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2  
3 MAGNESIUM SOLUTION PHASE CATHOLYTE

4 SEAWATER ELECTROCHEMICAL SYSTEM

5  
6 STATEMENT OF GOVERNMENT INTEREST

7 The invention described herein may be manufactured and used  
8 by or for the Government of the United States of America for  
9 governmental purposes without the payment of any royalties  
10 thereon or therefor.

11  
12 BACKGROUND OF THE PRESENT INVENTION

13 (1) Field of the Invention

14 The present invention relates to an electrochemical system,  
15 in particular a magnesium solution phase catholyte seawater  
16 electrochemical system, and to a process for generating  
17 electrical power using said system.

18 (2) Description of the Prior Art

19 Magnesium-seawater batteries have been developed, all of  
20 which include solid cathodes, including silver chloride, cuprous  
21 chloride, lead chloride, cuprous iodide, cuprous thiocyanate and  
22 manganese dioxide. Further, primary batteries employing aqueous  
23 electrolytes have been developed by various governmental and  
24 commercial laboratories in the U.S. and elsewhere since the  
25 1940s. Emphasis has been placed on aluminum and magnesium anodes  
26 due to their high faradic capacity, low atomic weight, and high

1 standard potentials. Of particular interest is their application  
2 to undersea vehicles as a result of the availability of seawater  
3 to act as an electrolyte or electrolyte solution, thus further  
4 enhancing their effectiveness as an energy source on a systems  
5 basis.

6 Magnesium/cuprous chloride and magnesium silver chloride  
7 were used as cathode materials in prior art battery systems.  
8 Eventually they were replaced with lower cost alternative  
9 cathodes such as lead chloride and manganese dioxide; but with  
10 equally lower specific energy. The development of higher  
11 specific energy systems included replacing magnesium with  
12 aluminum while retaining the silver oxide cathode. This enabled  
13 exceptional specific power and energy but with increased cost.  
14 To reduce the cost without compromising specific energy, the  
15 expensive silver oxide cathode was replaced with solution phase  
16 catholytes, such as hydrogen peroxide or sodium hypochlorite.  
17 These advancements are extremely promising by virtue of the  
18 reduced cost of materials while achieving specific energies  
19 upwards of 100 Wh/lb at current densities of 100 - 1200 mA/cm<sup>2</sup>.

20 Other countries, notably Sweden and Norway, have  
21 successfully employed magnesium-seawater batteries whereby oxygen  
22 saturated in the seawater electrolyte is reduced on a catalytic  
23 cathode surface opposite the magnesium anode. This is highly  
24 efficient on a systems basis due to the fact that there is no  
25 sodium hydroxide required, greatly reducing the system weight.

1 However, limited oxygen availability limits specific energies to  
2 under 100 Wh/lb.

3 Various types of batteries are shown in the patent  
4 literature. For example, U.S. Patent No. 4,063,006 to Murphy  
5 illustrates an aqueous electrolyte battery in which liquid  
6 oxychlorides are fed to a cathode chamber. The oxychlorides flow  
7 through a porous carbon electrode. At the electrode, the  
8 oxychlorides are reduced and the reaction products dissolve in an  
9 aqueous electrolyte flowing by the face of the carbon electrode  
10 opposite to that in which the oxychlorides are introduced. Metal  
11 standoffs connect to the porous electrode for use as conductors  
12 while maintaining spacing in the cathode chamber.

13 U.S. Patent No. 4,822,698 to Jackovitz et al. relates to a  
14 battery having an anode selected from the group consisting of  
15 magnesium, zinc, and mixtures and alloys thereof, an oxygen  
16 electrode as the cathode, and means for maintaining the anode and  
17 the cathode in an electricity generating relationship when the  
18 battery is placed in salt water. The '698 patent also describes  
19 a method of producing electricity by positioning the anode and  
20 cathode in a saline electrolyte.

21 U.S. Patent No. 4,910,102 to Rao et al. relates to a battery  
22 assembly and a process for operating same. The battery assembly  
23 is comprised of bipolar electrodes disposed between an inert  
24 cathode current collector acting as a hydrogen electrode and an  
25 anode plate formed from material selected from the group  
26 consisting of aluminum, magnesium, aluminum alloys, magnesium

1 alloys and mixtures thereof. The battery is configured for  
2 electrolyte flow wherein the electrolyte includes hydrogen  
3 peroxide in an amount sufficient to provide 0.5 to about 30  
4 volume percent solution.

5 U.S. Patent No. 4,910,104 to Rao et al. relates to a  
6 deferred actuated battery assembly comprised of a plurality of  
7 bipolar electrodes disposed between an inert cathode current  
8 collector acting as a hydrogen electrode and an anode plate  
9 formed from a material selected from the group consisting of  
10 aluminum, magnesium, aluminum alloys, magnesium alloys, and  
11 mixtures thereof and configured for electrolyte flow  
12 therebetween.

13 U.S. Patent No. 5,314,766 to Witherspoon et al. relates to a  
14 lead acid battery electrode and a method of manufacturing same.  
15 The positive plates are prepared by forming partially oxidized  
16 tetrabasic lead sulfate having at least a part of the oxide  
17 portion in the form of alpha lead dioxide and forming beta lead  
18 dioxide. Next the oxidized tetrabasic lead sulfate and the beta  
19 lead dioxide are intermingled in a wet mixture. The wet mixture  
20 is applied to the oxidized surface of a lead support substrate.  
21 Then, it is heated and pressed for a time and at a temperature  
22 and compressive load sufficient to form an adhered or retained  
23 coating of active material on the substrate. The oxidized  
24 tetrabasic lead sulfate is formed by reaction of tetrabasic lead  
25 sulfate with magnesium hydroxide and sodium persulfate.  
26 Preferably, beta lead dioxide is formed by reacting red lead

1 oxide with nitric acid to provide an oxidation product, at least  
2 a major portion of which is beta lead oxide, and which has a  
3 surface area of at least 10 m<sup>2</sup>/gram.

4 U.S. Patent No. 5,445,905 to Marsh relates to a dual flow  
5 battery comprising an aqueous hydrogen peroxide catholyte, an  
6 aqueous anolyte, a porous solid electrocatalyst capable of  
7 reducing the hydrogen peroxide and separating said anolyte, and  
8 an aluminum anode positioned within said anolyte. Separation of  
9 catholyte and anolyte chambers prevents hydrogen peroxide  
10 poisoning of the aluminum anode.

11 Many of these prior art batteries are expensive to  
12 manufacture and inordinately large. Further, many of these prior  
13 art batteries are unreliable.

#### 14 15 SUMMARY OF THE INVENTION

16 Accordingly, it is an object of the present invention to  
17 provide an electrochemical system for generating electrical power  
18 which is particularly applicable to low current density, long  
19 endurance applications.

20 It is a further object of the present invention to provide  
21 an electrochemical system as above which is relatively small and  
22 less expensive to produce.

23 It is yet another object of the present invention to provide  
24 an electrochemical system as above which has increased  
25 reliability.

1           It is still another object of the present invention to  
2 provide an improved process for generating electrical power.

3           The foregoing objects are attained by the electrochemical  
4 system and the process of the present invention.

5           In accordance with the present invention, an electrochemical  
6 system is provided which comprises cells incorporating bipolar  
7 electrodes. Each of the electrodes is formed by an anode portion  
8 formed from a magnesium containing material and an  
9 electrocatalytic cathode substrate material joined to a back  
10 surface of the anode. The electrochemical system also comprises  
11 means for introducing a seawater-catholyte solution into a space  
12 between the anode portion of one bipolar electrode and the  
13 cathode portion of a second bipolar electrode to initiate the  
14 reduction of the seawater-catholyte solution at the electrodes  
15 and to create electrical power. In a preferred embodiment, the  
16 seawater-catholyte solution is a seawater-hydrogen peroxide or  
17 seawater-sodium hypochlorite solution.

18           The process for generating electrical power of the present  
19 invention broadly comprises providing cells incorporating bipolar  
20 electrodes with at least one of the electrodes comprising an  
21 anode portion formed from a magnesium containing material;  
22 mixing a solution containing seawater and a solution phase  
23 catholyte; and introducing the seawater-catholyte solution into a  
24 space between the anode portion and cathode portion of the

1 bipolar electrodes to initiate the reduction of the seawater-  
2 catholyte solution at the electrodes and to create electrical  
3 power.

4 Other details of the electrochemical system and the process  
5 of the present invention, as well as other objects and advantages  
6 attendant thereto, are set forth in the following detailed  
7 description and the accompanying drawings, wherein like reference  
8 numerals depict like elements.

9  
10 BRIEF DESCRIPTION OF THE DRAWINGS

11 FIG. 1 is a schematic representation of an electrochemical  
12 system in accordance with the present invention; and

13 FIG. 2 is an enlarged view of a single cell showing the  
14 bipolar electrodes and showing the reactions which take place at  
15 the anode surface and at the electrocatalyst cathode surface for  
16 a seawater-sodium hypochlorite catholyte solution.

17  
18 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

19 Referring now to the drawings, FIG. 1 illustrates an  
20 electrochemical system 10 in accordance with the present  
21 invention. The electrochemical system 10 is formed by a  
22 plurality of components including an anode end plate 11 formed  
23 from a suitable metal or metal alloy such as silver or a silver  
24 alloy, a cathode end plate 12 formed from a suitable metal or  
25 metal alloy such as magnesium or a magnesium alloy, and a  
26 plurality of spaced apart bipolar electrodes 14 positioned



1 between the anode end plate 11 and the cathode end plate 12  
2 forming a plurality of cells 13. Each cell 13 further includes a  
3 separator system, picots 15, for insuring separation between the  
4 electrodes. The separator system picots 15 is preferably formed  
5 by a plurality of spaced apart separators made of an epoxy-based  
6 material such as URALITE as manufactured by HEXCEL Chemical  
7 Products of Chatsworth, CA.

8 A distribution manifold 16 is provided for introducing an  
9 aqueous electrolyte into the spaces 18 formed between adjacent  
10 electrodes 14, between the anode end plate 11 and a respective  
11 one of the electrodes 14, and between the cathode end plate 12  
12 and a respective one of the electrodes 14. An outlet manifold 20  
13 is provided for removing spent electrolyte from the spaces 18.

14 The distribution manifold 16 is in fluid communication via  
15 line 22 with a pump 24 connected on a suction side by a line 26  
16 with a source of an electrolyte such as sea water. Also  
17 connected by a line 28 under the control of a valve 30 to the  
18 suction side of the pump 24, there is provided a storage tank 32  
19 containing a solution phase catholyte, preferably selected from  
20 the group consisting of hydrogen peroxide, sodium hypochlorite  
21 and mixtures thereof. The valve 30 allows solution phase  
22 catholyte to be supplied at a desired rate of flow depending on  
23 the application. The solution phase catholyte is preferably  
24 admixed with the seawater electrolyte and supplied to the spaces  
25 18 via the distribution manifold 16.

1           The manifolds 16 and 20 provide for a substantially uniform  
2 flow of the electrolyte through the electrochemical system 10 and  
3 the collection and discharge of electrolyte via line 34 connected  
4 to the outlet manifold.

5           In a preferred construction of the present invention, the  
6 anode end plate 11 and the cathode end plate 12 form part of a  
7 casing (not shown) such that electrodes 14 are placed within the  
8 casing. Additionally, the anode end plate 11 and the cathode end  
9 plate 12 are each connected to a busbar (not shown) which is  
10 connected to a variable load (not shown) in a known manner.

11           As shown in FIG. 2, each of the bipolar electrodes 14 is  
12 formed by an anode portion 36 plated with conductive substrate  
13 and electrocatalyst 38. The anode portion 36 is preferably  
14 formed from a material selected from the group consisting of  
15 magnesium and magnesium alloys. The electrocatalyst 38 is  
16 preferably formed from a material capable of carrying out the  
17 reduction of the catholyte and of forming a conductive substrate.

18           Suitable materials for the electrocatalyst include silver,  
19 nickel, and carbon materials and alloys thereof.

20           In operation, electrical connection (not shown) is made to  
21 the anode end plate 11 and the cathode end plate 12 to initiate  
22 the reduction of the solution phase catholyte. A mixture of the  
23 solution phase catholyte and the seawater electrolyte, giving  
24 catholyte concentrations in the range of 0.1 molar to 1.0 molar,  
25 is fed into each space 18 via manifold 16. The desired mixture  
26 is created by causing the solution phase catholyte to flow from

1 the concentrated source at a rate of from about 2 lpm to about  
 2 4 lpm and mix with the seawater. The mixture of the solution  
 3 phase catholyte and the seawater electrolyte is then fed into the  
 4 spaces 18 at a rate in the range of from about 10 lpm to about  
 5 25 lpm.

6 The resulting magnesium solution phase couples are achieved:

|    |                                                                                                                      |           |            |
|----|----------------------------------------------------------------------------------------------------------------------|-----------|------------|
| 7  | (1) <u>Magnesium-Hydrogen Peroxide System (Mg-H<sub>2</sub>O<sub>2</sub>):</u>                                       | <u>E°</u> |            |
| 8  | Anode: Mg -----> Mg <sup>2+</sup> + 2e-                                                                              |           | 2.70 V (1) |
| 9  | Cathode: HO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O + 2e- -----> 3OH <sup>-</sup>                               |           | 0.88 V (2) |
| 10 | Cell Reaction: Mg + HO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O -----> Mg <sup>2+</sup> + 3OH <sup>-</sup>       |           | 3.58 V (3) |
| 11 |                                                                                                                      |           |            |
| 12 |                                                                                                                      |           |            |
| 13 |                                                                                                                      |           |            |
| 14 | (2) <u>Magnesium-Hypochlorite System (Mg-OCl<sup>-</sup>):</u>                                                       |           |            |
| 15 | Anode: Mg -----> Mg <sup>2+</sup> + 2e-                                                                              |           | 2.70 V (4) |
| 16 | Cathode: OCl <sup>-</sup> + H <sub>2</sub> O + 2e- -----> Cl <sup>-</sup> + 2OH <sup>-</sup>                         |           | 0.90 V (5) |
| 17 | Cell Reaction: Mg + OCl <sup>-</sup> + H <sub>2</sub> O -----> Mg <sup>2+</sup> + Cl <sup>-</sup> + 2OH <sup>-</sup> |           | 3.60 V (6) |
| 18 |                                                                                                                      |           |            |
| 19 |                                                                                                                      |           |            |
| 20 |                                                                                                                      |           |            |
| 21 |                                                                                                                      |           |            |
| 22 |                                                                                                                      |           |            |

23 The theoretical charge capacities and energy densities for  
 24 several electrochemical couples are listed below in Table I for  
 25 comparison purposes. It is evident that the magnesium-hydrogen  
 26 peroxide and the magnesium-sodium hypochlorite systems of the  
 27 present invention have higher theoretical potentials and higher  
 28 corresponding charge capacities and energy densities in  
 comparison with established magnesium and aluminum systems

TABLE I

| SYSTEM                             | CELL POTENTIAL<br>(Theoretical) | CHARGE CAPACITY* | ENERGY DENSITY* |
|------------------------------------|---------------------------------|------------------|-----------------|
| Al - H <sub>2</sub> O <sub>2</sub> | 3.23 V                          | 2.10 Ahr/g       | 6.78 Whr/g      |
| Al - NaOCl                         | 3.25 V                          | 1.54 Ahr/g       | 5.01 Whr/g      |
| Al - AgO                           | 2.92 V                          | 0.60 Ahr/g       | 1.75 Whr/g      |
| Mg - H <sub>2</sub> O <sub>2</sub> | 3.58 V                          | 1.87 Ahr/g       | 6.69 Whr/g      |
| Mg - NaOCl                         | 3.60 V                          | 1.42 Ahr/g       | 5.11 Whr/g      |
| Mg - AgCl                          | 2.92 V                          | 0.35 Ahr/g       | 1.02 Whr/g      |
| Mg - CuCl                          | 2.84 V                          | 0.48 Ahr/g       | 1.36 Whr/g      |

\*THEORETICAL (per mass of reactants (grams))

The resulting electrical output as shown in FIG. 2 may be used to power a desired load 40.

It has been found that the magnesium-hydrogen peroxide or magnesium-sodium hypochlorite electrochemical systems of the present invention are useful for very low rate, 10 to 50 mA/cm<sup>2</sup>, long endurance (greater than four hours and up to forty hours) systems.

It has also been found that the performance of the electrochemical couple is effected by temperature and electrolyte flow rates. With regard to temperature, it has been found that current densities approaching 100 mA/cm<sup>2</sup> with corresponding cell potentials of 1.0 Volt can be achieved at a temperature of 60°C. At room temperature, it has been found that a cell potential of 0.8V at 100 mA/cm<sup>2</sup> can be achieved. The electrolyte flow rate is optimized to achieve maximum electrochemical efficiency, e.g., low flow rates for low rate systems and higher flow rates for high rate (100 mA/cm<sup>2</sup>) systems.

1 One of the advantages to the electrochemical systems of the  
2 present invention is a significant reduction in size on a system  
3 basis. The reduction in size comes about from the fact that a  
4 caustic/sodium hydroxide storage tank is not necessary since  
5 seawater from the ocean is being used to activate the magnesium.

6 The elimination of the sodium hydroxide enables an increase of  
7 50% in specific energies, thus to 250 Wh/lb, or 6 -7 times that  
8 of silver zinc. Another advantage over current technology is the  
9 reduced cost over the present state of the cathode materials  
10 (sodium hypochlorite or hydrogen peroxide vs. silver oxide  
11 cathodes). Still another advantage is the increased reliability.

12 While it is preferred to form the anode portion 36 from  
13 magnesium or a magnesium alloy, it is also possible to form the  
14 magnesium alloy by replacing a portion of the magnesium with  
15 lithium, calcium or aluminum.

16 It is apparent that there has been provided in accordance  
17 with the present invention a magnesium solution phase catholyte  
18 seawater electrochemical system which fully meets the objects,  
19 advantages, and means set forth hereinbefore. While the  
20 invention has been described in combination with specific  
21 embodiments thereof, it is evident that many alternatives,  
22 modifications, and variations will be apparent to those skilled  
23 in the art in light of the foregoing description. Accordingly,  
24 it is intended to embrace all such alternatives, modifications  
25 and variations .

2

3

MAGNESIUM SOLUTION PHASE CATHOLYTE

4

SEAWATER ELECTROCHEMICAL SYSTEM

5

6

ABSTRACT OF THE DISCLOSURE

7

8 In accordance with the present invention, an electrochemical  
9 system is provided which comprises a plurality of cells, the  
10 cells being formed by spaced apart bipolar electrodes. Each of  
11 the electrodes is formed by an anode portion formed from a  
12 magnesium containing material and an electrocatalytic material  
13 joined to a surface of the anode. The electrodes are spaced such  
14 that the anode portion of one electrode faces the  
15 electrocatalytic material of the adjacent electrode. The  
16 electrochemical system also comprises a manifold system for  
17 introducing a seawater-catholyte solution into the spaces between  
18 the electrodes. An electrical connection is provided across the  
19 cells so as to initiate the reduction of the seawater-catholyte  
20 solution at the electrodes and to create electrical power. In a  
21 preferred embodiment, the seawater-catholyte solution is a  
22 seawater-hydrogen peroxide or seawater-sodium hypochlorite  
23 solution. A process for generating electrical power using the  
24 electrochemical system of the present invention is also  
described.

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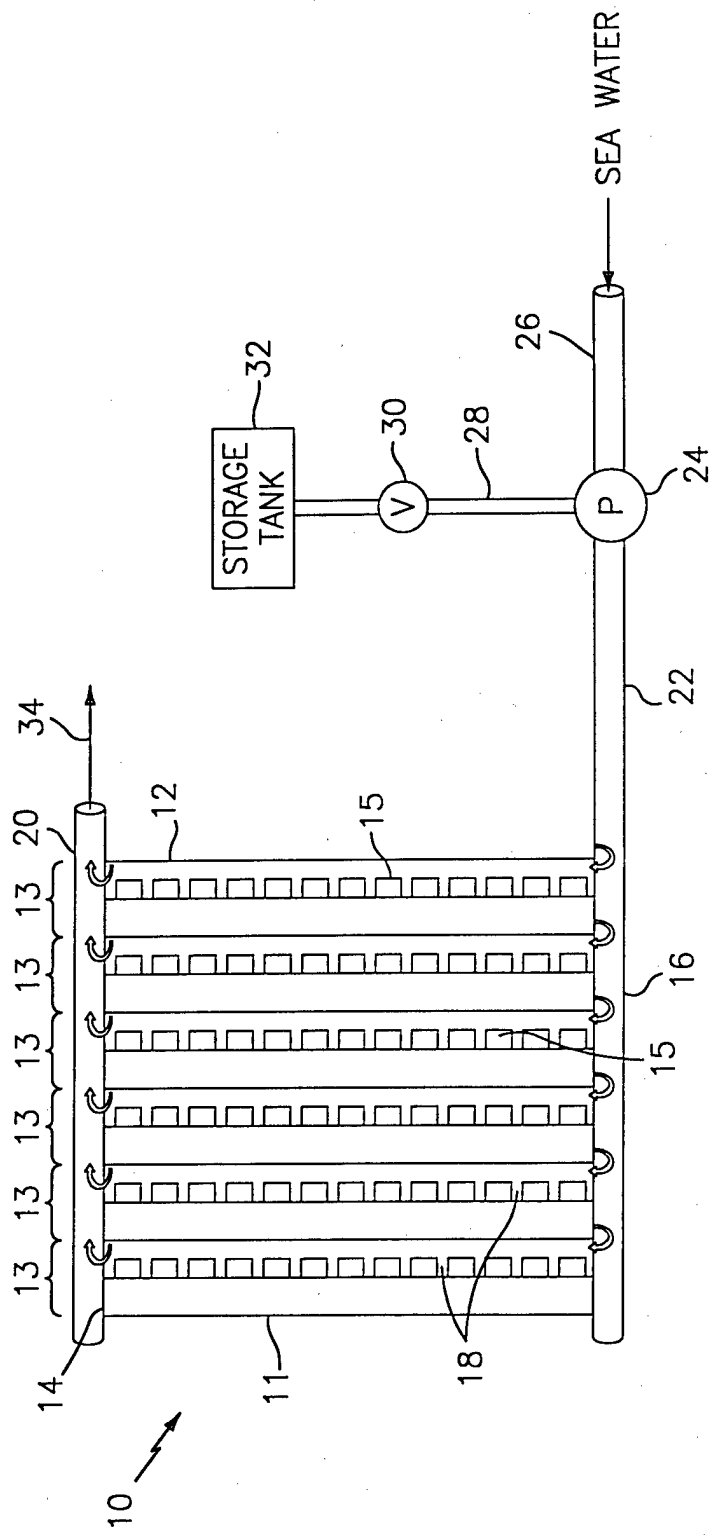
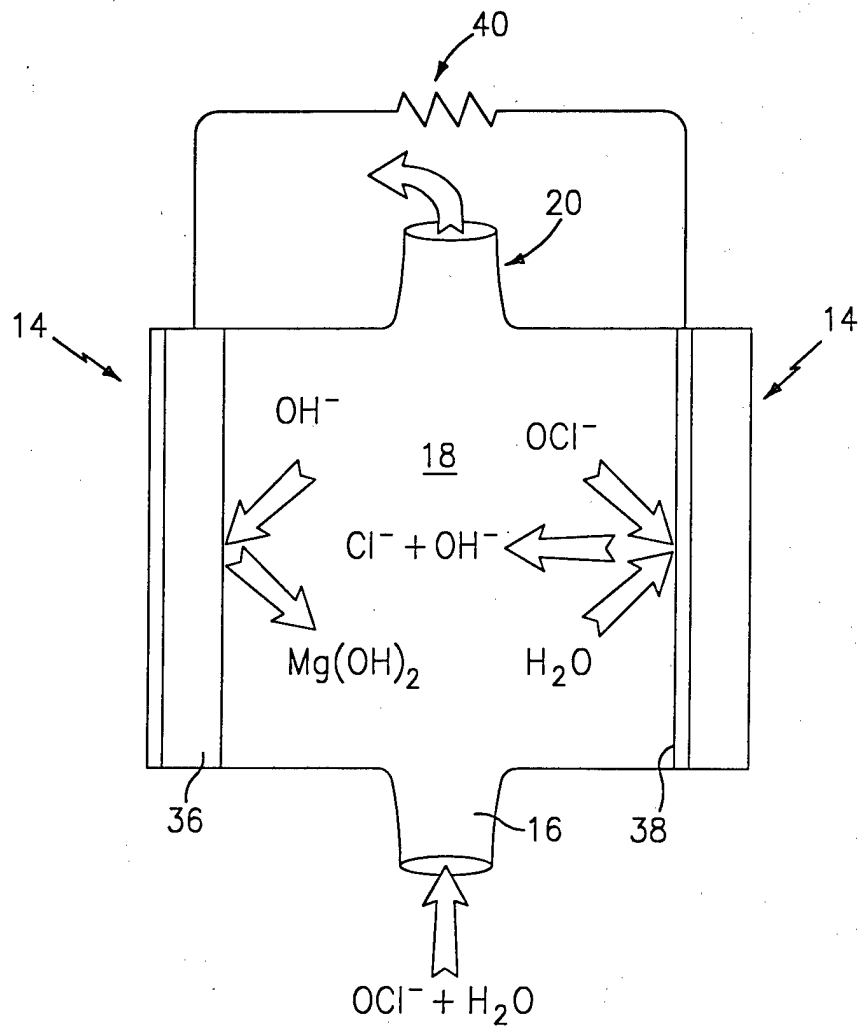


FIG. 1

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**FIG. 2**