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(54) **ELECTROLYSIS CELL COMPRISING SULFUR DIOXIDE-DEPOLARIZED ANODE AND METHOD OF USING THE SAME IN HYDROGEN GENERATION**

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(76) Inventors: **Simon G. Stone**, Arlington, MA (US); **Lawrence J. Gestaut**, Hopkinton, MA (US)

(57) **ABSTRACT**

Electrolysis cell and method of using the same in hydrogen generation. According to one embodiment, the electrolysis cell includes a frame having an interior. A proton exchange membrane (PEM) is disposed within the frame to divide the interior into two chambers. An anode in the form of a gas diffusion electrode is disposed within the interior of the frame and is spaced apart from the PEM, the space between the anode and the PEM being filled with an aqueous sulfuric acid. A cathode is disposed within the interior of the frame and is ionically coupled to the PEM. In use, gaseous sulfur dioxide is delivered to the side of the anode facing away from the sulfuric acid solution, and a current is supplied to the electrolysis cell. Consequently, sulfur dioxide is oxidized at the anode, and molecular hydrogen is generated at the cathode.

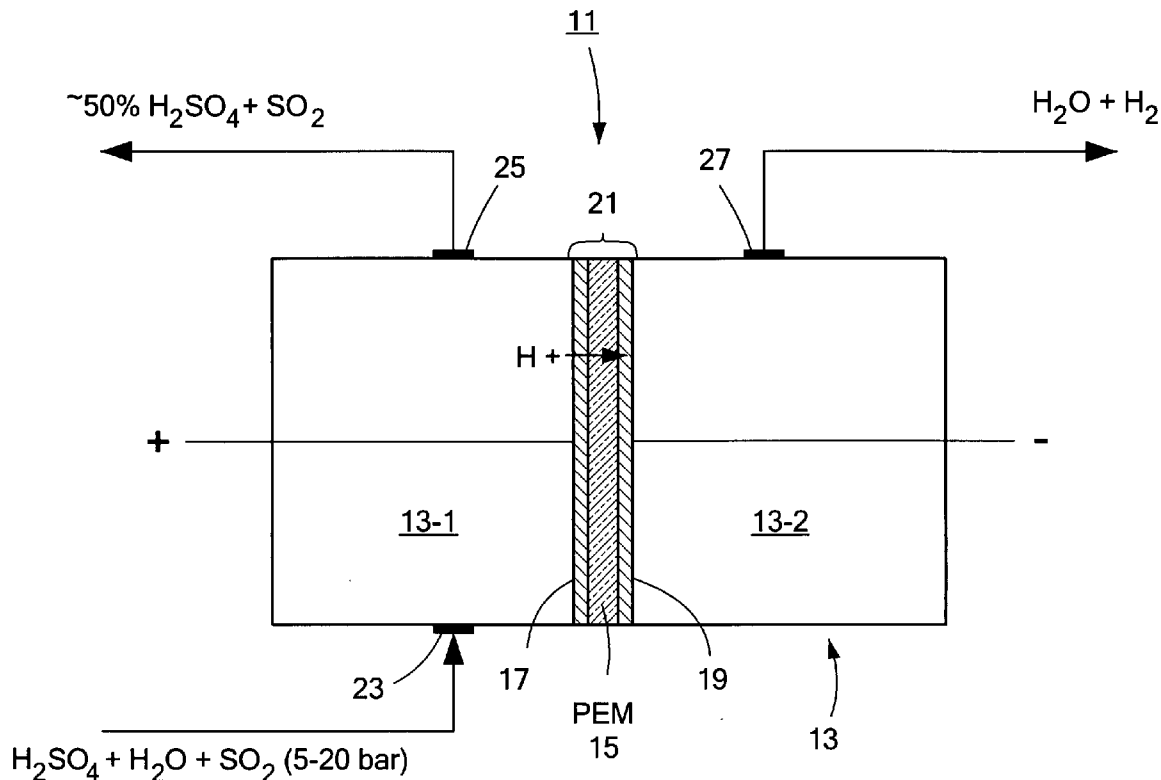
Correspondence Address:
KRIEGSMAN & KRIEGSMAN
30 TURNPIKE ROAD, SUITE 9
SOUTHBOROUGH, MA 01772 (US)

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(60) Provisional application No. 60/963,478, filed on Aug. 3, 2007.



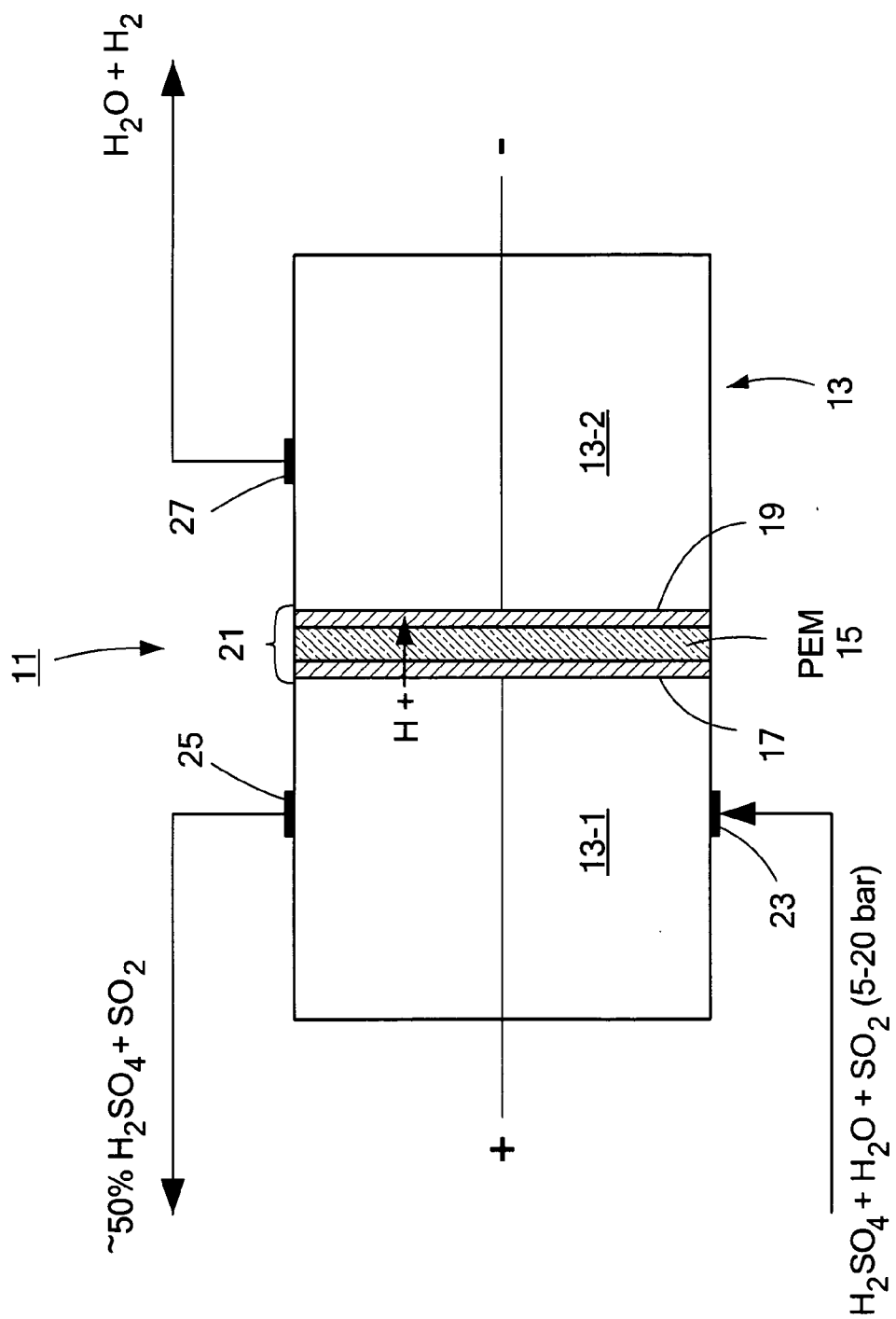


FIG. 1

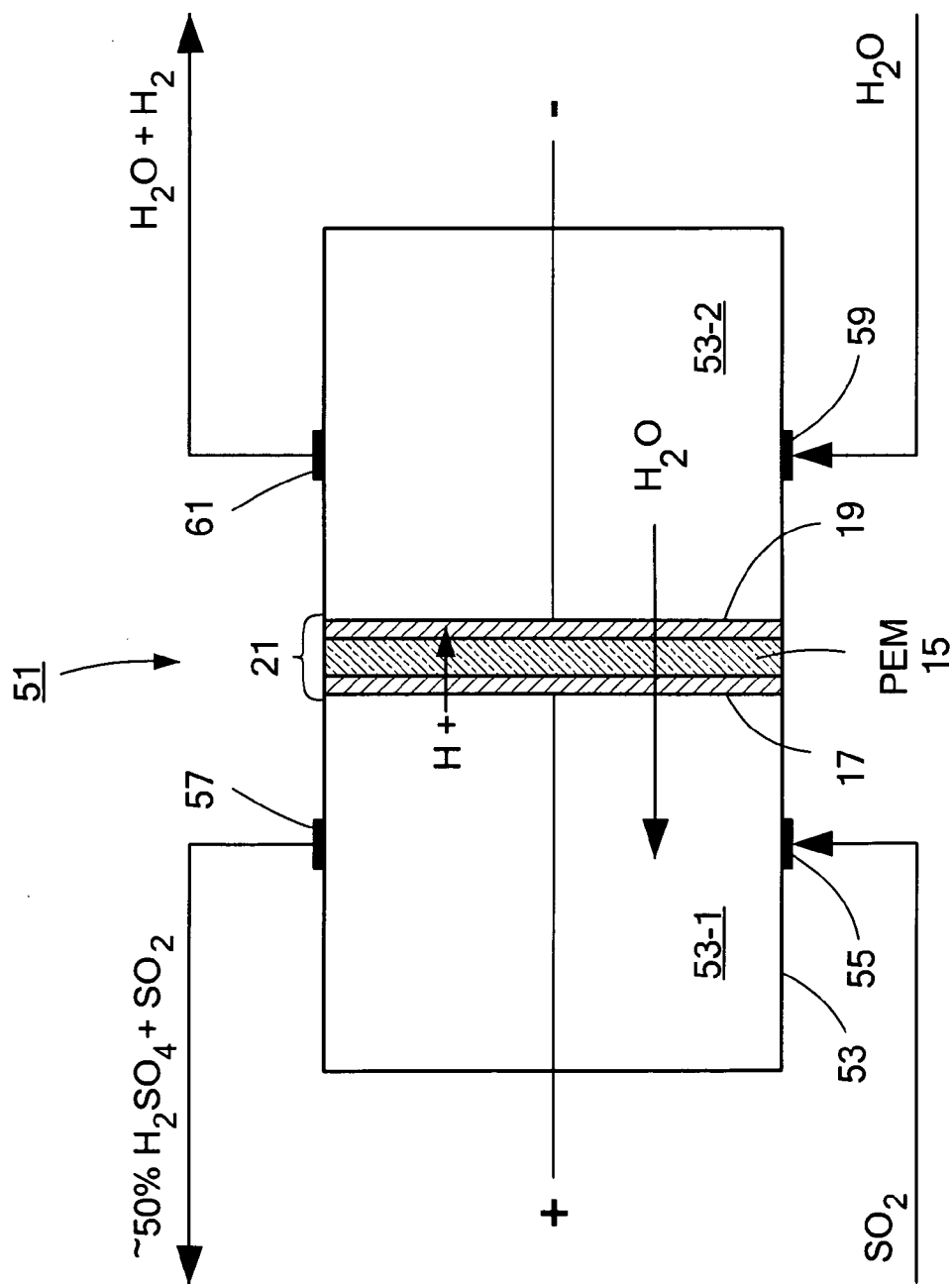


FIG. 2

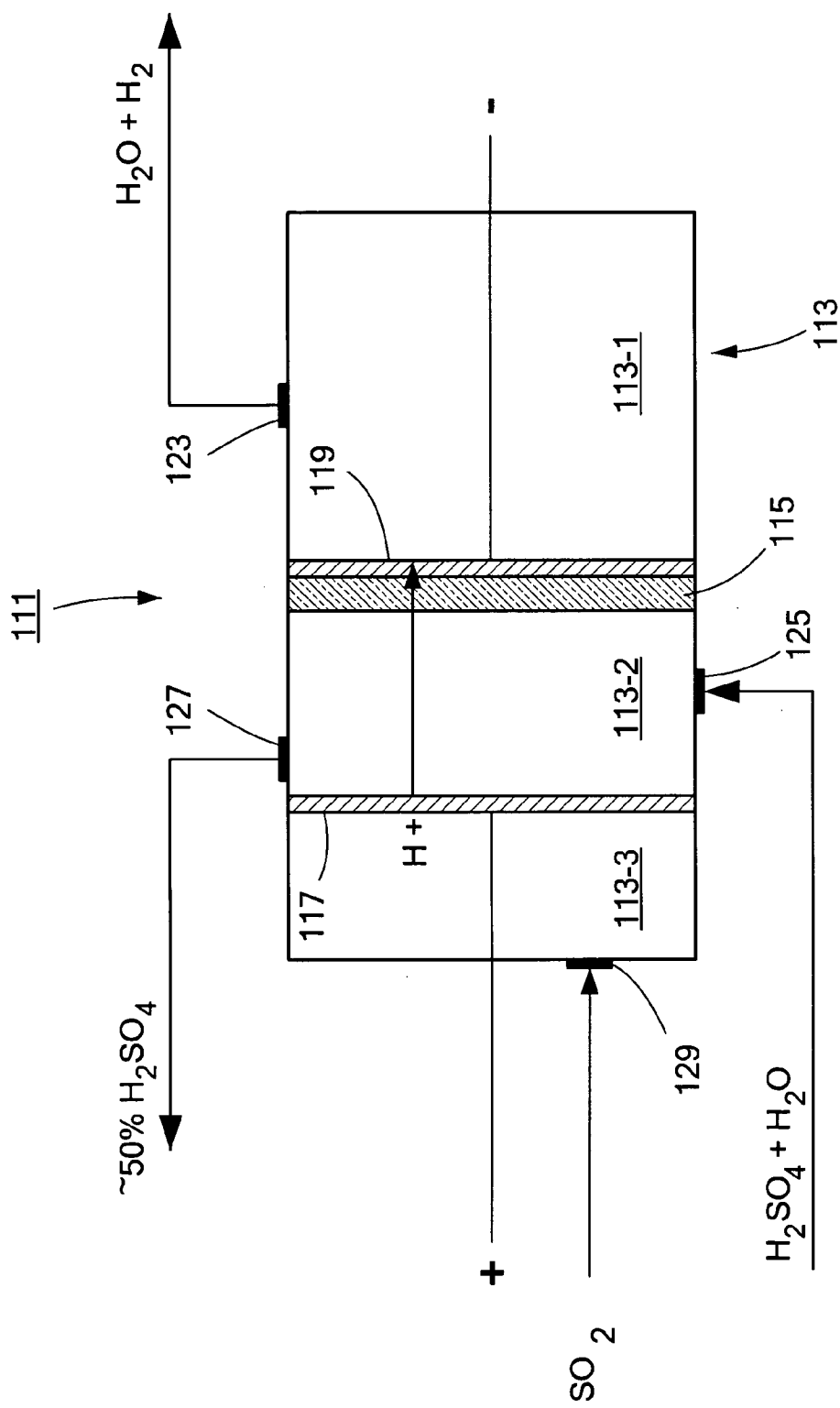


FIG. 3

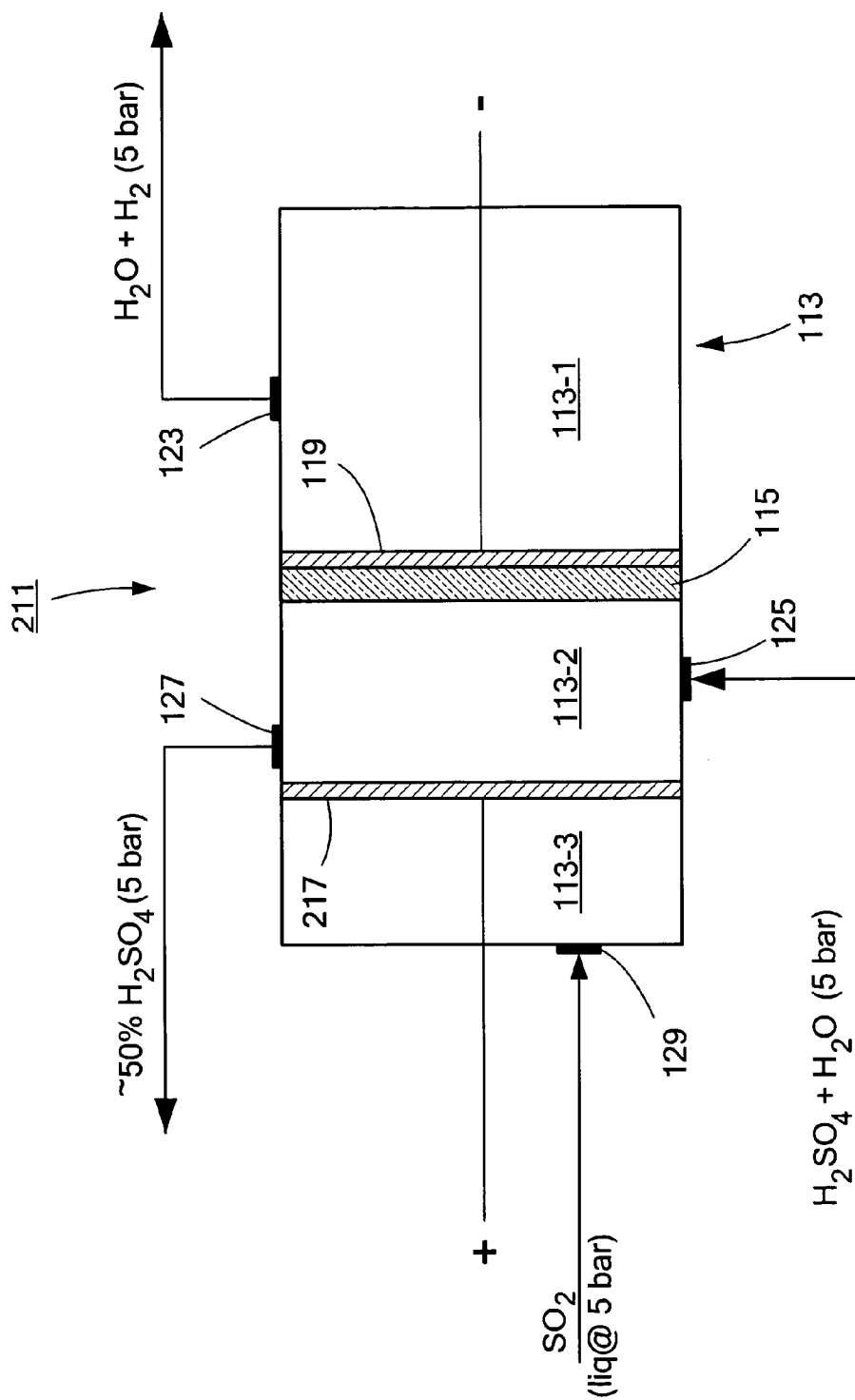


FIG. 4

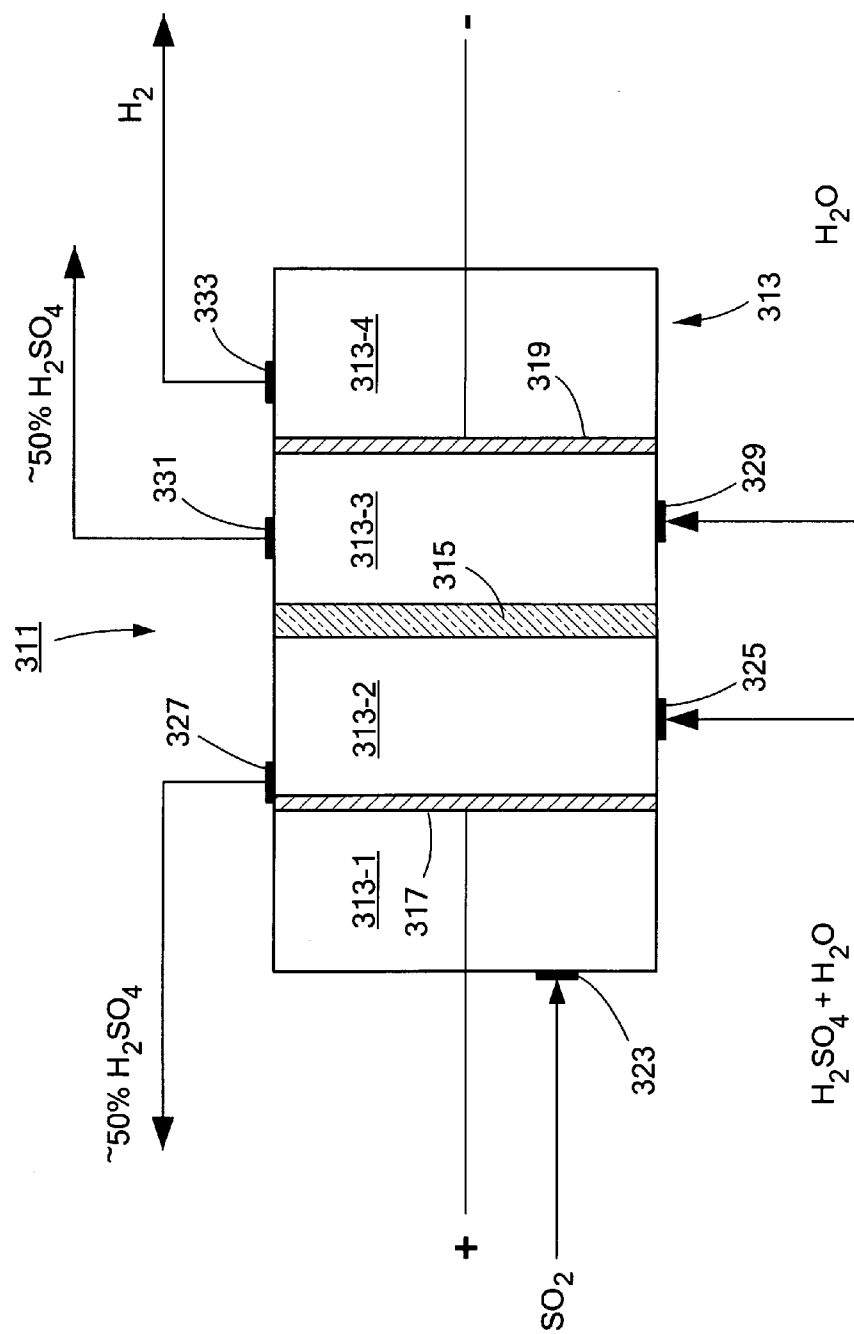


FIG. 5

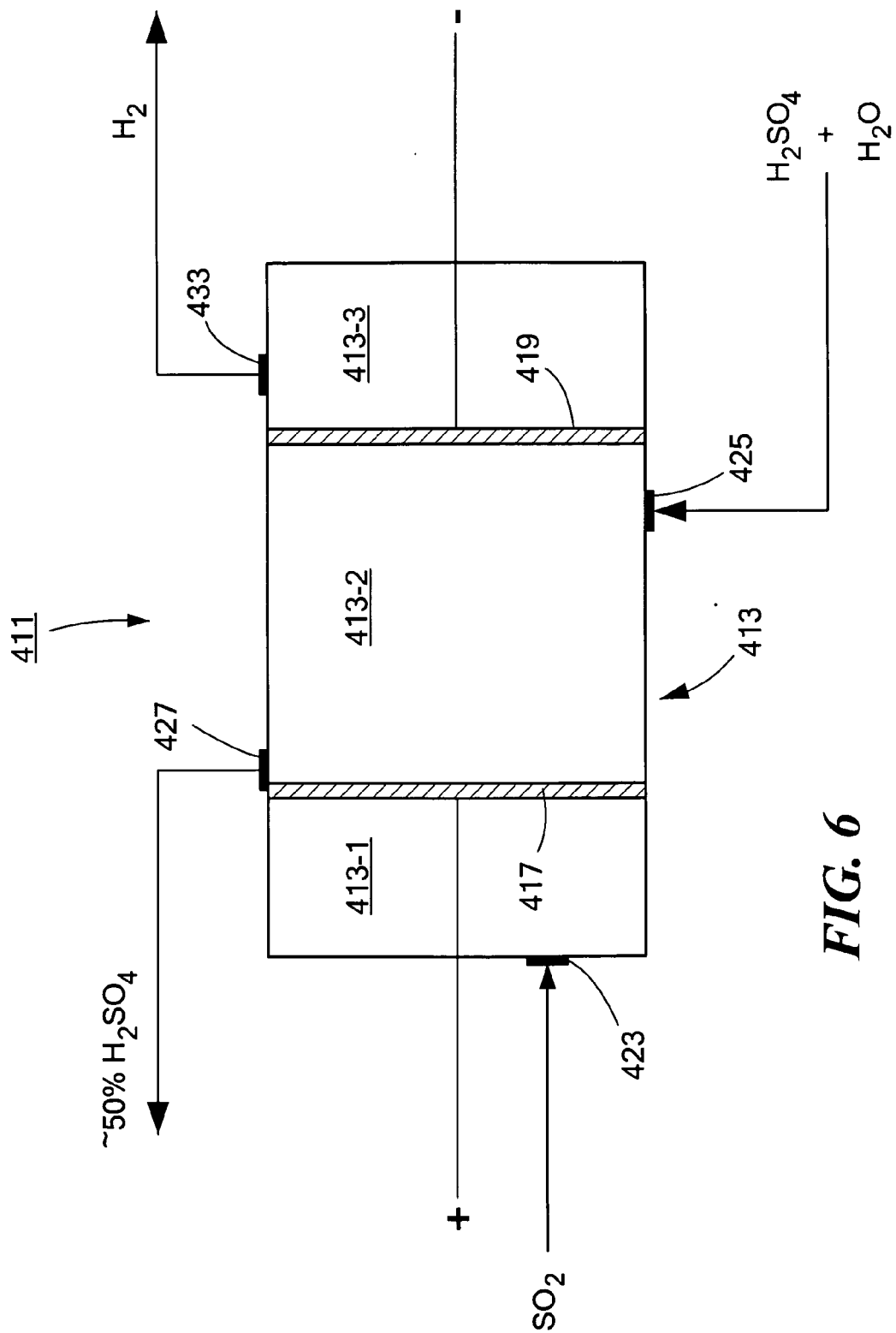


FIG. 6

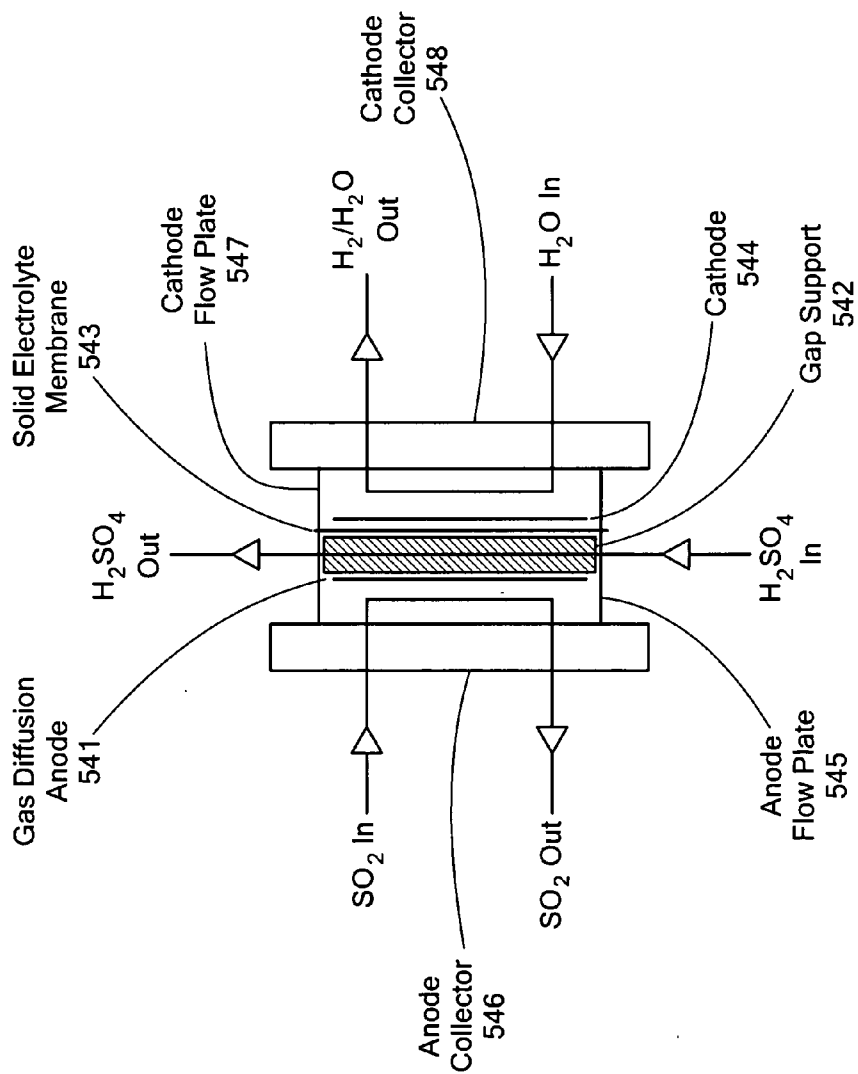


FIG. 7

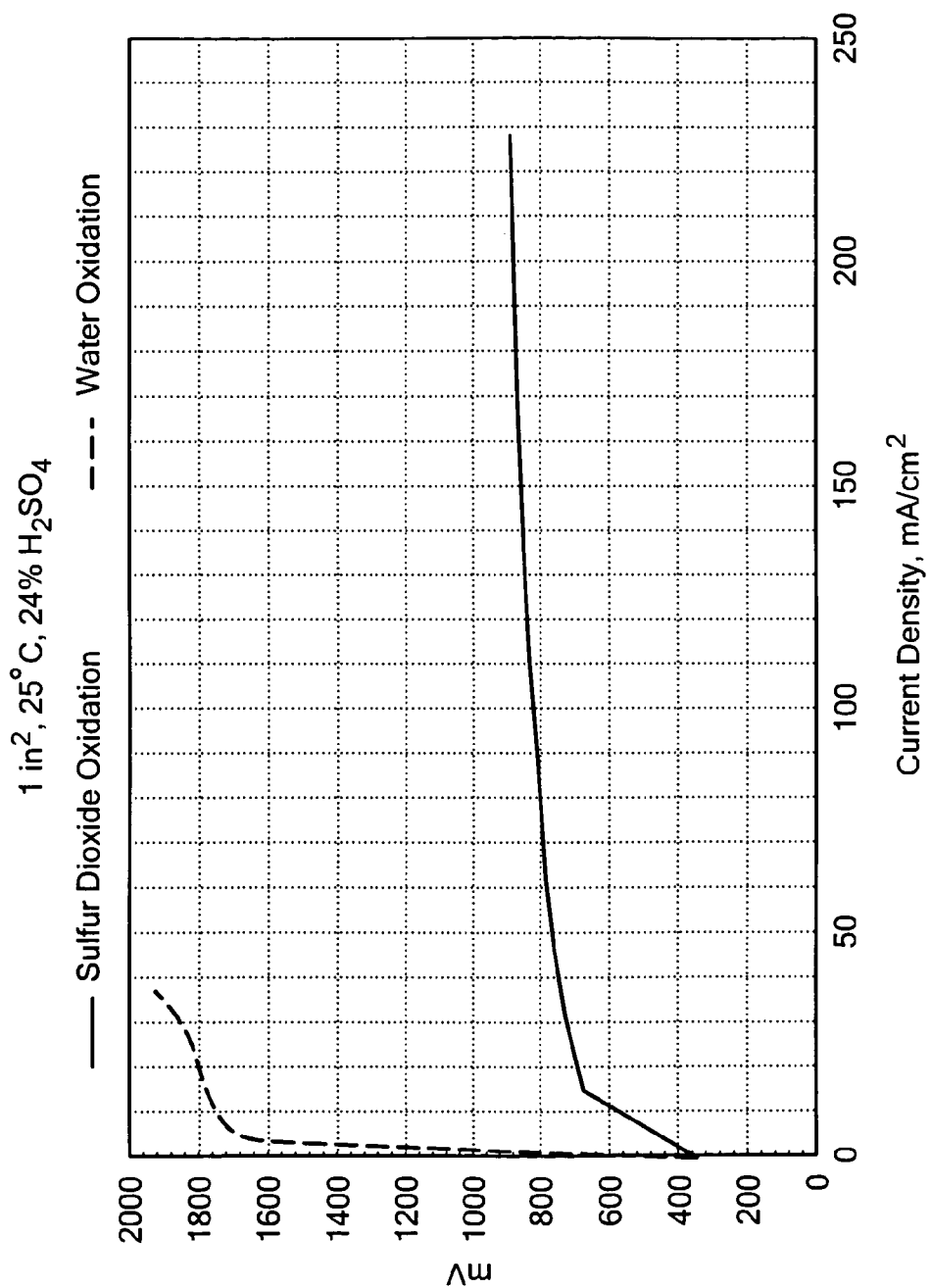


FIG. 8

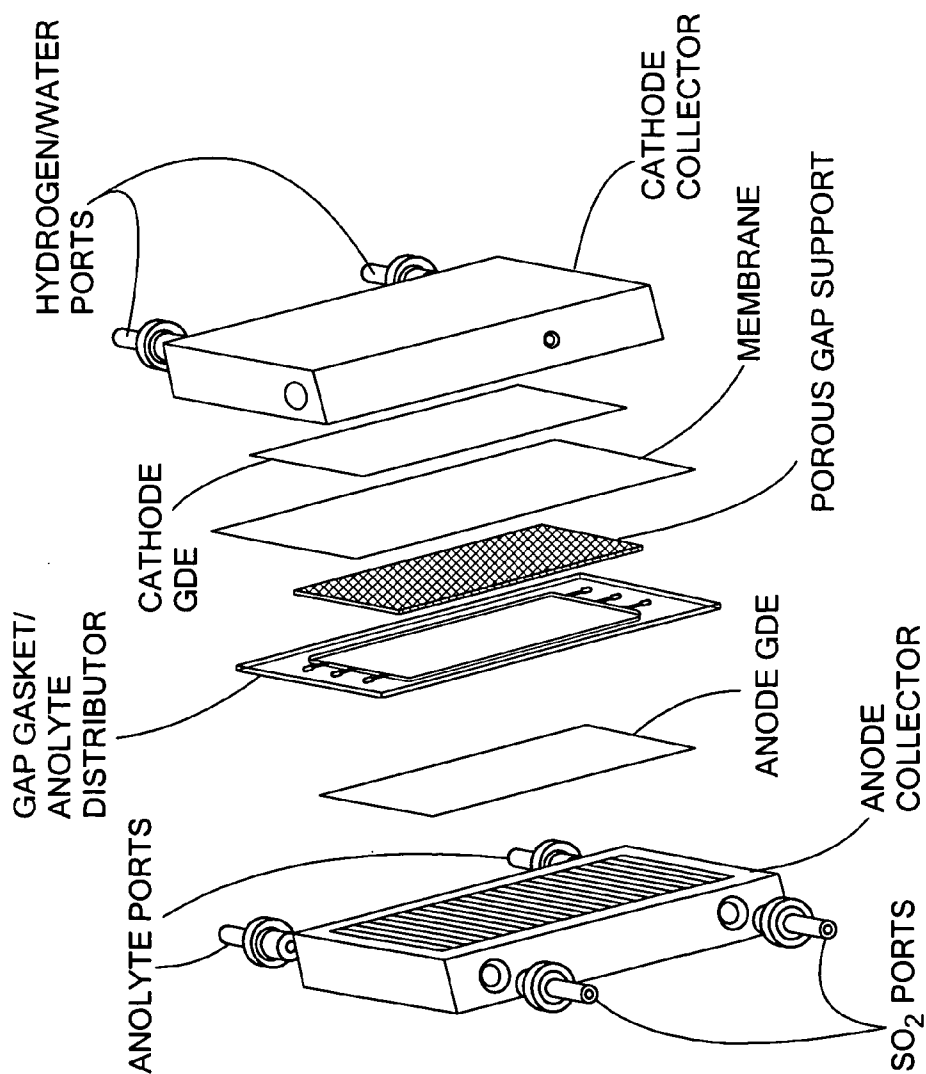


FIG. 9(a)

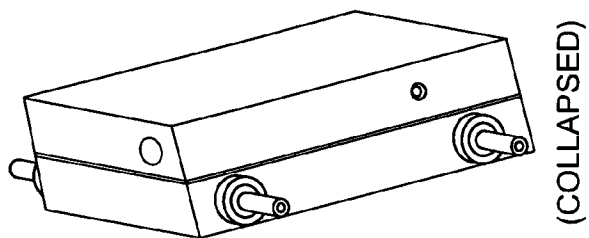


FIG. 9(b)

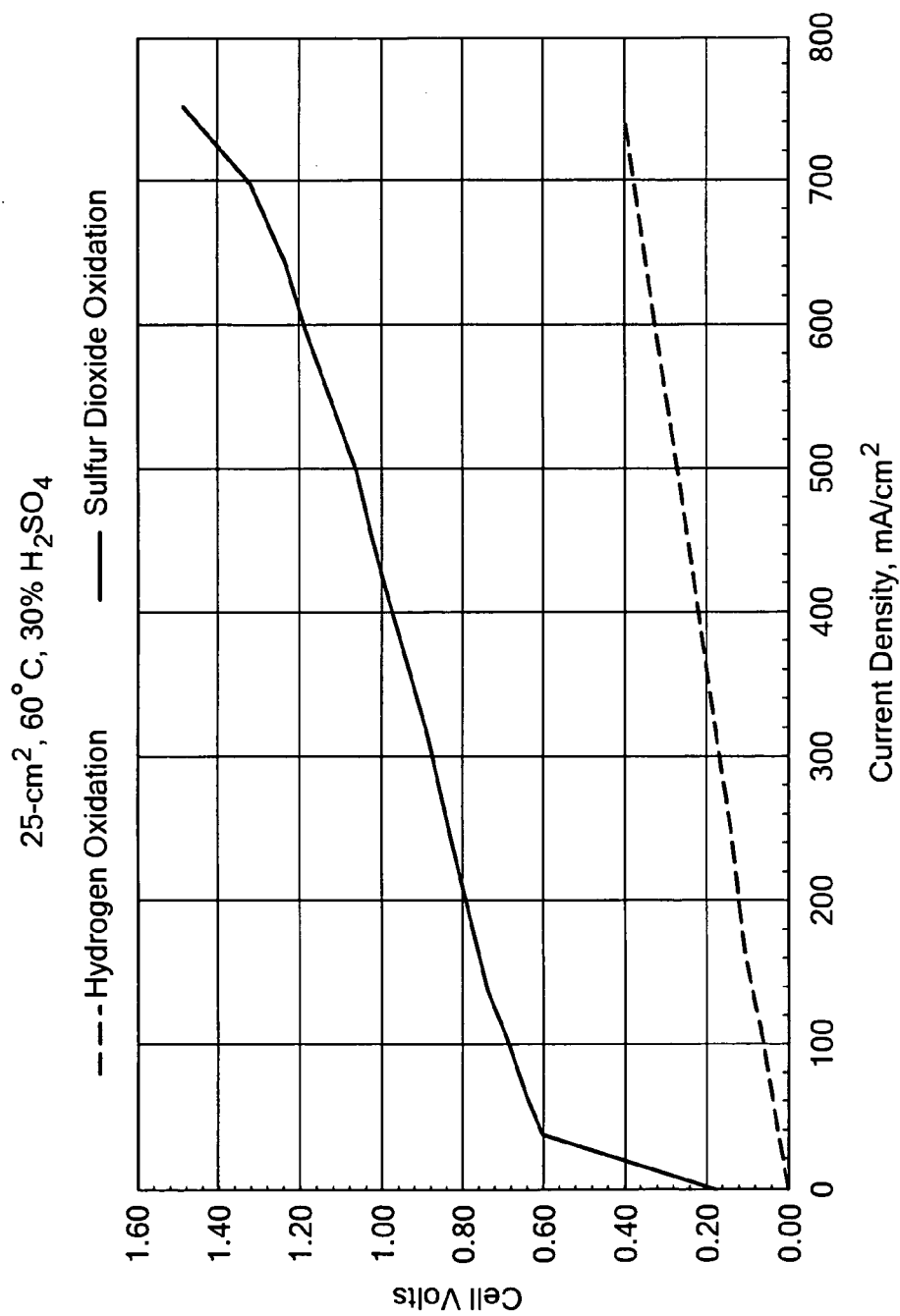


FIG. 10

**ELECTROLYSIS CELL COMPRISING
SULFUR DIOXIDE-DEPOLARIZED ANODE
AND METHOD OF USING THE SAME IN
HYDROGEN GENERATION**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. 119(e) of U.S. Provisional Patent Application No. 60/963,478, filed Aug. 3, 2007, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates generally to electrolysis cells and relates more particularly to a novel electrolysis cell comprising a sulfur dioxide-depolarized anode and to a method of using said electrolysis cell to generate molecular hydrogen from water.

[0003] As the availability of petroleum and natural gas reserves has diminished and as concerns of global climate change have deepened, interest in exploring alternative sources of energy and fuels has grown. Example of such alternative sources of energy include hydroelectric, nuclear, photovoltaic, wind, and geothermal. Although these alternative sources of energy hold varying degrees of promise as new or expanded supplies, none matches the ability of hydrocarbon fuels to serve as easily storable and transportable sources of energy. Therefore, it would be desirable to develop methods by which energy from the above-referenced sources could be stored until required. Examples of vehicles for storing such energy have included batteries, flywheels, and pumped water systems. Nevertheless, the most promising method for storing such energy would appear to be storing the energy in the form of molecular hydrogen, either as a compressed gas or as a cryogenic liquid. However, in order for it to be practical to store energy in the form of molecular hydrogen, there must be an efficient method for producing molecular hydrogen for subsequent storage.

[0004] Current nuclear reactors typically utilize water as a heat transfer medium, but future reactors, referred to as Generation IV, will operate at higher temperatures and involve the use of a gas as a coolant. Such high temperature gas-cooled (HTGC) reactors are capable of utilizing novel processes to store the thermal energy of the heated gas, expected to be helium, in the form of molecular hydrogen. According to one such process, which is sometimes referred to in the art as "the sulfur-iodine process," the thermal energy of the heated helium gas from the nuclear reactor is initially used in the thermal decomposition of sulfuric acid, which decomposition is represented as follows:



[0005] The sulfur trioxide of above Reaction (1) is then decomposed as follows:



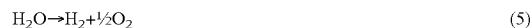
[0006] The sulfur dioxide of above Reaction (2) is then used to reduce molecular iodine as follows:



[0007] Lastly, the hydrogen iodide of above Reaction (3) is decomposed at an elevated temperature as follows:



[0008] The net reaction of above Reactions (1) through (4) is as follows (with the sulfuric acid and iodine reactants being regenerated in Reactions (3) and (4), respectively):



[0009] Therefore, as can be seen, the above-described sulfur-iodine process uses thermal energy from a nuclear reaction to store energy in the form of molecular hydrogen. Unfortunately, however, the sulfur-iodine process has not fully realized its potential as a method for storing energy in the form of molecular hydrogen. This is largely due to difficulties encountered with the iodine reactions of the process.

[0010] An alternative process to the sulfur-iodine process is a process sometimes referred to in the art as "the hybrid sulfur process." As seen below, the hybrid sulfur process begins like the sulfur-iodine process with the decomposition of sulfuric acid into water and sulfur trioxide and with the subsequent decomposition of sulfur trioxide into molecular oxygen and sulfur dioxide.



[0011] However, the hybrid sulfur process then differs from the sulfur-iodine process in that the hybrid sulfur process then uses an electrolyzer to conduct the following reactions at its anode and at its cathode, respectively:



[0012] Like the sulfur-iodine process, the net result of the hybrid sulfur process is as follows (with the initial sulfuric acid reactant being regenerated in Reaction (8)):



[0013] Referring now to FIG. 1, there is schematically shown a first conventional hybrid sulfur electrolysis cell for performing above Reactions (8) and (9), the first conventional hybrid sulfur electrolysis cell being represented generally by reference numeral 11. (For simplicity and clarity, certain standard elements of electrolysis cell 11 are not shown or described herein.)

[0014] Electrolysis cell 11 comprises a frame 13. A proton exchange membrane (PEM) 15 is appropriately positioned within frame 13, and an anode 17 and a cathode 19 are positioned against opposing surfaces of PEM 15. Each of anode 17 and cathode 19 typically consists of a metallic material or another electrically-conductive structure. PEM 15, anode 17 and cathode 19 collectively define an electrode membrane assembly 21, assembly 21 dividing the interior of frame 13 into an anode chamber 13-1 and a cathode chamber 13-2. Anode chamber 13-1 includes an inlet 23 and an outlet 25, and cathode chamber 13-2 includes an outlet 27. In use, inlet 23 is used to admit into anode chamber 13-1 a solution of gaseous sulfur dioxide dissolved in aqueous sulfuric acid, and outlet 25 is used to remove from anode chamber 13-1 the excess aqueous sulfuric acid, as well as any excess sulfur dioxide. At the same time, outlet 27 is used to remove from cathode chamber 13-2 the molecular hydrogen generated at cathode 19, as well as any excess water.

[0015] As noted above, electrolysis cell 11 utilizes dissolved sulfur dioxide as the electroactive species for the anode. Unfortunately, however, sulfur dioxide is sparingly soluble in aqueous sulfuric acid. Consequently, there is a

limited ability for the solvent to carry the electroactive species to the electrode, which, in turn, results in a low limiting current. One technique that has been used to mitigate this problem has been to increase the pressure of the gaseous species over the supporting electrolyte. Thus, as shown in FIG. 1, the sulfur dioxide is typically introduced at a high pressure, such as 20 bar. However, the introduction of sulfur dioxide at such a high pressure requires that electrolyzer system 11 and, in particular, frame 13 be engineered to contain gas safely at such a high pressure. Unfortunately, however, operation of electrolysis cell 11, particularly frame 13, presents safety and cost limitations, and measures to mitigate this shortcoming are not commercially viable at this time. In addition, another problem associated with the above operation of electrolysis cell 11 is that the dissolved sulfur dioxide is capable of permeating PEM 15 and reaching cathode 19, where it may be reduced to elemental sulfur and/or hydrogen sulfide. The formation of elemental sulfur poses significant problems in cathode performance, sulfur dioxide utilization and process sulfur conservation.

[0016] Referring now to FIG. 2, there is schematically shown a second conventional hybrid sulfur electrolysis cell for performing above Reactions (8) and (9), the second conventional hybrid sulfur electrolysis cell being represented generally by reference numeral 51. (For simplicity and clarity, certain standard elements of electrolysis cell 51 are not shown or described herein.)

[0017] Electrolysis cell 51 is similar in structure to electrolysis cell 11, the principal structural difference between the two electrolysis cells being that electrolysis cell 51 includes a frame 53 divided by assembly 21 into an anode chamber 53-1 and a cathode chamber 53-2, anode chamber 53-1 comprising an inlet 55 and an outlet 57, cathode chamber 53-2 comprising an inlet 59 and an outlet 61. In use, inlet 55 is used to admit into anode chamber 53-1 gaseous sulfur dioxide, and outlet 57 is used to remove from anode chamber 53-1 the aqueous sulfuric acid generated at anode 17, as well as any excess sulfur dioxide. At the same time, inlet 59 is used to admit water into cathode chamber 53-2, and outlet 61 is used to exit from cathode chamber 53-2 the molecular hydrogen generated at cathode 19, as well as any excess water present in cathode chamber 53-2.

[0018] As can be seen, when using electrolysis cell 51 in the above manner, the water required for the reaction at anode 17 must be supplied by water diffusing through PEM 15 to anode 17 from cathode chamber 53-2. However, the protons formed at anode 17 must simultaneously be transported through PEM 15 in the opposite direction to enable the formation of molecular hydrogen at cathode 19. These protons are transported through PEM 15 to cathode 19 in their hydrated form, thereby reducing the effectiveness of water transport through PEM to anode 17. The result is a current density limitation arising from the limited water available to anode 17. In addition, in a fashion similar to that described in connection with electrolysis cell 11, electrolysis cell 51 also shares the shortcoming that unreacted sulfur dioxide from anode chamber 53-1 may cross PEM 15 to cathode 19, where it may be reduced to elemental sulfur and/or hydrogen sulfide.

[0019] Patents and publications of interest may include the following, all of which are incorporated herein by reference: U.S. Pat. No. 7,261,874 B2, inventors Lahoda et al., which issued Aug. 28, 2007; U.S. Patent Application Publication No. US 2007/0007147 A1, inventor Lahoda, which was published Jan. 11, 2007; U.S. Pat. No. 5,512,144, inventor

Stauffer, which issued Apr. 30, 1996; U.S. Pat. No. 4,357,224, inventors Hardman et al., which issued Nov. 2, 1982; U.S. Pat. No. 4,330,378, inventors Boltersdorf et al., which issued May 18, 1982; U.S. Pat. No. 4,191,619, inventor Struck, which issued Mar. 4, 1980; U.S. Pat. No. 4,059,496, inventors Schulten et al., which issued Nov. 22, 1977; U.S. Pat. No. 3,888,750, inventors Brecher et al., which issued Jun. 10, 1975; U.S. Pat. No. 3,824,163, inventor Maget, which issued Jul. 16, 1974; PCT International Publication Number WO 2006/110780A2, published Oct. 19, 2006; Sivasubramanian et al., "Electrochemical hydrogen production from thermochemical cycles using a proton exchange membrane electrolyzer," *International Journal of Hydrogen Energy*, 32(4):463-468 (2007); and Staser et al., "Effect of Water on the Electrochemical Oxidation of Gas-Phase SO₂ in a PEM Electrolyzer for H₂ Production," *Electrochemical and Solid-State Letters*, 10(11):E17-19 (2007).

SUMMARY OF THE INVENTION

[0020] It is an object of the present invention to provide a new electrochemical technique for the simultaneous oxidation of sulfur dioxide and production of molecular hydrogen.

[0021] It is another object of the present invention to provide a technique as described above that overcomes at least some of the shortcomings associated with conventional techniques for the simultaneous oxidation of sulfur dioxide and production of molecular hydrogen.

[0022] According to one aspect of the invention, there is provided an electrolysis cell suitable for oxidizing sulfur dioxide at an anode and for generating molecular hydrogen at a cathode, the electrolysis cell comprising (a) a frame, said frame having an interior; (b) a separator disposed within the interior of said frame to divide said interior into a plurality of chambers, said separator being ionically-conductive, said separator having an anodic-facing surface and a cathodic-facing surface; (c) an anode disposed within the interior of said frame and spaced apart from said anodic-facing surface of said separator to form a first electrolyte chamber therebetween, said anode comprising a fluid diffusion electrode; (d) a first electrolytic solution present in said first electrolyte chamber; and (e) a cathode disposed within the interior of said frame and ionically coupled to the cathodic-facing surface of the separator.

[0023] According to another aspect of the invention, there is provided an electrolysis cell suitable for oxidizing sulfur dioxide at an anode and for generating molecular hydrogen at a cathode, the electrolysis cell comprising (a) a frame, said frame having an interior; (b) an anode disposed within the interior of said frame, said anode being a fluid diffusion electrode; (c) a cathode disposed within the interior of said frame and spaced apart from said anode, said cathode being a gas diffusion electrode, wherein said cathode and said anode define an electrolyte chamber therebetween, a sulfur dioxide chamber being formed on the opposite side of said anode, and a hydrogen chamber being formed on the opposite side of said cathode; and (d) an electrolytic solution present in said electrolyte chamber.

[0024] According to yet another aspect of the invention, there is provided a method for generating molecular hydrogen, said method comprising the steps of: (a) providing an electrolysis cell, said electrolysis cell comprising (i) a separator, said separator being ionically-conductive, said separator having an anodic-facing surface and a cathodic-facing surface; (ii) an anode spaced apart from said anodic-facing

surface of said separator to form a first space, said anode comprising a fluid diffusion electrode; and (iii) a cathode ionically coupled to the cathodic-facing surface of the separator; (b) filling the first space between said anode and said separator with an aqueous electrolytic solution; (c) supplying sulfur dioxide to the anode from the side opposite the aqueous electrolytic solution; and (d) supplying current to the electrolysis cell, whereby sulfur dioxide is oxidized at the anode and molecular hydrogen is generated at the cathode.

[0025] According to still yet another aspect of the invention, there is provided a method for generating molecular hydrogen, said method comprising the steps of: (a) providing an electrolysis cell, said electrolysis cell comprising an anode and a cathode, the anode and the cathode being spaced apart from one another by a space, the space being filled with an aqueous electrolytic solution, the anode comprising a fluid diffusion electrode, the cathode comprising a gas diffusion electrode; (b) supplying sulfur dioxide to the anode from the side opposite the aqueous electrolytic solution; and (c) supplying current to the electrolysis cell, whereby sulfur dioxide is oxidized at the anode and molecular hydrogen is generated at the cathode.

[0026] Additional objects, as well as aspects, features and advantages, of the present invention will be set forth in part in the description which follows, and in part will be obvious from the description or may be learned by practice of the invention. In the description, reference is made to the accompanying drawings which form a part thereof and in which is shown by way of illustration various embodiments for practicing the invention. The embodiments will be described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that structural changes may be made without departing from the scope of the invention. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is best defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The accompanying drawings, which are hereby incorporated into and constitute a part of this specification, illustrate various embodiments of the invention and, together with the description, serve to explain the principles of the invention. In the drawings wherein like reference numerals represent like parts:

[0028] FIG. 1 is a schematic diagram of a first example of a conventional hybrid sulfur electrolysis cell, said conventional hybrid sulfur electrolysis cell using an aqueous sulfur dioxide/sulfuric acid liquid electrolyte feed;

[0029] FIG. 2 is a schematic diagram of a second example of a conventional hybrid sulfur electrolysis cell, said conventional hybrid sulfur electrolysis cell using a direct sulfur dioxide gas feed;

[0030] FIG. 3 is a schematic diagram of a first embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention;

[0031] FIG. 4 is a schematic diagram of a second embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention;

[0032] FIG. 5 is a schematic diagram of a third embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention;

[0033] FIG. 6 is a schematic diagram of a fourth embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention;

[0034] FIG. 7 is a schematic diagram of a fifth embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention;

[0035] FIG. 8 is a current-voltage plot, illustrating the performance of the electrolysis cell described in Example 1;

[0036] FIGS. 9(a) and 9(b) are exploded perspective and perspective views, respectively, of the electrolysis cell used in Example 2; and

[0037] FIG. 10 is a current-voltage plot, illustrating the performance of the electrolysis cell described in Example 2.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0038] The present invention is based, at least in part, on the discovery that an improvement in the performance of an electrolysis cell of the type in which sulfur dioxide is oxidized and molecular hydrogen is produced substantially simultaneously therewith may be achieved by utilizing as the anode a porous fluid diffusion electrode (i.e., a gas-diffusion electrode or a liquid-liquid electrode) and by supplying pure sulfur dioxide to the anode from one side thereof while simultaneously providing water and an electrolyte substantially free of sulfur dioxide to the opposite side thereof, said opposite side lying between the anode and the cathode. In this manner, the sulfur dioxide that ultimately reaches the cathode may be limited. In addition, the supply of substantially pure sulfur dioxide to the anode also enables the achievement of substantially higher current densities than would be attainable if the sulfur dioxide were supplied as an aqueous solution. The electrolysis cells of the present invention may utilize separated and unseparated electrolyte compartments. The separators, if used, may include but are not limited to, cation exchange membranes, anion exchange membranes, and electrolyte-containing porous barriers, either installed during assembly or formed in situ.

[0039] Referring now to FIG. 3, there is schematically shown a first embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention, said hybrid sulfur electrolysis cell being represented generally by reference numeral 111. (For simplicity and clarity, certain standard elements of electrolysis cell 111 are not shown or described herein.)

[0040] Electrolysis cell 111 comprises a frame 113. A separator 115 is appropriately positioned within frame 113 to divide the interior of frame 113 into a pair of chambers, one of the two chambers being a cathodic chamber 113-1. Separator 115 may be an ion exchange membrane and preferably is a proton exchange membrane (PEM), such as a perfluorinated ion exchange membrane of the type commercially available from E.I. du Pont de Nemours and Company (Wilmington, Del.) as NAFION® membrane. Alternatively, separator 115 may be a porous, chemically inert, non-electrically-conductive material whose pores are filled with electrolyte to permit ionic species to be conducted through the pores from one chamber to the other.

[0041] A porous gas diffusion electrode 117, which serves as an anode, is positioned in the chamber that is located opposite to cathodic chamber 113-1, porous gas diffusion electrode 117 being spaced away from separator 115 to subdivide the non-cathodic chamber into an electrolyte chamber 113-2 and a sulfur dioxide chamber 113-3. Gas diffusion

electrode **117** may be a conventional gas diffusion electrode but is not limited thereto. Preferably, electrode **117** possesses some or all of the following properties: (1) It is mechanically stable and is capable of sustaining whatever operating differential pressures it encounters; (2) It is sufficiently electrically conductive to serve as a current collector without substantially increasing the cell voltage; (3) It is sufficiently wettable by the electrolyte to be partially wetted internally; (4) It is sufficiently resistant to electrolyte wetting such that the electrolyte is incapable of wetting through to the gas side of the electrode; (5) It is sufficiently catalytically active to promote the oxidation of sulfur dioxide at meaningful rates; and (6) It is dimensionally stable under the operating conditions and voltages that it encounters.

[0042] Examples of gas diffusion electrodes of the type that may be suitable for use in electrolysis cell **111** are disclosed in the following patents, all of which are incorporated herein by reference: U.S. Pat. No. 5,047,133, inventor Allen, which issued Sep. 10, 1991; U.S. Pat. No. 4,877,694, inventor Solomon et al., which issued Oct. 31, 1989; U.S. Pat. No. 4,459,197, inventor Solomon, which issued Jul. 10, 1984; U.S. Pat. No. 4,440,617, inventor Solomon, which issued Apr. 3, 1984; U.S. Pat. No. 4,431,567, inventors Gestaut et al., which issued Feb. 14, 1984; U.S. Pat. No. 4,377,496, inventor Solomon, which issued Mar. 22, 1983; U.S. Pat. No. 4,370,284, inventor Solomon, which issued Jan. 25, 1983; U.S. Pat. No. 4,293,396, inventors Allen et al., which issued Oct. 6, 1981; and U.S. Pat. No. 4,248,682, inventors Lindstrom et al., which issued Feb. 3, 1981.

[0043] It should be noted that gas diffusion electrode **117** may contain materials, such as carbon, that would not normally be utilized in anode structures for industrial electrolysis applications. In applications such as water electrolysis or chlor-alkali generation, the anode potential raises to a point that carbon can be directly oxidized to carbon dioxide. Thus, in those applications, specialized valve metal based electrodes are utilized to provide dimensionally stable catalytic structures. However, the oxidation of sulfur dioxide occurs at potentials less positive than the oxidation of carbon and, under that circumstance, carbon is an acceptable structural material.

[0044] A cathode **119** is positioned within cathodic chamber **113-1** and is ionically coupled to with the cathodically-facing surface of separator **115**. Cathode **119** may consist of a conventional, freestanding, metallic electrode, or cathode **119** may take the form of a catalytic decal or structure affixed either by pressure or by bonding to the surface of separator **115**. Alternatively, cathode **119** may be a gas diffusion electrode, for example, a porous bonded structure containing platinum and/or carbon. In those instances in which cathode **119** is a gas diffusion electrode, such an electrode is preferably fabricated to possess some or all of the following properties: (a) mechanically stable, capable of sustaining whatever operating differential pressures it encounters; (b) sufficiently electrically conductive to serve as a current collector without substantially increasing the cell voltage; (c) sufficiently wettable by the electrolyte to be partially wetted internally; (d) sufficiently resistant to electrolyte wetting such that the electrolyte is incapable of wetting through to the gas side of the electrode; (e) capable of providing gas paths to the side of the GDE opposite the membrane/separator such that the hydrogen gas generated by the GDE is released to that side; (f) sufficiently catalytically active to promote the elec-

trochemical generation of hydrogen at meaningful rates; and (g) dimensionally stable under the operating conditions and voltages that it encounters.

[0045] In addition to possessing the features described above, the components of electrolysis cell **111** should also be stable in the environments to be encountered and should be capable of operating for sustained periods without corrosion or extraordinary maintenance.

[0046] Cathode chamber **113-1** includes an outlet **123**, electrolyte chamber **113-2** includes an inlet **125** and an outlet **127**, and sulfur dioxide chamber **113-3** includes an inlet **129**. In use, inlet **129** is used to admit sulfur dioxide gas into sulfur dioxide chamber **113-3**, and inlet **125** is used to admit aqueous sulfuric acid into electrolyte chamber **113-2**. The water from electrolyte chamber **113-2** and the sulfur dioxide from sulfur dioxide chamber **113-3** react with one another within the pores of gas diffusion electrode **117**, thereby resulting in the production of sulfuric acid, protons and electrons (as described in Reaction (8) above). These products then empty from gas diffusion electrode **117** and into electrolyte chamber **113-2**, with some of the sulfuric acid eventually exiting electrolyte chamber **113-2** through outlet **127** and with the protons being transported across separator **115** to cathode **119**, where they are then converted into molecular hydrogen. The thus-formed molecular hydrogen, together with excess water, then exits cathodic chamber **113-1** through outlet **123**.

[0047] As can readily be appreciated, electrolysis cell **111** possesses several advantages over electrolysis cells **11** and **51**. These advantages include the following: First, in electrolysis cell **111**, pure gaseous sulfur dioxide is supplied to and diffuses into the reaction zone within the high-surface-area, porous gas diffusion electrode **117**. Thus, the limitations associated with the dissolution of sulfur dioxide into an aqueous sulfuric acid electrolyte are obviated. Second, as there are no unreactive species (such as a solvent) in the sulfur dioxide supply, the consumption of sulfur dioxide results in a pressure loss which actively resupplies additional sulfur dioxide without diffusion limitations. Third, the gap between the gas diffusion electrode **117** and separator **115** presents an additional barrier to the crossover of unreacted sulfur dioxide to cathode **119**.

[0048] Referring now to FIG. 4, there is schematically shown a second embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention, said hybrid sulfur electrolysis cell being represented generally by reference numeral **211**. (For simplicity and clarity, certain standard elements of electrolysis cell **211** are not shown or described herein.)

[0049] Electrolysis cell **211** is similar in most respects to electrolysis cell **111**, the principal difference between the two electrolysis cells being that porous gas diffusion electrode **117** of electrolysis cell **111** is replaced with porous liquid-liquid electrode **217** in electrolysis cell **211**. Porous liquid-liquid electrode **217** may be similar or even identical in construction to gas diffusion electrode **117**, provided that electrode **117** is capable of being partially permeated by liquid sulfur dioxide.

[0050] Electrolysis cell **211** may be used in a manner similar to that described above for electrolysis cell **111**, except that sulfur dioxide in liquid form, as opposed to sulfur dioxide in gaseous form, is provided to sulfur dioxide chamber **113-3** through inlet **129**.

[0051] The fluids within electrolysis cell **211** may be pressurized, preferably in a balanced fashion. While additional

complexities may arise from the containment of the pressure, there are additional advantages associated with electrolysis cell 211: First, the pressure differential across separator 115 can be near zero. Second, the supply of liquid sulfur dioxide further reduces mass transfer limitations associated with its supply to the anode reaction.

[0052] Referring now to FIG. 5, there is schematically shown a third embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention, said hybrid sulfur electrolysis cell being represented generally by reference numeral 311. (For simplicity and clarity, certain standard elements of electrolysis cell 311 are not shown or described herein.)

[0053] Electrolysis cell 311 comprises a frame 313. A separator 315, which may be identical to separator 115 of electrolysis cell 111, is appropriately positioned within frame 313 to divide the interior of frame 313 into a pair of chambers.

[0054] A porous fluid diffusion electrode 317, serving as an anode, is positioned in one of the two chambers defined by separator 315, fluid diffusion electrode 317 being spaced from separator 315 and subdividing the chamber into a sulfur dioxide chamber 313-1 and an electrolyte chamber 313-2. Depending on whether sulfur dioxide is supplied to fluid diffusion electrode 317 in a gaseous state or a liquid state, fluid diffusion electrode 317 may be a gas diffusion electrode like gas diffusion electrode 117 or may be a liquid-liquid electrode like liquid-liquid electrode 217, respectively.

[0055] A gas diffusion electrode 319, serving as a cathode, is positioned within the other of the two chambers defined by separator 315, gas diffusion electrode 319 being spaced from separator 315 and subdividing the chamber into an electrolyte chamber 313-3 and a hydrogen chamber 313-4. Gas diffusion electrode 319 may be similar or identical to electrode 117.

[0056] Sulfur dioxide chamber 313-1 includes an inlet 323, electrolyte chamber 313-2 includes an inlet 325 and an outlet 327, electrolyte chamber 313-3 includes an inlet 329 and an outlet 331, and hydrogen chamber 313-4 includes an outlet 333. In use, inlet 329 is used to admit sulfur dioxide into sulfur dioxide chamber 313-1, and inlet 325 is used to admit aqueous sulfuric acid into electrolyte chamber 313-2. The water from electrolyte chamber 313-2 and the sulfur dioxide from sulfur dioxide chamber 313-1 react with one another within the pores of fluid diffusion electrode 317, thereby resulting in the production of sulfuric acid, protons and electrons (as described in Reaction (8) above). These products then empty from gas diffusion electrode 317 and into electrolyte chamber 313-2, with some of the sulfuric acid eventually exiting electrolyte chamber 313-2 through outlet 327 and with the protons being transported across separator 315 into electrolyte chamber 313-3. Electrolyte chamber 313-3 is filled with aqueous sulfuric acid entering through inlet 329 and exiting through outlet 331. The protons passing through electrolyte chamber 313-3 to gas diffusion electrode 319 are reduced at gas diffusion electrode 319 to form molecular hydrogen, which is then released into hydrogen chamber 313-4 from the un-wetted side of gas diffusion electrode 319.

[0057] As can readily be appreciated, because of the design of electrolysis cell 311, the molecular hydrogen formed is released to the side of gas diffusion electrode 319 that is opposite to separator 315. Such a design permits the in situ separation of the molecular hydrogen within cell 311.

[0058] Referring now to FIG. 6, there is schematically shown a fourth embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present

invention, said hybrid sulfur electrolysis cell being represented generally by reference numeral 411. (For simplicity and clarity, certain standard elements of electrolysis cell 411 are not shown or described herein.)

[0059] Electrolysis cell 411 comprises a frame 413. A porous fluid diffusion electrode 417, serving as an anode, is disposed within frame 413, and a gas diffusion electrode 419, serving as a cathode, is disposed within frame 413, electrodes 417 and 419 being appropriately positioned within frame 413 to divide the interior of frame 413 into a sulfur dioxide chamber 413-1, an electrolyte chamber 413-2, and a hydrogen chamber 413-3. Depending on whether sulfur dioxide is supplied to fluid diffusion electrode 417 in a gaseous state or a liquid state, fluid diffusion electrode 417 may be a gas diffusion electrode like gas diffusion electrode 117 or may be a liquid-liquid electrode like liquid-liquid electrode 217, respectively.

[0060] Sulfur dioxide chamber 413-1 includes an inlet 423, electrolyte chamber 413-2 includes an inlet 425 and an outlet 427, and hydrogen chamber 413-3 includes an outlet 433. In use, inlet 423 is used to admit sulfur dioxide into sulfur dioxide chamber 413-1. Inlet 425 is used to admit aqueous sulfuric acid into electrolyte chamber 413-2. The water from electrolyte chamber 413-2 and the sulfur dioxide from sulfur dioxide chamber 413-1 react with one another within the pores of fluid diffusion electrode 417, thereby resulting in the production of sulfuric acid, protons and electrons (as described in Reaction (8) above). These products then empty from gas diffusion electrode 417 and into electrolyte chamber 413-2, with some of the sulfuric acid eventually exiting electrolyte chamber 413-2 through outlet 427 and with the protons being transported through the sulfuric acid solution to gas diffusion electrode 419. At gas diffusion electrode 419, the protons are reduced to form molecular hydrogen, which is then released into hydrogen chamber 413-3 from the un-wetted side of gas diffusion electrode 419.

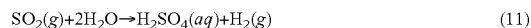
[0061] As can be appreciated, it is advantageous that the cathode of cell 411 is a gas diffusion electrode since any hydrogen released to the electrolyte has an opportunity to be re-oxidized at the anode.

[0062] One benefit of electrolysis cell 411, as compared to the above-described electrolysis cells comprising a separator, is that the elimination of the separator will eliminate a major source of cell internal resistance. As a result, the voltage required to operate the cell will be reduced. Such a reduction will be a major advantage to the overall process economics.

[0063] Referring now to FIG. 7, there is schematically shown a fifth embodiment of a hybrid sulfur electrolysis cell constructed according to the teachings of the present invention, said hybrid sulfur electrolysis cell being represented generally by reference numeral 511. (For simplicity and clarity, certain standard elements of electrolysis cell 511 are not shown or described herein.)

[0064] Electrolysis cell 511 is similar in most respects to electrolysis cell 111 and operates in substantially the same manner. Accordingly, electrolysis cell 511 includes a gas diffusion anode 541 that is used in conjunction with a cathode 544 immediately adjacent to a membrane/separator 543. Gaseous sulfur dioxide is provided to a chamber formed by the side of the anode 541 opposite the membrane/separator 543 and an anode flow plate 545. The sulfur dioxide is oxidized within the anode according to Reaction (8) above. The sulfuric acid thus produced accumulates in the aqueous sulfuric acid electrolyte within a gap support 542 and is removed via

channels in a gasket about the gap support **542** or in the anode flow plate **545** while the hydrogen ions are transported through the membrane/separator **543** to be reduced at the cathode **544** according to Reaction 9 above. This yields the following net reaction.



[0065] The cathode flow plate **547** serves the following functions: (i) directs flow of optional water (for membrane hydration) from the cell cathode inlet across the cathode active area; (ii) directs product hydrogen and excess water across the cathode active area and towards the cell cathode outlet; and (iii) provides electrical conductivity to a cathode collector **548**, which serves as the negative terminal of the entire assembly. An anode collector **546** serves as the positive terminal and is in mechanical and electrical contact with the anode flow plate **545**, which provides electrical conductivity between the anode **541** and the anode collector **546**.

[0066] The following examples are illustrative only and do not limit the present invention.

EXAMPLE 1

[0067] A porous gas diffusion electrode for use as a gas diffusion anode was fabricated by depositing 4 mg/cm² of platinum black (Engelhard) suspended in a NAFION® (1100EW) ionomer-containing media onto a hydrophobic woven carbonaceous backing (ETEK ELAT). The backing was laminated under elevated temperature and pressure to form a gas diffusion anode. This anode was placed in an unseparated cell equipped with a platinized titanium cathode.

[0068] As a control, this configuration was operated with hydrogen as the depolarizing gas: hydrogen was supplied to the side of the gas diffusion anode opposite the membrane and a current-voltage curve was obtained. Due to the low polarization of the hydrogen electrode reactions, the current-voltage curve so obtained is an approximation of the resistive losses within the cell.

[0069] As an additional control, reactive gases were excluded from the anode so as to effect the oxidation of water in the aqueous sulfuric acid to oxygen when current was applied to the cell. Thus, a current-voltage curve for the water oxidation reaction was obtained.

[0070] Subsequently, sulfur dioxide was supplied to the side of the gas diffusion anode opposite the membrane and a voltage-current curve was obtained. Subtraction of the hydrogen pump voltage from the experimentally obtained sulfur dioxide oxidation and water oxidation voltages yields the resistance-corrected voltages of those reactions. These corrected current-voltage curves are shown in FIG. 8.

[0071] The successful use of the sulfur dioxide gas diffusion anode is demonstrated by the approximately 1 volt potential reduction when compared to water oxidation.

EXAMPLE 2

[0072] A porous gas diffusion electrode for use as a gas diffusion anode was fabricated by depositing 4 mg/cm² of platinum black (Engelhard) suspended in a NAFION® (1100EW) ionomer-containing media onto a hydrophobic woven carbonaceous backing (ETEK ELAT). The backing was laminated under elevated temperature and pressure to form a gas diffusion anode. This anode was placed in a test

cell, equipped with a) a plastic electrolyte gap frame (PEEK), b) a coarse plastic mesh gap support (HDPE), c) a NAFION® 117 membrane, and d) a platinized cathode (see FIGS. 9(a) and 9(b)). As a control, this configuration was operated with hydrogen as the depolarizing gas, as performed in Example 1 above: hydrogen was supplied to the side of the gas diffusion anode opposite the membrane and a current-voltage curve was obtained, said curve being shown in FIG. 10.

[0073] Subsequently, sulfur dioxide was supplied to the side of the gas diffusion anode opposite the membrane and a voltage-current curve was obtained, said curve being shown in FIG. 10.

[0074] The resultant curves in FIG. 10 demonstrate sulfur dioxide oxidation with accompanying cathodic hydrogen evolution at potentials below that of water electrolysis.

EXAMPLE 3

[0075] In a fashion similar to Example 2, a liquid-liquid depolarized anode could be incorporated into a membrane cell. The membrane cell could be pressurized to approximately 5 atmospheres and liquid sulfur dioxide could be introduced into the non-electrolyte side of the anode, wherein it would permeate into the porous liquid-liquid anode. The electrolysis would be initiated and the pressure on the catholyte would rise due to the generation of hydrogen gas. Upon reaching a pressure equal to the anolyte pressure, the catholyte would exit the cell, thereby establishing a balanced pressure across the membrane.

EXAMPLE 4

[0076] A cell could be constructed in an identical fashion to that described in Example 2 except that an asymmetric gas diffusion cathode could be substituted for the platinized titanium cathode. The asymmetric cathode could be fabricated by laminating a porous hydrophilic carbon-polymer layer to a porous, conductive hydrophobic layer with a layer of high surface area platinum deposited onto the side to be joined to the hydrophilic layer. The laminated gas diffusion cathode so fabricated could be operated such that the hydrogen generated would escape the structure to the non-electrolyte side of the cathode, thereby effecting the phase separation of the hydrogen gas from the electrolyte.

EXAMPLE 5

[0077] A cell could be fabricated as described in Example 4 except that no membrane would be included. In this manner, a common sulfuric acid electrolyte would be established between the anode and the cathode. As the sulfur dioxide utilized to depolarize the anode would be supplied to the gas diffusion anode to the non-electrolyte side and as the hydrogen generated at the cathode would be released to the non-electrolyte side, electrolysis in the absence of a separator would proceed.

[0078] The embodiments of the present invention described above are intended to be merely exemplary and those skilled in the art shall be able to make numerous variations and modifications to it without departing from the spirit of the present invention. All such variations and modifications are intended to be within the scope of the present invention as defined in the appended claims.

What is claimed is:

1. An electrolysis cell suitable for oxidizing sulfur dioxide at an anode and for generating molecular hydrogen at a cathode, the electrolysis cell comprising:

- (a) a frame, said frame having an interior;
- (b) a separator disposed within the interior of said frame to divide said interior into a plurality of chambers, said separator being ionically-conductive, said separator having an anodic-facing surface and a cathodic-facing surface;
- (c) an anode disposed within the interior of said frame and spaced apart from said anodic-facing surface of said separator to form a first electrolyte chamber therebetween, said anode comprising a fluid diffusion electrode;
- (d) a first electrolytic solution present in said first electrolyte chamber; and
- (e) a cathode disposed within the interior of said frame and ionically coupled to the cathodic-facing surface of the separator.

2. The electrolysis cell as claimed in claim **1** wherein said separator is an ion exchange membrane.

3. The electrolysis cell as claimed in claim **2** wherein said ion exchange membrane is a proton exchange membrane.

4. The electrolysis cell as claimed in claim **1** wherein said fluid diffusion electrode is a gas diffusion electrode.

5. The electrolysis cell as claimed in claim **1** wherein said fluid diffusion electrode is a liquid-liquid electrode.

6. The electrolysis cell as claimed in claim **1** wherein said first electrolytic solution is aqueous sulfuric acid.

7. The electrolysis cell as claimed in claim **1** wherein said cathode is in direct contact with said cathodic-facing surface of said separator.

8. The electrolysis cell as claimed in claim **1** wherein said cathode is spaced apart from said cathodic-facing surface of said separator to define a second electrolyte chamber, said electrolysis cell further comprising a second electrolytic solution in said second electrolyte chamber.

9. The electrolysis cell as claimed in claim **8** wherein said second electrolytic solution is aqueous sulfuric acid.

10. The electrolysis cell as claimed in claim **8** wherein said cathode comprises a gas diffusion electrode.

11. The electrolysis cell as claimed in claim **1** wherein said frame and said anode form a sulfur dioxide chamber and wherein said frame includes an inlet that opens into said sulfur dioxide chamber to permit sulfur dioxide to be introduced into said sulfur dioxide chamber.

12. The electrolysis cell as claimed in claim **1** wherein said frame includes an inlet opening into said first electrolyte chamber and an outlet exiting from said first electrolyte chamber.

13. An electrolysis cell suitable for oxidizing sulfur dioxide at an anode and for generating molecular hydrogen at a cathode, the electrolysis cell comprising:

- (a) a frame, said frame having an interior;
- (b) an anode disposed within the interior of said frame, said anode being a fluid diffusion electrode;
- (c) a cathode disposed within the interior of said frame and spaced apart from said anode, said cathode being a gas diffusion electrode, wherein said cathode and said anode define an electrolyte chamber therebetween, a sulfur dioxide chamber being formed on the opposite side of

said anode, and a hydrogen chamber being formed on the opposite side of said cathode; and

- (d) an electrolytic solution present in said electrolyte chamber.

14. The electrolysis cell as claimed in claim **13** wherein said electrolytic solution is aqueous sulfuric acid.

15. The electrolysis cell as claimed in claim **14** wherein said frame includes a first inlet that opens into said sulfur dioxide chamber to permit sulfur dioxide to be introduced into said sulfur dioxide chamber, wherein said frame includes a second inlet that opens into said electrolyte chamber to permit the electrolytic solution to be introduced into the electrolyte chamber and a first outlet that removes the electrolytic solution from said electrolyte chamber, and wherein said frame includes a second outlet to permit molecular hydrogen to be removed from said hydrogen chamber.

16. The electrolysis cell as claimed in claim **13** wherein said anode is a gas diffusion electrode.

17. The electrolysis cell as claimed in claim **13** wherein said anode is a liquid-liquid electrode.

18. A method for generating molecular hydrogen, said method comprising the steps of:

- (a) providing an electrolysis cell, said electrolysis cell comprising
 - i. a separator, said separator being ionically-conductive, said separator having an anodic-facing surface and a cathodic-facing surface;
 - ii. an anode spaced apart from said anodic-facing surface of said separator to form a first space, said anode comprising a fluid diffusion electrode; and
 - iii. a cathode ionically coupled to the cathodic-facing surface of the separator;
- (b) filling the first space between said anode and said separator with an aqueous electrolytic solution;
- (c) supplying sulfur dioxide to the anode from the side opposite the aqueous electrolytic solution; and
- (d) supplying current to the electrolysis cell, whereby sulfur dioxide is oxidized at the anode and molecular hydrogen is generated at the cathode.

19. The method as claimed in claim **18** wherein the sulfur dioxide supplied to the anode is in liquid form and wherein the fluid diffusion electrode is a liquid-liquid electrode.

20. The method as claimed in claim **18** wherein the sulfur dioxide supplied to the anode is in gaseous form and wherein the fluid diffusion electrode is a gas diffusion electrode.

21. The method as claimed in claim **18** wherein the cathode is in direct contact with the cathodic-facing surface of the separator.

22. The method as claimed in claim **18** wherein the cathode is a gas diffusion electrode and is spaced apart from the cathodic-facing surface of the separator to form a second space, said method further comprising filling said second space with an aqueous electrolytic solution.

23. The method as claimed in claim **18** wherein said separator is an ion exchange membrane.

24. The method as claimed in claim **23** wherein said ion exchange membrane is a proton exchange membrane.

25. The method as claimed in claim **18** wherein the aqueous electrolytic solution is aqueous sulfuric acid.

26. A method for generating molecular hydrogen, said method comprising the steps of:

- (a) providing an electrolysis cell, said electrolysis cell comprising an anode and a cathode, the anode and the

cathode being spaced apart from one another by a space, the space being filled with an aqueous electrolytic solution, the anode comprising a fluid diffusion electrode, the cathode comprising a gas diffusion electrode;

- (b) supplying sulfur dioxide to the anode from the side opposite the aqueous electrolytic solution; and
- (c) supplying current to the electrolysis cell, whereby sulfur dioxide is oxidized at the anode and molecular hydrogen is generated at the cathode.

27. The method as claimed in claim **26** wherein the sulfur dioxide supplied to the anode is in liquid form and wherein the fluid diffusion electrode is a liquid-liquid electrode.

28. The method as claimed in claim **26** wherein the sulfur dioxide supplied to the anode is in gaseous form and wherein the fluid diffusion electrode is a gas diffusion electrode.

29. The method as claimed in claim **26** wherein the aqueous electrolytic solution is a solution of aqueous sulfuric acid.

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