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(71) Applicant (*for all designated States except US*): **IDAT-ECH, LLC** [US/US]; P.O. Box 5339, Bend, OR 97708-5339 (US).

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(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **EDLUND, David, J.** [US/US]; 1698 Davenport, Bend, OR 97701 (US).

(74) Agent: **D'ASCENZO, David, S.**; Kolisch, Hartwell, Dickinson, McCormack & Heuser, P.C., Suite 200, 520 S.W. Yamhill Street, Portland, OR 97204 (US).

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(54) Title: FUEL CELLS AND FUEL CELL SYSTEMS CONTAINING NON-AQUEOUS ELECTROLYTES

(57) Abstract: The present invention provides fuel cells and fuel cell systems that include a non-aqueous electrolyte. Fuel cells according to the present invention include an anode region adapted to receive a hydrogen stream, a cathode region adapted to receive a stream containing oxygen, and an electrolytic barrier that separates the anode region from the cathode region and which contains a non-aqueous electrolyte. The non-aqueous electrolyte is preferably acidic or basic, with the electrolyte having an acid ionization constant ( $K_a$ ) greater than  $5 \times 10^{-6}$  at 25 °C if the non-aqueous electrolyte is an acid and a base ionization constant ( $K_b$ ) greater than  $5 \times 10^{-6}$  at 25 °C if the non-aqueous electrolyte is a base. The fuel cell has an operating temperature of less than 300 °C, and may operate at temperatures above, at, and below 100 °C.



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## FUEL CELLS AND FUEL CELL SYSTEMS CONTAINING NON-AQUEOUS ELECTROLYTES

### Field of the Invention

The present invention relates generally to fuel cells and fuel cell  
5 systems, and more particularly to fuel cells and fuel cell systems that contain a non-aqueous electrolyte.

### Background of the Invention

An electrochemical fuel cell is a device that reacts a fuel source with  
an oxidizing agent to produce an electric current. Commonly, the fuel source is  
10 hydrogen gas, and the oxidizing agent is oxygen. An example of a fuel cell utilizing  
these reactants is a proton exchange membrane fuel cell (PEMFC or PEM fuel cell),  
in which hydrogen gas is catalytically dissociated in the fuel cell's anode chamber  
into protons and electrons. The liberated protons are drawn through an electrolytic  
membrane into the fuel cell's cathode chamber. The electrons cannot pass through  
15 the membrane and instead must travel through an external circuit to reach the cathode  
chamber. In the cathode chamber, the protons and electrons react with oxygen to  
form water. The net flow of electrons from the anode to the cathode chamber  
produces an electric current, which can be used to meet the electrical load being  
applied to the fuel cell by an associated electrical, or energy-consuming, device, such  
20 as a vehicle, boat, light, appliance, household, etc.

The fuel cell's ability to transport hydrogen ions across the electrolytic  
membrane is a function of the hydration of the membrane. In the case of low-  
temperature fuel cells, such as PEM fuel cells and alkaline fuel cells (AFCs), the  
ionically-conductive electrolyte is a water-swollen, strongly acidic polymeric  
25 membrane (PEMFC) or an aqueous solution of a strong base such as potassium  
hydroxide (AFC). These ionically-conductive electrolytes are susceptible to drying  
(losing water) or flooding (absorbing excess water). Either occurrence can lead to  
poor performance of the fuel cell and premature failure. U.S. Patent No. 6,059,943,  
which is incorporated herein by reference in its entirety for all purposes, describes  
30 many of the problems related to maintaining a correct water balance in  
electrochemical devices such as fuel cells.

### Summary of the Invention

The present invention provides fuel cells and fuel cell systems that include a non-aqueous electrolyte. Fuel cells according to the present invention include an anode region adapted to receive a hydrogen stream, a cathode region adapted to receive a stream containing oxygen, and an electrolytic barrier that separates the anode region from the cathode region and which contains a non-aqueous electrolyte. The non-aqueous electrolyte is preferably acidic or basic, with the electrolyte having an acid ionization constant ( $K_a$ ) greater than  $5 \times 10^{-6}$  at 25° C if the non-aqueous electrolyte is an acid and a base ionization constant ( $K_b$ ) greater than  $5 \times 10^{-6}$  at 25° C if the non-aqueous electrolyte is a base. The fuel cell has an operating temperature of less than 300° C, and may operate at temperatures above, at, and below 100° C.

Many features of the present invention will become manifest to those versed in the art upon making reference to the detailed description which follows and the accompanying sheets of drawings in which preferred embodiments incorporating the principles of this invention are disclosed as illustrative examples only.

### Brief Description of the Drawings

Fig. 1 is a schematic diagram of a fuel cell system constructed according to the present invention.

Fig. 2 is a schematic diagram of another fuel cell system constructed according to the present invention.

Fig. 3 is a schematic diagram of a fuel cell constructed according to the present invention.

Fig. 4 is a schematic diagram of a fuel processor suitable for use in the fuel cell system shown in Fig. 2.

Fig. 5 is a schematic diagram of another fuel processor suitable for use in the fuel cell system shown in Fig. 2.

### Detailed Description and Best Mode of the Invention

A fuel cell system according to the present invention is shown in Fig. 1 and generally indicated at 10. System 10 includes a fuel cell stack 12 and a source 14 of an anode feedstock 16, which is delivered to fuel cell stack 12 as stream 17. Anode feedstock 16 is any suitable composition or compositions that contain chemically bound hydrogen and which liberate protons at the anode of a fuel cell. An example of

a suitable anode feedstock 16 is hydrogen gas. Other examples include methanol, hydrazine, ethanol and formaldehyde. Source 14 may include a storage tank or other reservoir containing feedstock 16, which is delivered to fuel cell stack 12 through any suitable mechanism, such as by pumping or by gravity flow. For example, source 14  
5 may be a tank of compressed hydrogen gas, a tank or other fluid-holding container of methanol, etc. Another example is a hydride bed, which contains stored hydrogen gas.

Alternatively, source 14 may include one or more devices that are adapted to produce anode feedstock 16, such as by a chemical reaction. An example  
10 of such a source 14 is shown in Fig. 2 and includes at least one fuel processor 18. Fuel processor 18 is adapted to receive a feed stream 20 that contains the feedstock for the fuel processor and is delivered to the fuel processor by any suitable mechanism, such as by pumping or by gravity flow. Fuel processor 18 produces an anode feedstock 16 in the form of hydrogen gas 22 from feed stream 20. Preferably,  
15 the fuel processor is adapted to produce substantially pure hydrogen gas, and even more preferably, the fuel processor is adapted to produce pure hydrogen gas. For the purposes of the present invention, substantially pure hydrogen gas is greater than 90% pure, preferably greater than 95% pure, more preferably greater than 99% pure, and even more preferably greater than 99.5% pure. Suitable fuel processors for producing  
20 hydrogen gas are disclosed in U.S. Patent Nos. 6,221,117, 5,997,594 and 5,861,137, and U.S. Provisional Patent Application Serial No. 60/188,993, which was filed on March 13, 2000 and is entitled "Fuel Processor," each of which is incorporated by reference in its entirety for all purposes.

Non-exclusive examples of suitable mechanisms by which fuel  
25 processor 18 produces hydrogen gas 22 include steam reforming, autothermal reforming, pyrolysis, partial oxidation, electrolysis and dissociation by irradiation. The composition and number of individual streams forming feed stream 20 will tend to vary depending on the mechanism by which fuel processor 18 is adapted to produce hydrogen gas 22. For example, if fuel processor 18 produces hydrogen gas by steam  
30 or autothermal reforming, feed stream 20 contains a carbon-containing feedstock 24 and water 26, such as shown in Fig. 2. If fuel processor 18 produces hydrogen gas by pyrolysis, irradiation or catalytic partial oxidation of a carbon-containing feedstock, feed stream 20 contains a carbon-containing feedstock and does not include water. If

fuel processor 18 produces hydrogen gas by electrolysis, feed stream 20 contains water and does not contain a carbon-containing feedstock. When the feed stream contains water and a carbon-containing feedstock that is soluble with water, the feed stream may be a single stream, such as shown in a solid line in Fig. 2. When the  
5 carbon-containing feedstock is not miscible in water, the water and carbon-containing feedstock are delivered in separate feed streams 20, such as shown in dashed lines in Fig. 2.

Examples of carbon-containing feedstocks 24 include alcohols and hydrocarbons. Illustrative examples of suitable hydrocarbons include methane,  
10 propane, natural gas, diesel, kerosene, gasoline and the like. Illustrative examples of suitable alcohols include methanol, ethanol, propanol, and polyols, such as ethylene glycol and propylene glycol. A preferred, but by no means exclusive, feedstock for a fuel processor in the form of a steam reformer is methanol, and more particularly, fuel-cell grade methanol. Generally, catalysts that are used for conducting the water-  
15 gas shift reaction are suitable for steam reforming methanol. Commonly used (and commercially available) methanol steam-reforming catalysts consist of mixtures of copper and zinc oxide, and copper and chromium oxide. These catalyst formulations are very rapidly and completely poisoned by compounds of sulfur, compounds of phosphorous, volatile heavy metals (e.g., cadmium, mercury), and compounds of  
20 heavy metals. Therefore, the methanol is preferably free from these compounds so that the reforming catalyst is not poisoned. Similarly, other carbon-containing feedstocks should be sufficiently free from these or other compounds that will poison the reforming or other catalysts used to produce hydrogen gas therefrom.

Fuel cell stack 12 is adapted to produce an electric current 28 from the  
25 portion of anode feedstock 16 (or hydrogen gas 22) delivered thereto. Illustrative examples of suitable conventional fuel cells include proton exchange membrane (PEM) fuel cells and alkaline fuel cells. Fuel cell stack 12 typically includes a plurality of fuel cells 30 integrated together between common end plates 32, which contain fluid delivery/removal conduits (not shown). The number of cells in stack 12  
30 may vary, such as depending upon such factors as the desired power output, the size limitations of the system, and the maximum available hydrogen (or other anode feedstock) supply. However, it is within the scope of the present invention that fuel cell stack 12 may include a single fuel cell 30, or multiple fuel cells 30. Typically,

fuel cell stack 12 receives all or at least a substantial portion of stream 17 and produces electric current 28 therefrom. This current can be used to provide electrical power to an associated energy-consuming device 34, such as a vehicle or a house or other residential or commercial dwelling.

5            Illustrative examples of devices 34 include, but should not be limited to, a motor vehicle, recreational vehicle, boat, tools, lights or lighting assemblies, appliances (such as household or other appliances), household, signaling or communication equipment, etc. It should be understood that device 34 is schematically illustrated in Figs. 1 and 2 and is meant to represent one or more  
10 devices or collection of devices that are adapted to draw electric current from the fuel cell system. By "associated," it is meant that device 34 is adapted to receive electrical power generated by stack 12. It is within the scope of the invention that this power may be stored, modulated or otherwise treated prior to delivery to device 34. Similarly, device 34 may be integrated with stack 12, or simply configured to draw  
15 electric current produced by stack 12, such as via electrical power transmission lines.

          In Fig. 3, an illustrative example of a fuel cell 30 constructed according to the present invention is shown. Fuel cell 30 includes an anode region 36 and a cathode region 38. The regions respectively include anode and cathode electrodes 40 and 42, which are schematically illustrated in Fig. 3. Any suitable electrode  
20 construction may be used. As an illustrative example, the electrodes may be porous and contain an electrocatalyst 44 and an electrically conductive support 46 that is in electrical communication with a current collection device 48 from which energy-consuming device 34 may directly or indirectly draw electric current 28.

          The anode region 36 of the fuel cell receives at least a portion of  
25 stream 17. Anode region 36 is periodically purged, and releases a purge stream 50, which may contain hydrogen gas. Alternatively, hydrogen gas may be continuously vented from the anode region of the fuel cell. The purge streams may be vented to the atmosphere, combusted, used for heating, fuel or as a feedstock for the fuel processing assembly. The fuel cells of a fuel cell stack may exhaust a common purge stream  
30 consisting of the purge streams from the individual fuel cells contained therein. The purge streams from the fuel cells may be integrated into a suitable collection assembly through which the combined purge stream may be used for fuel, feedstock, heating, or otherwise harvested, utilized or stored.

Cathode region 38 receives a stream 52 containing oxygen 54, such as a stream of pure oxygen, an air stream, or an air stream that has been enriched with oxygen gas, and releases a cathode air exhaust stream 56 that is partially or substantially depleted in oxygen. The relative flow rate of air will generally be  
5 greater than that of pure oxygen because of the lower relative concentration of oxygen atoms provided.

The anode and cathode regions are separated by an electrolytic barrier 60 through which hydrogen ions (protons) may pass. Electrons liberated from hydrogen gas 22 (or other composition or compositions that contain chemically bound  
10 hydrogen and which liberate protons at the anode of the fuel cell stack) cannot pass through barrier 60, and instead must pass through an external circuit 61, thereby producing electric current 28 that may be used to meet the load applied by device 34. Current 28 may also be used to power the operation of the fuel cell system. The power requirements of the fuel cell system are collectively referred to as the balance  
15 of plant requirements of the fuel cell system.

Electrolytic barrier 60 includes a non-aqueous electrolyte 62 and a support structure, or containment structure, 64. Illustrative examples of suitable support structures 64 include absorbent media that absorb electrolyte 62 and porous structures. Illustrative examples of absorbent media include swollen polymer mats  
20 and films. Examples of suitable polymers are sold by DuPont under the trade name NAFION<sup>TM</sup>, which is available in varying thicknesses, such as between 0.001 inches to 0.011 inches. Generally thinner sheets are preferred because they decrease the diffusion distance across the electrolyte. Illustrative examples of porous structures include mats, meshes, or channels, which contain the electrolyte by capillary action  
25 and/or the surface tension between the electrolytes and the porous structures. The support structure may be saturated with the electrolyte. Alternatively, less than full saturation may be used without adversely affecting the conductivity of the electrolyte, especially when the electrolyte is hydrophobic.

Electrolyte 62 may have a low or even exceptionally low vapor  
30 pressure, low viscosity, a melting point that is less than 100° C and preferably less than 25° C. The electrolyte may have a high ionic conductivity and a range of electrochemical potential of at least 0.6 V and preferably at least 1.5 V, over which

components of the electrolyte (other than protons or hydroxide ions) are neither oxidized nor reduced at the electrodes.

In conventional low-temperature fuel cells with water-based electrolytes, water is volatile at the operating temperature of the fuel cell. As used  
5 herein, the term "low-temperature" is used to refer to temperatures less than 100° C, "high-temperature" is used to refer to temperatures greater than 300° C, with "moderate-temperature" referring to temperatures between 100° C and 300° C. Because water is volatile at the operating temperature of low-temperature fuel cells, the amount of water in the electrolyte must be continuously monitored to ensure the  
10 electrolyte is not dried from too little water or flooded from too much water. Too little water decreases the ionic conductivity of the electrolyte, while too much water results in droplets that impede the conduction of ions across the electrolyte. Furthermore, in fuel cells in which aqueous electrolytes are used, the fuel cell is typically configured to remove formed water so that water does not significantly  
15 increase the volume of the electrolyte. This water monitoring and maintenance requires significant monitoring and/or control to maintain the fuel cell's operability and efficiency.

A method for managing and removing excess water is to operate the fuel cell, or fuel stack, at an operating temperature at or above 100° C. Operating the  
20 fuel cell at this temperature results in water being vaporized. As a result, the water cannot significantly add to the volume of the electrolyte. However, low-temperature water-based electrolytes cannot be used above 100° C, and high-temperature inorganic electrolytes do not have sufficient ionic conductivity to function at low and/or moderate temperatures. In fact, some high-temperature electrolytes are not  
25 even liquids at low or even moderate temperatures. Examples of fuel cells that operate at temperatures greater than 100° C include phosphoric acid fuel cells (180-200° C), molten carbonate fuel cells (450-550° C) and solid oxide fuel cells (600-700° C).

Electrolyte 62 may exhibit very low solubility for water by using  
30 hydrophobic anions and cations. Because non-aqueous electrolyte 62 is insoluble or only slightly soluble in water, it produces a fuel cell 30 in which the amount of water in the electrolytic barrier 60 does not need to be managed.



Non-aqueous electrolyte 62 enables fuel cell 30 to be operated at moderate temperatures as well as at the low-temperature conditions at which aqueous electrolytes are typically operated. Worded another way, the ionic conductivity of fuel cells 30 is acceptable for operation of the fuel cells at both low and moderate  
5 temperatures. Therefore, it is within the scope of the invention that fuel cell 30 (and stack 12) will be operated at a range of temperatures in the range of 0° C (or approximately 0° C) and 300° C (or approximately 300° C). In many embodiments, fuel cell 30 will be operated at temperatures in the range of approximately 15° C and approximately 200° C, and more typically in the range of approximately 15° C and  
10 approximately 150° C. It is also within the scope of the present invention that the fuel cell, or fuel cell stack, may be operated at temperatures in the range of 0° C or 15° C and 100° C, at 100° C, and at temperatures greater than 100° C, such as temperatures up to 200° C or 300° C.

An advantage of operating at an elevated temperature is that the  
15 efficiency of the fuel cell increases with increases in its operating temperature. As the temperature increases, the electrocatalysts on the anode and cathode sides become more active. Also, the anode catalyst becomes less sensitive to gas-phase impurities. Another result of operating the fuel cell at a higher operating temperature is that the exhaust streams will be at a higher temperature than corresponding streams of a low-  
20 temperature fuel cell. Accordingly, these streams will have an increased heating value, which may be harvested through heat exchange or which may remove or lessen the need to heat these streams prior to downstream use. Similarly, feed streams 17 and 52 may be delivered at a higher temperature than conventionally used with low-temperature fuel cells, thereby reducing or eliminating the need to cool these streams  
25 if they are available at temperatures higher than the temperatures acceptable for use in low-temperature fuel cells.

Non-aqueous electrolyte 62 may be either a pure compound or a mixture of compounds in which water is not a major component. Typically, the non-aqueous electrolyte should be less than 5% water on a molar basis. Because the  
30 electrolyte serves as a barrier to electrons, but not protons, the non-aqueous electrolyte should be a poor electrical conductor and a good ionic conductor. The non-aqueous electrolyte should have low volatility, meaning that the normal boiling point of the electrolyte is at least 90° C and preferably at least 130° C, and more

preferably at least 150° C. The non-aqueous electrolyte should have a melting point of less than 5° C and more preferably less than 0° C.

Examples of non-aqueous electrolytes 62 are inorganic acids such as phosphoric acid or sulfuric acid, and low volatility hydrocarbons such as decane or hexadecane. Alternatively, the non-aqueous electrolyte may be a mixture of several compounds. These mixtures may include a hydrocarbon solvent combined with an acidic or basic solute, a polyalcohol solvent combined with an acidic or basic solute, a polyether solvent combined with an acidic or basic solute, an organic ionic liquid solvent combined with an acidic or basic solute, or any organic solvent with a normal boiling point of greater than 90° C combined with an acidic or basic solute. The acidic solute should be a solute that is ionized in solution to yield protons. The basic solute should be a solute that is ionized in solution to yield hydroxide ions. Examples of suitable solvents are hexadecane, decane, kerosene, propylene carbonate, propylene glycol, o-dichlorobenzene, and 1,3,5-trichlorobenzene. Examples of suitable acidic solutes are hydrogen hexafluorophosphate, hydrogen tetrphenylborate, sulfuric acid, and perchloric acid. Examples of suitable basic solutes are tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide and other tetraalkylammonium hydroxides.

Another example of a non-aqueous electrolyte is an organic ionic liquid. Organic ionic liquids are discussed, for example, in M. Freemantle, "Eyes on Ionic Liquids," *Chemical Engineering and News*, May 15, 2000, p. 37-50, which is hereby incorporated by reference in its entirety for all purposes. In general an organic ionic liquid includes an organic salt that is liquid at room temperature, (i.e. the melting point of the salt is lower than room temperature) and ionization occurs when the salt is molten or dissolved.

The chemistry behind an organic ionic liquid forming the electrolyte in a fuel cell is illustrated below. Consider, for example, 1-ethyl-3-methyl-imidazoleum tetrafluoroborate, which is an organic ionic liquid (melting point 15° C and boiling point > 350° C) that is commercially available from Aldrich Chemical Co. in Milwaukee, Wisconsin. For this compound to serve as the electrolyte in a PEM fuel cell, the conjugate base would be the tetrafluoroborate ion ( $\text{BF}_4^-$ ), which is protonated at the anode to form the conjugate acid  $\text{HBF}_4$ . Other anions can be selected rather than tetrafluoroborate for use with the 1-ethyl-3-methyl-imidazoleum cation. For example,

other suitable anions include tetraphenylborate ( $\text{BPh}_4^-$ ), and hexafluorophosphate ( $\text{PF}_6^-$ ).

Examples of organic ionic liquids include 1,3-dialkylimidazoleum cations coupled to hydrophobic anions or hydrophilic anions. Specific examples include 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butylpyridinium nitrate, 1-ethyl-3-methylimidazoleum bis(trifluoromethanesulfonate), and 1-ethyl-3-methylimidazoleum bis(trifluoromethanesulfonyl)imide. The organic ionic liquid or liquids may themselves form electrolyte 62 or they may be the solvent for an acid or base, such as these discussed herein.

A preferred non-aqueous electrolyte 62 is either a strong acid or a strong base, since the electrolyte must serve as either a proton donor or a hydroxide-ion donor. For the purposes of the present invention, a strong acid is defined as an acid having an ionization constant ( $K_a$ ), or first ionization constant if it is a polyprotic acid, greater than  $5 \times 10^{-6}$ , preferably greater than  $1 \times 10^{-4}$ , and more preferably, greater than  $1 \times 10^{-2}$  at  $25^\circ \text{C}$ . Likewise, for the purposes of the present invention, a strong base is defined as a base having an ionization constant ( $K_b$ ) greater than  $5 \times 10^{-6}$ , preferably greater than  $1 \times 10^{-4}$ , and more preferably, greater than  $1 \times 10^{-2}$  at  $25^\circ \text{C}$ . As used herein, the term "acid" shall refer to a proton donor or Bronsted-Lowry acid and "base" shall refer to a hydroxide ion donor or Bronsted-Lowry base.

Strongly acidic non-aqueous electrolytes are used when the fuel cell relies on proton ions, for example proton exchange membrane fuel cells (PEMFCs), while strongly basic non-aqueous electrolytes are used when the fuel cell relies on hydroxide ions, such as in alkaline fuel cells (AFCs). Thus, non-aqueous electrolytes suitable for use in the present invention are typically strong acids and bases. Alternatively, non-aqueous electrolytes, such as those described in U.S. Patent No. 5,965,054, which is hereby incorporated by reference in its entirety for all purposes, that are weak acids and bases may be modified by the addition of electrochemically active ions, i.e. protons or hydroxide ions, to form strongly acidic or strongly basic non-aqueous electrolytes.

As discussed above, fuel processor 18 may utilize any suitable hydrogen-producing mechanism including steam reforming, autothermal reforming, electrolysis, irradiation, pyrolysis and catalytic partial oxidation. An example of a suitable fuel processor 18 is a steam reformer. An example of a suitable steam

reformer is shown in Fig. 4 and indicated generally at 130. Reformer 130 includes a reforming, or hydrogen-producing, region 132 that includes a steam reforming catalyst 134. Alternatively, reformer 130 may be an autothermal reformer that includes an autothermal reforming catalyst. In reforming region 132, a reformate stream 136 is produced from the water and carbon-containing feedstock forming feed stream 20. The reformate stream typically contains hydrogen gas and impurities, and therefore is delivered to a separation region, or purification region, 138, where the hydrogen gas is purified. In separation region 138, the hydrogen-containing stream is separated into one or more byproduct streams, which are collectively illustrated at 140, and a hydrogen-rich stream 142 by any suitable pressure-driven separation process. In Fig. 4, hydrogen-rich stream 142 is shown forming stream 17.

An example of a suitable structure for use in separation region 138 is a membrane module 144, which contains one or more hydrogen permeable metal membranes 146. Examples of suitable membrane modules formed from a plurality of hydrogen-selective metal membranes are disclosed in U.S. Patent No. 6,221,117, the complete disclosure of which is hereby incorporated by reference in its entirety for all purposes. In that patent, a plurality of generally planar membranes are assembled together into a membrane module having flow channels through which an impure gas stream is delivered to the membranes, a purified gas stream is harvested from the membranes and a byproduct stream is removed from the membranes. Gaskets, such as flexible graphite gaskets, are used to achieve seals around the feed and permeate flow channels. Also disclosed in the above-identified application are tubular hydrogen-selective membranes, which also may be used. Other suitable membranes and membrane modules are disclosed in U.S. Patent Application Serial No. 09/618,866, which was filed on July 19, 2000 and is entitled "Hydrogen-Permeable Metal Membrane and Method for Producing the Same," the complete disclosure of which is hereby incorporated by reference in its entirety for all purposes. Other suitable fuel processors are also disclosed in the incorporated patent applications.

The thin, planar, hydrogen-permeable membranes are preferably composed of palladium alloys, most especially palladium with 35 wt% to 45 wt% copper. These membranes, which also may be referred to as hydrogen-selective membranes, are typically formed from a thin foil that is approximately 0.001 inches thick. It is within the scope of the present invention, however, that the membranes

may be formed from hydrogen-selective metals and metal alloys other than those discussed above, hydrogen-permeable and selective ceramics, or carbon compositions. The membranes may have thicknesses that are larger or smaller than discussed above. For example, the membrane may be made thinner, with  
5 commensurate increase in hydrogen flux. The hydrogen-permeable membranes may be arranged in any suitable configuration, such as arranged in pairs around a common permeate channel as is disclosed in the incorporated patent applications. The hydrogen permeable membrane or membranes may take other configurations as well, such as tubular configurations, which are disclosed in the incorporated patents.

10 Another example of a suitable pressure-separation process for use in separation region 138 is pressure swing absorption (PSA). In a pressure swing adsorption (PSA) process, gaseous impurities are removed from a stream containing hydrogen gas. PSA is based on the principle that certain gases, under the proper conditions of temperature and pressure, will be adsorbed onto an adsorbent material  
15 more strongly than other gases. Typically, it is the impurities that are adsorbed and thus removed from reformat stream 136. The success of using PSA for hydrogen purification is due to the relatively strong adsorption of common impurity gases (such as CO, CO<sub>2</sub>, hydrocarbons including CH<sub>4</sub>, and N<sub>2</sub>) on the adsorbent material. Hydrogen adsorbs only very weakly and so hydrogen passes through the adsorbent  
20 bed while the impurities are retained on the adsorbent. Impurity gases such as NH<sub>3</sub>, H<sub>2</sub>S, and H<sub>2</sub>O adsorb very strongly on the adsorbent material and are therefore removed from stream 136 along with other impurities. If the adsorbent material is going to be regenerated and these impurities are present in stream 136, separation region 138 preferably includes a suitable device that is adapted to remove these  
25 impurities prior to delivery of stream 136 to the adsorbent material because it is more difficult to desorb these impurities.

Adsorption of impurity gases occurs at elevated pressure. When the pressure is reduced, the impurities are desorbed from the adsorbent material, thus regenerating the adsorbent material. Typically, PSA is a cyclic process and requires  
30 at least two beds for continuous (as opposed to batch) operation. Examples of suitable adsorbent materials that may be used in adsorbent beds are activated carbon and zeolites, especially 5 Å (5 angstrom) zeolites. The adsorbent material is commonly in the form of pellets and it is placed in a cylindrical pressure vessel

utilizing a conventional packed-bed configuration. It should be understood, however, that other suitable adsorbent material compositions, forms and configurations may be used.

Reformer 130 may, but does not necessarily, further include a polishing region 148, such as shown in Fig. 5. Polishing region 148 receives hydrogen-rich stream 142 from separation region 138 and further purifies the stream by reducing the concentration of, or removing, selected compositions therein. For example, when stream 142 is intended for use in a fuel cell stack, such as stack 12, compositions that may damage the fuel cell stack, such as carbon monoxide and carbon dioxide, may be removed from the hydrogen-rich stream. The concentration of carbon monoxide should be less than 10 ppm (parts per million) to prevent the control system from isolating the fuel cell stack. Preferably, the system limits the concentration of carbon monoxide to less than 5 ppm, and even more preferably, to less than 1 ppm. The concentration of carbon dioxide may be greater than that of carbon monoxide. For example, concentrations of less than 25% carbon dioxide may be acceptable. Preferably, the concentration is less than 10%, even more preferably, less than 1%. Especially preferred concentrations are less than 50 ppm. It should be understood that the acceptable minimum concentrations presented herein are illustrative examples, and that concentrations other than those presented herein may be used and are within the scope of the present invention. For example, particular users or manufacturers may require minimum or maximum concentration levels or ranges that are different than those identified herein.

Region 148 includes any suitable structure for removing or reducing the concentration of the selected compositions in stream 142. For example, when the product stream is intended for use in a PEM fuel cell stack or other device that will be damaged if the stream contains more than determined concentrations of carbon monoxide or carbon dioxide, it may be desirable to include at least one methanation catalyst bed 150. Bed 150 converts carbon monoxide and carbon dioxide into methane and water, both of which will not damage a PEM fuel cell stack. Polishing region 148 may also include another hydrogen-producing device 152, such as another reforming catalyst bed, to convert any unreacted feedstock into hydrogen gas. In such an embodiment, it is preferable that the second reforming catalyst bed is upstream

from the methanation catalyst bed so as not to reintroduce carbon dioxide or carbon monoxide downstream of the methanation catalyst bed.

Steam reformers typically operate at temperatures in the range of 200° C and 700° C, and at pressures in the range of 50 psi and 1000 psi, although  
5 temperatures outside of this range are within the scope of the invention, such as depending upon the particular type and configuration of fuel processor being used. Any suitable heating mechanism or device may be used to provide this heat, such as a heater, burner, combustion catalyst, or the like. The heating assembly may be external the fuel processor or may form a combustion chamber that forms part of the  
10 fuel processor. The fuel processing system, fuel cell system, an external source, or a combination thereof, may provide the fuel for the heating assembly.

It is within the scope of the present invention that any other type of fuel processor may be used, such as those discussed above, and that any other suitable source of hydrogen gas may be used. Examples of other sources of hydrogen include  
15 a storage device, such as a storage tank or hydride bed, containing a stored supply of hydrogen gas.

Although discussed above in terms of a PEM fuel cell, it is within the scope of the present invention that non-aqueous Bronsted-Lowry electrolyte 60 may be implemented with other forms of fuel cells. For example, the system may be  
20 implemented with other low and moderate temperature fuel cells, such as alkaline fuel cells (AFCs) or direct methanol fuel cells (DMFCs).

#### Industrial Applicability

The present invention is applicable to energy-producing systems, and more particularly to fuel cells and fuel cell systems.

25 It is believed that the disclosure set forth above encompasses multiple distinct inventions with independent utility. While each of these inventions has been disclosed in its preferred form, the specific embodiments thereof as disclosed and illustrated herein are not to be considered in a limiting sense as numerous variations are possible. The subject matter of the inventions includes all novel and non-obvious  
30 combinations and subcombinations of the various elements, features, functions and/or properties disclosed herein. Similarly, where the claims recite “a” or “a first” element or the equivalent thereof, such claims should be understood to include incorporation

of one or more such elements, neither requiring nor excluding two or more such elements.

It is believed that the following claims particularly point out certain combinations and subcombinations that are directed to one of the disclosed inventions and are novel and non-obvious. Inventions embodied in other combinations and subcombinations of features, functions, elements and/or properties may be claimed through amendment of the present claims or presentation of new claims in this or a related application. Such amended or new claims, whether they are directed to a different invention or directed to the same invention, whether different, broader, narrower or equal in scope to the original claims, are also regarded as included within the subject matter of the inventions of the present disclosure.



**I CLAIM:**

1. A fuel cell, comprising:  
an anode region adapted to receive a hydrogen stream;  
a cathode region adapted to receive a stream containing oxygen; and  
an electrolytic barrier separating the anode region from the cathode region, wherein the electrolytic barrier includes an acidic or basic non-aqueous electrolyte, wherein the non-aqueous electrolytic has an acid ionization constant ( $K_a$ ) greater than  $5 \times 10^{-6}$  at 25° C if the non-aqueous electrolyte is an acid and a base ionization constant ( $K_b$ ) greater than  $5 \times 10^{-6}$  25° C if the non-aqueous electrolyte is a base; and further wherein the fuel cell has an operating temperature of less than 300° C.
2. The fuel cell of claim 1, wherein the non-aqueous electrolyte is an acid.
3. The fuel cell of claim 1, wherein the non-aqueous electrolyte is a base.
4. The fuel cell of claim 1, wherein the non-aqueous electrolyte includes an organic ionic liquid.
5. The fuel cell of claim 1, wherein the non-aqueous electrolyte includes sulfuric acid.
6. The fuel cell of claim 1, wherein the non-aqueous electrolyte includes a mixture of a solvent combined with an acidic or basic solute.
7. The fuel cell of claim 6, wherein the solvent includes an organic ionic liquid.
8. The fuel cell of claim 6, wherein the solvent is selected from the group consisting of: a hydrocarbon, a polyalcohol, a polyether, an organic ionic liquid, and an organic liquid with a normal boiling point greater than 90° C.

9. The fuel cell of claim 6, wherein the solvent is selected from the group consisting of: hexadecane, decane, kerosene, propylene carbonate, propylene glycol, o-dichlorobenzene, and 1,3,5-trichlorobenzene.

10. The fuel cell of claim 6, wherein the acidic solute is selected from the group consisting of: hydrogen hexafluorophosphate, hydrogen tetraphynylborate, sulfuric acid, and perchloric acid.

11. The fuel cell of claim 6, wherein the basic solute is a tetraalkylammonium hydroxide.

12. The fuel cell of claim 1, wherein the non-aqueous electrolyte has a  $K_a$  greater than  $1 \times 10^{-2}$  at  $25^\circ \text{C}$  if the electrolyte is an acid and a  $K_b$  greater than  $1 \times 10^{-2}$   $25^\circ \text{C}$  if the electrolyte is a base.

13. The fuel cell of claim 1, wherein the non-aqueous electrolyte has a  $K_a$  greater than  $1 \times 10^{-4}$  at  $25^\circ \text{C}$  if the electrolyte is an acid and a  $K_b$  greater than  $1 \times 10^{-4}$   $25^\circ \text{C}$  if the electrolyte is a base.

14. The fuel cell of claim 1, wherein the non-aqueous electrolyte contains less than 5% water on a molar basis.

15. The fuel cell of claim 1, wherein the boiling point of the non-aqueous electrolyte is at least  $90^\circ \text{C}$ .

16. The fuel cell of claim 1, wherein the boiling point of the non-aqueous electrolyte is at least  $130^\circ \text{C}$ .

17. The fuel cell of claim 1, wherein the boiling point of the non-aqueous electrolyte is at least  $150^\circ \text{C}$ .

18. The fuel cell of claim 1, wherein the melting point of the non-aqueous electrolyte is less than  $5^\circ \text{C}$ .

19. The fuel cell of claim 1, wherein the melting point of the non-aqueous electrolyte is less than 0° C.

20. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is between 0° C and 300° C.

21. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is between 15° C and 200° C.

22. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is between 15° C and 150° C.

23. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is between 0° C and 100° C.

24. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is above 100° C.

25. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is between 150° C and 300° C.

26. The fuel cell of claim 1, wherein the operating temperature of the fuel cell is above the boiling point of water at the operating conditions of the fuel cell.

27. A fuel cell system, comprising:  
a fuel processor comprising:  
a hydrogen-producing region adapted to receive a feed stream that includes a carbon-containing feedstock and to produce therefrom a mixed gas stream containing hydrogen gas and other gasses; and  
a separation region adapted to receive the mixed gas stream and to separate the mixed gas stream into an at least substantially pure hydrogen stream and a byproduct stream containing substantially the other gasses;  
a fuel cell stack containing at least one fuel cell comprising:  
an anode region adapted to receive at least a portion of the at least substantially pure hydrogen stream;  
a cathode region adapted to receive a stream containing oxygen; and  
an electrolytic barrier separating the cathode region and the anode region, wherein the electrolytic barrier includes a non-aqueous electrolyte that is either acidic or basic, and further wherein the non-aqueous electrolyte has a  $K_a$  greater than  $5 \times 10^{-6}$  at  $25^\circ \text{C}$  if the non-aqueous electrolyte is acidic, or a  $K_b$  greater than  $5 \times 10^{-6}$  at  $25^\circ \text{C}$  if the non-aqueous electrolyte is basic.
28. The fuel cell system of claim 27, wherein the separation region includes at least one hydrogen-selective membrane.
29. The fuel cell system of claim 27, wherein the hydrogen-producing region includes a reforming region containing a reforming catalyst.
30. The fuel cell system of claim 27, wherein the fuel processor includes a polishing catalyst bed adapted to increase the purity of the at least substantially pure hydrogen stream prior to delivery of the stream to the fuel cell stack.
31. The fuel cell system of claim 27, wherein the non-aqueous electrolyte has a  $K_a$  greater than  $1 \times 10^{-2}$  at  $25^\circ \text{C}$  if the electrolyte is acidic and a  $K_b$  greater than  $1 \times 10^{-2}$  at  $25^\circ \text{C}$  if the electrolyte is basic.

32. The fuel cell system of claim 27, wherein the non-aqueous electrolyte has a  $K_a$  greater than  $1 \times 10^{-4}$  at 25° C if the electrolyte is acidic and a  $K_b$  greater than  $1 \times 10^{-4}$  25° C if the electrolyte is basic.

33. The fuel cell system of claim 27, wherein the non-aqueous electrolyte is an acid.

34. The fuel cell system of claim 27, wherein the non-aqueous electrolyte is a base.

35. The fuel cell system of claim 27, wherein the non-aqueous electrolyte includes an organic ionic liquid.

36. The fuel cell system of claim 27, wherein the non-aqueous electrolyte includes a mixture of a solvent combined with an acidic or basic solute.

37. The fuel cell system of claim 27, wherein the solvent includes an organic ionic liquid.

38. The fuel cell system of claim 27, wherein the non-aqueous electrolyte contains less than 5% water on a molar basis.

39. The fuel cell system of claim 27, wherein the boiling point of the non-aqueous electrolyte is at least 90° C.

40. The fuel cell system of claim 27, wherein the boiling point of the non-aqueous electrolyte is at least 130° C.

41. The fuel cell system of claim 27, wherein the boiling point of the non-aqueous electrolyte is at least 150° C.

42. The fuel cell system of claim 27, wherein the melting point of the non-aqueous electrolyte is less than 5° C.

43. The fuel cell system of claim 27, wherein the melting point of the non-aqueous electrolyte is less than 0° C.

44. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is between 0° C and 300° C.

45. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is between 15° C and 200° C.

46. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is between 15° C and 150° C.

47. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is between 0° C and 100° C.

48. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is above 100° C.

49. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is between 150° C and 300° C.

50. The fuel cell system of claim 27, wherein the operating temperature of the fuel cell is above the boiling point of water at the operating conditions of the fuel cell.

51. A fuel cell system, comprising:
- a source of an anode feedstock, wherein the anode feedstock includes at least one composition that contains chemically bound hydrogen and which liberates protons at an anode of a fuel cell;
  - a fuel cell stack adapted to receive a stream containing the anode feedstock and containing at least one fuel cell comprising:
    - an anode region adapted to receive at least a portion of the stream containing the anode feedstock;
    - a cathode region adapted to receive a stream containing oxygen; and
    - an electrolytic barrier separating the cathode region and the anode region, wherein the electrolytic barrier includes a non-aqueous electrolyte that is either acidic or basic, and further wherein the non-aqueous electrolyte has a  $K_a$  greater than  $5 \times 10^{-6}$  at 25° C if the non-aqueous electrolyte is acidic, or a  $K_b$  greater than  $5 \times 10^{-6}$  25° C if the non-aqueous electrolyte is basic.
52. The fuel cell system of claim 51, wherein the anode feedstock includes hydrogen gas.
53. The fuel cell system of claim 51, wherein the anode feedstock includes methanol.
54. The fuel cell system of claim 51, wherein the anode feedstock includes hydrazine.
55. The fuel cell system of claim 51, wherein the anode feedstock includes formaldehyde.
56. The fuel cell system of claim 51, wherein the anode feedstock includes ethanol.
57. The fuel cell system of claim 51, wherein the source includes a storage tank.

58. The fuel cell system of claim 51, wherein the source includes a device adapted to produce the anode feedstock through a chemical reaction.

59. The fuel cell system of claim 51, wherein the source includes a fuel processor and the anode feedstock is at least substantially pure hydrogen gas.

60. The fuel cell system of claim 59, wherein the fuel processor is a steam reformer that includes a reforming catalyst.

61. The fuel cell system of claim 59, wherein the fuel processor is adapted to produce the anode feedstock by partial oxidation of a carbon-containing feedstock.

62. The fuel cell system of claim 59, wherein the fuel processor is adapted to produce the anode feedstock by electrolysis of water.

63. The fuel cell system of claim 59, wherein the fuel processor is adapted to produce the anode feedstock by irradiation of a carbon-containing feedstock.



64. A fuel cell system, comprising:

a fuel processor comprising:

a hydrogen-producing region adapted to receive a feed stream that includes a carbon-containing feedstock and to produce therefrom a mixed gas stream containing hydrogen gas and other gasses; and

a separation region adapted to receive the mixed gas stream and to separate the mixed gas stream into an at least substantially pure hydrogen stream and a byproduct stream containing substantially the other gasses;

a fuel cell stack containing at least one fuel cell comprising:

an anode region adapted to receive at least a portion of the at least substantially pure hydrogen stream;

a cathode region adapted to receive a stream containing oxygen; and

electrolytic means for separating the anode and the cathode regions.

Fig. 1

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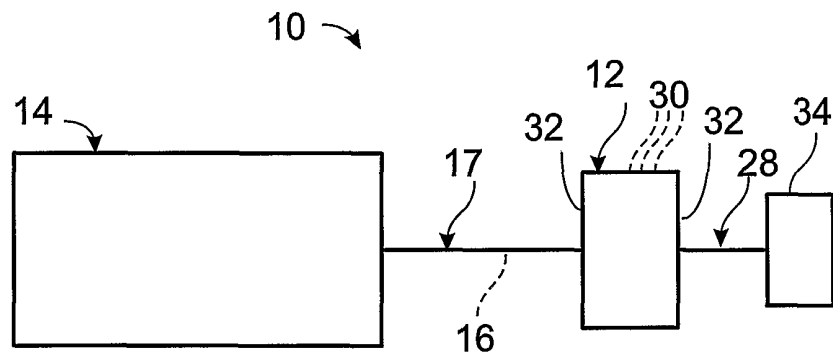


Fig. 2

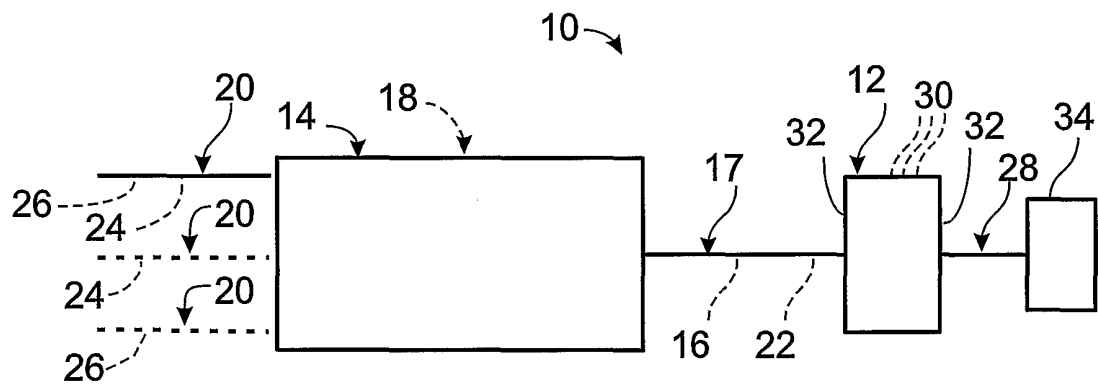


Fig. 3

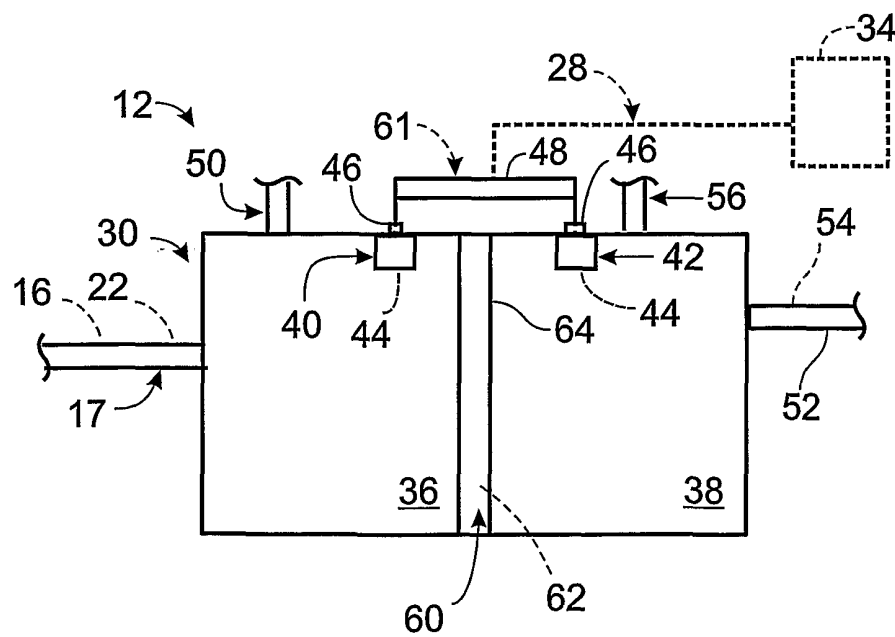


Fig. 4

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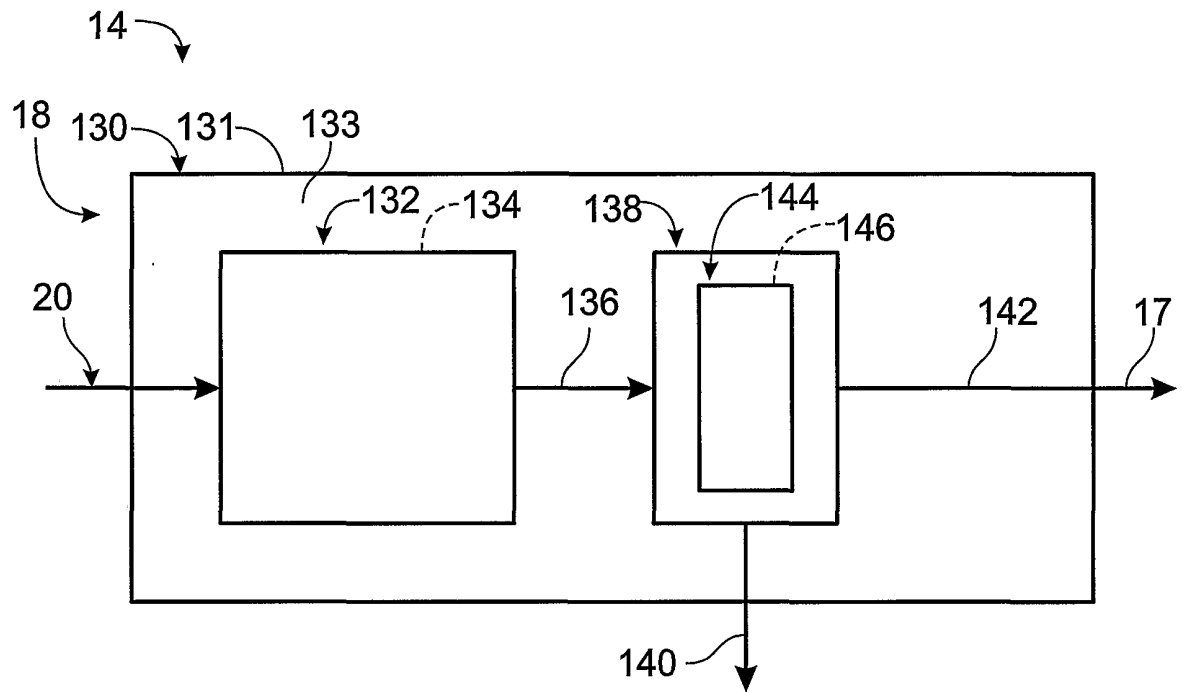
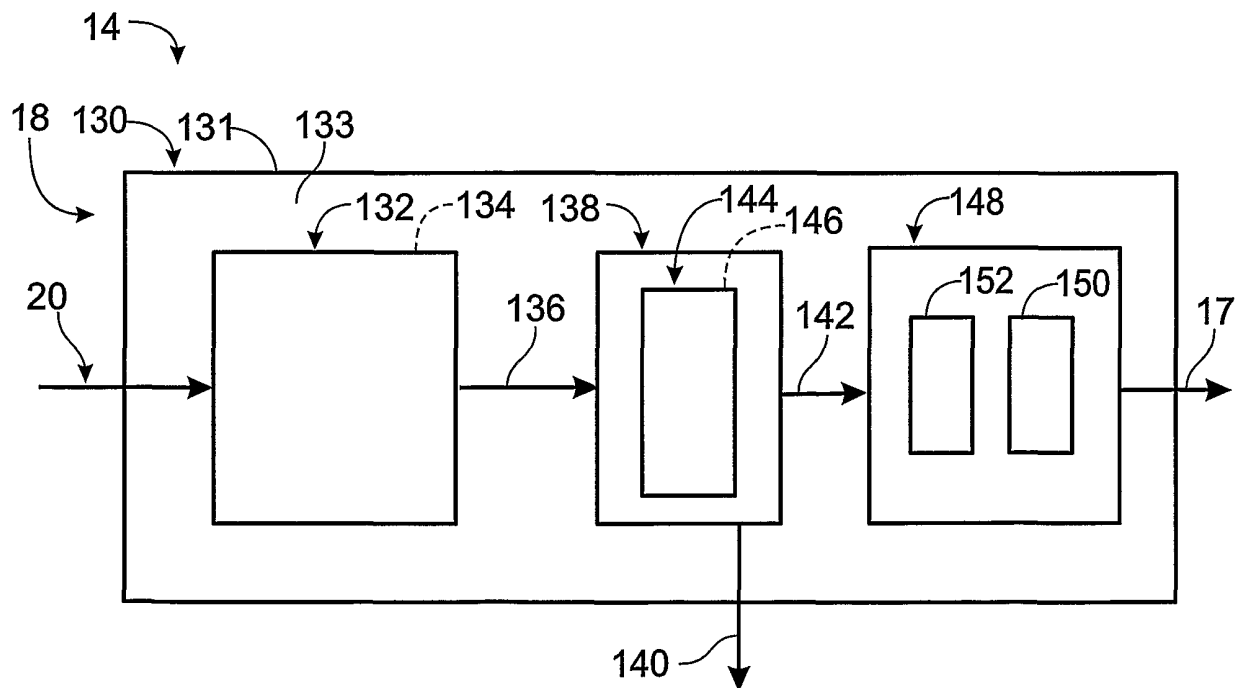


Fig. 5



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/18002

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/46, 13, 15, 41, 29; 48/76, 61, 127.5; 423/652, 655, 658.3; 422/211

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

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

WEST, EAST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y --- X	US 5,997,594 A (EDLUND et al) 7 December 1999, abstract, figure 1, col. 55-65.	27-30, 51-53, 57-62, 64 --- 44-45, 50, 56
Y --- X	US 3,877,989 A (WALDMAN et al) 15 April 1975, Figure 4, col. 3, lines 25-30 & lines 53-60, col. 5, lines 37-42, claim 1.	1-2, 4-7, 10, 27-30, 51-53, 57-62, 64 --- 33, 35-37

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

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 24 JULY 2001	Date of mailing of the international search report <b>14 SEP 2001</b>
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer DEBORAH THOMAS PARALEGAL SPECIALIST RAYMOND ALEJANDRO Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/18002

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ---- X	US 5,599,638 A (SURAMPUDI et al) 4 February 1997, col. 4, lines 54-60; col. 13, lines 64-67; col. 16, lines 27-35; col. 20, lines 21-25.	1-2, 4-7, 10, 14, 52-53, 57 ---- 55
Y,P ---- X,P	US 6,183,914 A (YAO et al) 6 February 2001, col. 1, lines 28-30; col. 8, lines 15-42.	1, 4, 6-7, 14 ---- 3, 8, 11
A	US RE33,149 A (PETROW et al) 16 January 1990.	1-2, 12-13

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/18002

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

H01M 08/14, 08/08, 08/00, 08/04, 04/86, 04/00; C10J 03/68; B01J 07/00, 08/02; C01B 03/32, 03/26, 03/12, 03/50

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

429/46, 13, 15, 41, 29; 48/76, 61, 127.5; 423/652, 655, 658.3; 422/211