reformate" gas includes CO which is converted to CO_2 at the anode via an oxidation process similar to that performed on the hydrogen. Reformed gasoline is a commonly used fuel in automotive fuel cell applications.

[0003] A single cell is capable of generating a relatively small voltage and wattage, typically between about 0.5 volt and about 1.0 volt, depending upon load, and less than about 2 watts per cm^2 of cell surface. Therefore, in practice it is usual to stack together, in electrical series, a plurality of cells. Because each anode and cathode must have a free space for passage of gas over its surface, the cells are separated by perimeter spacers which are vented to permit flow of gas to the anodes and cathodes as desired but which form seals on their axial surfaces to prevent gas leakage from the sides of the stack. The perimeter spacers include dielectric layers to insulate the interconnects from each other. Adjacent cells are connected electrically by "interconnect" elements in the stack, the outer surfaces of the anodes and cathodes being electrically connected to their respective interconnects by electrical contacts disposed within the gas-flow space, typically by a metallic foam which is readily gas-permeable or by conductive filaments. The outermost, or end, interconnects of the stack define electric terminals, or "current collectors," which may be connected across a load.

[0004] A complete SOFC system typically includes auxiliary subsystems for, among other requirements, generating fuel by reforming hydrocarbons; tempering the reformate fuel and air entering the stack; providing air to the hydrocarbon reformer; providing air to the cathodes for reaction with hydrogen in the fuel cell stack; providing air for cooling the fuel cell stack; providing combustion air to an afterburner for unspent fuel exiting the stack; and providing cooling air to the afterburner and the stack. A complete SOFC assembly also includes appropriate piping and valving, as well as a programmable electronic control unit (ECU) for managing the activities of the subsystems simultaneously.

[0005] The anodes of cells in a fuel cell assembly typically include metallic nickel and/or a nickel cermet (Ni—YSZ) which are readily oxidized. During operation of an assembly, the anodes are in a reduced state. A problem exists in that the anodes are vulnerable to oxidation by atmospheric oxygen which can enter the stacks via the reformate passageways during cool-down of the assembly. The grain growth and contraction of the metallic nickel in the anode during the oxidation/reduction cycle is not readily managed by the ceramic component. Repeated oxidation and reduction of nickel in the anodes can lead to unwanted structural changes and can result in catastrophic cracking of the anodes.

[0006] It is a principal object of the present invention to protect the nickel anodes of a fuel cell from structural degradation by periodic oxidation and reduction of the nickel.

[0007] It is a further object of the present invention, through such prevention, to improve the reliability and extend the lifetime of solid oxide fuel cells.

BRIEF DESCRIPTION OF THE INVENTION

[0008] Briefly described, in a fuel cell assembly, for example, a solid-oxide fuel cell assembly, metallic nickel in a Ni—YSZ based anode is readily oxidized when exposed to oxygen as may happen through atmospheric invasion of the assembly during cool-down following shutdown of the assembly. Anodes are in an oxidized equilibrium state when the assembly is fabricated and are then reduced by reformate when the assembly is first turned on. Repeated anode oxidation and reduction can be destructive of the three-dimensional structure of the anodes and can lead to cracking and failure of the anodes and thus the entire assembly. To prevent such oxygen migration and re-oxidation, oxygen getter devices, themselves containing oxygen-scavenging material such as metallic nickel, are provided in the reformate passageways leading to and from the anodes. When oxidized, the oxygen-gettering material is readily reversed through reduction by reformate when the assembly is restarted.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] These and other features and advantages of the invention will be more fully understood and appreciated from the following description of certain exemplary embodiments of the invention taken together with the accompanying drawings, in which:

[0010] **FIG. 1** is a schematic cross-sectional view of a two-cell stack of solid oxide fuel cells;

[0011] **FIG. 2** is a schematic elevational view of two fuel cell stacks electrically connected in series; and

[0012] **FIG. 3** is a schematic mechanization diagram of an SOFC assembly, showing the incorporation of oxygen getters in fuel passageways leading into and out of the anodes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] Referring to **FIG. 1, a** fuel cell stack **10** includes elements known in the art of solid oxide fuel cell stacks comprising more than one fuel cell. The example shown includes two identical fuel cells **11**, connected in series, and is of a class of such fuel cells said to be "anode-supported" in that the anode is a structural element having the electrolyte and cathode deposited upon it. Element thicknesses as shown are not to scale.

[0014] Each fuel cell **11** includes an electrolyte element **14** separating an anodic element **16** and a cathodic element **18**. Each anode and cathode is in direct chemical contact with its respective surface of the electrolyte, and each anode and cathode has a respective free surface **20,22** forming one wall of a respective passageway **24,26** for flow of gas across the surface. Anode **16** of a first fuel cell **11** faces and is electrically connected to an interconnect **28** by filaments **30** extending across but not blocking passageway **24**. Similarly, cathode **18** of a second fuel cell **11** faces and is electrically connected to interconnect **28** by filaments **30** extending across but not blocking passageway **26**. Similarly, cathode **18** faces and is electrically connected to a cathodic current collector **32** by filaments **30** extending across but not blocking passageway **26**, and anode **16** faces and is electrically connected to an anodic current collector **34** by filaments **30** extending across but not blocking passageway **24**. Current collectors **32,34** may be connected across a load **35** in order that the fuel cell stack **10** performs electrical work. Passageways **24** are formed by anode spacers **36** between the perimeter of anode **16** and either interconnect **28** or anodic current collector **34**.

[0015] Passageways **26** are formed by cathode spacers **38** between the perimeter of electrolyte **14** and either interconnect **28** or cathodic current collector **32**. Anode spacer **36** and cathode spacer **38** are formed from sheet stock in such a way to yield the desired height of the anode passageways **24** and cathode passageways **26**.

[0016] Preferably, the interconnect and the current collectors are formed of an alloy, typically a "superalloy," which is chemically and dimensionally stable at the elevated temperatures necessary for fuel cell operation, generally about 750° C. or higher, for example, Hastelloy, Haynes 230, or a stainless steel. The electrolyte is formed of a ceramic oxide and preferably includes zirconia stabilized with yttrium oxide (yttria), known in the art as YSZ. The cathode is formed of, for example, porous lanthanum strontium manganate or lanthanum strontium iron, and the anode is formed of, for example, a mixture of nickel and YSZ.

[0017] In operation **(FIG. 1)**, reformate gas **21** is provided to passageways **24** at a first edge **25** of the anode free surface **20**, flows parallel to the surface of the anode across the anode in a first direction, and is removed at a second and opposite edge **29** of anode surface **20**. Hydrogen and CO diffuse into the anode to the interface with the electrolyte. Oxygen **31**, typically in air, is provided to passageways **26** at a first edge **39** of the cathode free surface **22**, flows parallel to the surface of the cathode in a second direction which can be orthogonal to the first direction of the reformate (second direction shown in the same direction as the first for clarity in **FIG. 1**), and is removed at a second and opposite edge **43** of cathode surface **22**. Molecular oxygen gas (O_2) diffuses into the cathode and is catalytically reduced to two O^{-2} ions by accepting four electrons from the cathode and the cathodic current collector **32** or the interconnect **28** via filaments **30**. The electrolyte ionically conducts or transports O^{-2} anions to the anode electrolyte innerface where they combine with four hydrogen atoms to form two water molecules, giving up four electrons to the anode and the anodic current collector **34** or the interconnect **28** via filaments **30**. Thus cells **11** are connected in series electrically between the two current collectors, and the total voltage and wattage between the current collectors is the sum of the voltage and wattage of the individual cells in a fuel cell stack.

[0018] Referring to **FIG. 2**, the cells **11** are arranged side-by-side rather than in overlapping arrangement as shown in **FIG. 1**. Further, the side-by-side arrangement may comprise a plurality of cells **11**, respectively, such that each of first stack **44** and second stack **46** shown in **FIG. 2** is a stack of identical fuel cells **11**. The cells **11** in stack **44** and stack **46** are connected electrically in series by interconnect **47**, and the stacks are connected in series.

[0019] Referring to **FIG. 3**, the diagram of a solid-oxide fuel cell assembly **12** includes auxiliary equipment and controls for stacks **44,46** electrically connected as in **FIG. 2**.

[0020] A conventional high speed inlet air pump **48** draws inlet air **50** through an air filter **52**, past a first MAF sensor **54**, through a sonic silencer **56**, and a cooling shroud **58** surrounding pump **48**.

[0021] Air output **60** from pump **48**, at a pressure sensed by pressure sensor **61**, is first split into branched conduits between a feed **62** and a feed **72**. Feed **62** goes as burner cooling air **64** to a stack afterburner **66** via a second MAF sensor **68** and a burner cool air control valve **70**.

[0022] Feed **72** is further split into branched conduits between an anode air feed **74** and a cathode air feed **75**. Anode feed **74** goes to a hydrocarbon fuel vaporizer **76** via a third MAF sensor **78** and reformer air control valve **80**. A portion of anode air feed **74** may be controllably diverted by control valve **82** through the cool side **83** of reformate pre-heat heat exchanger **84**, then recombined with the non-tempered portion such that feed **74** is tempered to a desired temperature on its way to vaporizer **76**.

[0023] Cathode air feed **75** is controlled by cathode air control valve **86** and may be controllably diverted by cathode air preheat bypass valve **88** through the cool side **90** of cathode air pre-heat heat exchanger **92** on its way to stacks **44,46**. After passing through the cathode sides of the cells in stacks **44,46**, the partially spent, heated air **93** is fed to burner **66**.

[0024] A hydrocarbon fuel feed pump **94** draws fuel from a storage tank **96** and delivers the fuel via a pressure regulator **98** and filter **100** to a fuel injector **102** which injects the fuel into vaporizer **76**. The injected fuel is combined with air feed **74**, vaporized, and fed to a reformer catalyst **104** in main fuel reformer **106** which reforms the fuel to, principally, hydrogen and carbon monoxide. Reformate **108** from catalyst **104** is fed to the anodes in stacks **44,46**. Unconsumed fuel **110** from the anodes is fed to afterburner **66** where it is combined with air supplies **64** and **93** and is burned. The hot burner gases **112** are passed through a cleanup catalyst **114** in main reformer **106**. The effluent **115** from catalyst **114** is passed through the hot sides **116,118** of heat exchangers **84**, **92**, respectively, to heat the incoming cathode and anode air. The partially-cooled effluent **115** is fed to a manifold **120** surrounding stacks **44,46** from whence it is eventually exhausted **122**.

[**0025**] Still referring to **FIG. 3, a** first oxygen getter device **124** is provided in the conduit feeding fuel such as, for example, pure hydrogen or reformate **108** to the anodes (not visible) in stacks **44,46**. A second and substantially identical oxygen getter device **126** is similarly provided in the conduit feeding spent fuel **110** from the anodes to afterburner **66**. As described above, during cool-down of the fuel cell stacks after shut-down of the assembly, it is important to prevent migration of oxygen into anode passages **24** wherein anode surface **20**, comprising metallic nickel in a ceramic matrix (nickelYSZ cermet), would be subject to damaging oxidation. Each getter includes a passageway **128** having an inlet **130** and an outlet **132** through which fuel is passed during operation of the fuel cell assembly. Within the passageway is a readily-oxidized material **134** (oxygen-reducing means), for example, nickel metal foam, nickel wire or nickel mesh, which is capable of gettering oxygen by reaction therewith but which does not present a significant obstruction to flow of fuel through the passageway. Nickel in the getters reacts with oxygen to produce nickel oxide, NiO, when the assembly is shut down, thus protecting the nickel-containing anodes from oxidation. When the assembly is turned back on, reformate is again produced which, in passing through the getters, reduces the NiO back to metallic nickel, allowing the getters to be used repeatedly.

[**0026**] An SOFC assembly in accordance with the invention is especially useful as an auxiliary power unit (APU) for vehicles **136** on which the APU may be mounted as shown in **FIG. 3**, such as cars and trucks, boats and ships, and airplanes, wherein motive power is supplied by a conventional engine and the auxiliary electrical power needs are met by an SOFC assembly.

[**0027**] An SOFC assembly in accordance with the invention is also useful as a stationary power plant such as, for example, in a household or for commercial usage.

[**0028**] While the invention has been described by reference to various specific embodiments, it should be understood that numerous changes may be made within the spirit and scope of the inventive concepts described. Accordingly, it is intended that the invention not be limited to the described embodiments, but will have full scope defined by the language of the following claims.

What is claimed is:

1. In a fuel cell assembly including nickel-containing anodes and passageways leading to and from the anodes for conducting fuel to and from the anodes, the improvement comprising oxygen getter means disposed in each of said passageways for preventing gaseous oxygen from reaching and oxidizing said nickel in said anodes.

2. An improvement in accordance with claim 1 wherein said getter means comprises:

a) a passageway having an inlet and an outlet for passage of gas therethrough; and

b) reducing means disposed within said passageway for reacting with oxygen.

3. A fuel cell assembly in accordance with claim 2 wherein said reducing means includes metallic nickel.

4. A fuel cell assembly in accordance with claim 2 wherein said reducing means includes nickel alloy.

5. A fuel cell assembly in accordance with claim 3 wherein said metallic nickel is in a form selected from the group consisting of nickel metal foam, nickel wire, and nickel mesh.

6. A fuel cell assembly in accordance with claim 4 wherein said nickel alloy is in a form selected from the group consisting of nickel metal foam, nickel wire, and nickel mesh.

7. A fuel cell assembly in accordance with claim I wherein said oxidation of said reducing means is reductively reversible by fuel.

8. A fuel cell assembly in accordance with claim 1 wherein said assembly is mounted on a vehicle.

9. A fuel cell assembly in accordance with claim 1 wherein said assembly is mounted stationary.

10. A fuel cell assembly in accordance with claim 8 wherein said vehicle is selected from the group consisting of car, truck, boat, and airplane.

11. A fuel cell assembly in accordance with claim 10 wherein said assembly is an auxiliary power unit for said vehicle.

12. A fuel cell assembly in accordance with claim 1 wherein said fuel cell is a solid-oxide fuel cell.

13. An automotive vehicle, comprising a fuel cell assembly for generating auxiliary power for said vehicle, the assembly including

nickel-containing anodes,

passageways leading to and from said anodes for conducting fuel to and from said anodes, and

oxygen getter means disposed in each of said passageways for preventing gaseous oxygen from reaching and oxidizing said nickel in said anodes.

* * * * *