

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 December 2005 (22.12.2005)

PCT

(10) International Publication Number
WO 2005/121412 A2

(51) International Patent Classification⁷: **C25C 1/02**

(21) International Application Number:
PCT/US2004/018894

(22) International Filing Date: 15 June 2004 (15.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/858,985 2 June 2004 (02.06.2004) US

(71) Applicant and

(72) Inventor: **KLEIN, Dennis, J.** [US/US]; 1725 Starlite Drive, Clearwater, FL 33755 (US).

(74) Agent: **LAPOINTE, Dennis, G.**; Mason Law, P.L., 17757 U.S. Hwy. 19 N., Ste.500, Clearwater, FL 33764 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROLYTIC SOLUTION FOR PROMOTING ELECTROLYSIS OF WATER

(57) Abstract: An electrolytic solution that increases the efficiency of energy use and gas production of a wide range of electrolytic devices, that can be adapted to specific devices and to changes in the metal composition and configuration of conductive elements in electrolytic systems, and that reduces maintenance of the such systems. The electrolytic solution comprising a major solute and a minor solute combined proportionately and dissolved in a predetermined quantity of water; said major solute comprising dry pellets, flakes or combinations thereof comprising about 83% to 87% potassium hydroxide and about 0.4% to 0.7 of a carbonate, and minimal amounts of iron compounds and minimal amounts of calcium. The minor solute comprises about 4.0% to 6.0% of a bicarbonate and up to 3.0% sodium chloride, wherein said solutes are combined with said predetermined quantity of water to yield the electrolytic solution.

WO 2005/121412 A2

ELECTROLYTIC SOLUTION FOR PROMOTING ELECTROLYSIS OF WATER

Field of the Invention

The present invention relates to the electrolysis of water to produce a combustible gas. More specifically, the present invention relates to electrolytic solutions that promote the electrolysis of water, and even more specifically, the present invention relates to an electrolytic solution that promotes the more efficient generation of hydrogen gas and oxygen through the electrolysis of water using well known devices and that also specifically promotes the generation of a new, combustible gas produced by a new electrolytic device.

Background of the Invention

Hydrogen gas is a nearly perfect fuel. When ignited, it releases nearly three times the energy of comparable amounts of fossil fuels and is generally environmentally "friendly" producing only water as a by-product of combustion. The supply of oxygen is nearly inexhaustible as the product of the electrolysis of water through which water is split into hydrogen and oxygen in an atomic ratio of 2:1. However, hydrogen as a fuel has one very serious drawback: it is highly explosive and thus dangerous to store and to transport in even moderate quantities. It has not been reasonably practical to use hydrogen gas as a fuel, or even as a fuel additive to increase energy output of fossil fuels. Unlike most common fuels, transporting an adequate quantity of hydrogen in a reasonable volume would require storage under high pressure (in excess of 1,000 psi) thereby increasing risk of serious explosions. If

adequate quantities could be produced on demand near or at the point of consumption, much of the risk would be overcome.

Much of the effort directed to the use of hydrogen as a fuel, or as a fuel additive has focused on hydrogenerators (frequently referred to as electrolyzer electrolysis devices, or electrolysis chambers. Most recently this emphasis is reflected in the explosive growth of research in the general field of hydrogen fuel cell technology as it relates to both the use of hydrogen as a fuel and to devices and systems that safely produce hydrogen for consumption directly or indirectly as a fuel.

Numerous patents illustrate the efforts and emphasis placed on improving the safety of use of hydrogen by improving the safety of electrolysis devices and systems that generate hydrogen gas. In related efforts, emphasis has also been placed on producing hydrogen at the point of consumption and on producing it more "on demand" to minimize the need for storing large quantities of the explosive gas and reduce exposure to risks at all levels from production to consumer to "by-standers".

For example, US patent No. 5,231,954 issued to Stowe in August 1993 describes a design for an electrolysis system with power to drive the system supplied by a vehicle electrical system.

The system rapidly moves hydrogen generated in an electrolysis chamber to the fuel delivery system of a vehicle, thereby minimizing the storage of the hydrogen. The system of the Stowe patent also includes a "pop-off" valve to vent excessive hydrogen and reduce storage of large quantities of hydrogen gas under pressure.

Deficiencies however include the absence of a means to regulate the level of hydrogen produced in terms of demand or even in terms of specific types of engines. There are also inefficiencies in hydrogen gas production associated with the design of

electrical conductor plates in the electrolyzer and the fact that the initiation of hydrogen gas production is delayed when the system is activated. Excessive heating in the electrolyzer chamber is also a problem. The Stowe patent fails to recognize possible relevance of the electrolytic solution as it relates to several of these deficiencies.

US patent No. 5,733,421 issued March 31, 1998 to Pettigrew, et al. overcomes several of the above cited deficiencies of the Stowe patent. Compared with the Stowe patent, the electrolysis unit of the Pettigrew patent reduces explosion hazard by a sealed system that is protected from explosions and from corrosive damage. However, the Pettigrew patent does not recognize the role the electrolytic solution plays in corrosion and related costs, nor apparently does the patent recognize that uniquely designed conductor plates may benefit from a uniquely formulated electrolytic solution.

The Stowe patent does note that a wide variety of electrolytic solutions can be used. These include potassium hydroxide, potassium nitrate, sodium sulfate, and sulfuric acid. Without explanation, potassium is suggested as preferred; sulfuric acid yielded the greatest outputs of hydrogen, but owing to its extreme corrosive potential is destructive to the system. According to the disclosure of the Stowe patent only water need be added to the electrolyzer once the electrolysis solution (potassium hydroxide) is supplied. The Stowe patent makes no claim or recommendation or other teaching as to superior electrolytic solutions.

US patent 5,843,292 issued December 1, 1998 to Spiros, describes a cell arrangement for the electrolysis of water (hydrogen production). The Spiros patent does address complex details of anode and cathode electrode elements. The relevance

of an electrolysis solution is “prior art” according to the Spiros patent. The Spiros patent acknowledges that electrolyzing water in the presence of an electrolyte is well known. Without explanation, the Spiros patent suggest potassium hydroxide and sodium hydroxide as appropriate electrolytes. The Spiros patent summarized the process of electrolysis in its simplest terms. Electrolyzing water in the presence of NaOH or KOH to liberate hydrogen involves applying a DC potential difference between two or more anode/cathode pairs and delivering the minimum energy to break the H--O bonds. Gases are produced in the stoichiometric chemical proportions of 2:l/H:O. The patent '292 teaches no uniqueness to specific types of electrolytes.

Although the Spiros patent failed to address the possible importance of the nature of the electrolyte, it describes a method to selectively adjust the water/electrolyte pressure differential on the respective sides of separation membranes in a hydrogen generator, thereby affecting the release of hydrogen and oxygen. Although apparently unrecognized at the time, this suggests far more than a simple, common role for any electrolyte, under at least some conditions.

There remains room in the art for improvement of the various elements of the emerging, complex hydrogen/oxygen generator (electrolysis) systems. Specifically, there remains room in the art for improvements in formulating specific electrolytic solutions that improve the efficiency or overall performance of any of the generally described systems as well as for electrolytes that are more specifically formulated for certain types or configurations of the anode and cathode electrical elements and related systems.

SUMMARY OF THE INVENTION

The present invention is intended for and adapted for use in various types of electrolysis systems. It has specific applications to the welding equipment described and claimed in US Patent No. 6,689,259 issued to Klein on February 10, 2004, which US Patent is hereby incorporated by reference in its entirety.

A first objective of the invention is described electrolytic solutions that increase the efficiency of all types of electrolysis hydrogen generating systems, including those used in welding systems, engine systems, among others.

A further objective of the invention is to provide electrolytic solutions that help minimize maintenance of and repairs to electrolysis hydrogen generating systems and also reduce hydrogen sludge production by such systems.

A still further objective of the invention is to provide electrolytic solutions adapted to hydrogen generators with conductive plates of unique configuration or composition of conductive materials.

An additional objective of the invention is to provide electrolytic solutions that generate higher amperage draw than generic electrolytic solutions.

And yet another objective of the invention is to provide electrolytic solutions that will allow the electrolysis system to operate at subfreezing temperatures.

A still further objective of the invention is to provide electrolytic solutions formulated from a major and a secondary set of solutes which are dissolved in water to produce desired electrolytic solutions of predictable performance with specified electrolysis systems.

These and other objectives, purposes and benefits can be achieved by the herein disclosed electrolytic solutions that are stable in the electrolysis system and the composition of which can readily be changed by altering the relative proportion of one

or more solutes in either the major or the secondary set of solutes prior to dissolving such salutes in water. These and other objectives are further satisfied by electrolytic solutions that generate an increased amperage draw and related increased hydrogen gas yield compared to a standard, and further by desired electrolytic solutions that because of their chemical composition have a freezing point below 32°F, and further by described electrolytic solutions that have minimum iron content and minimum calcium salts to reduce the accumulation of hydrogen sludge and reduce maintenance of the electrolysis system. Finally, these objectives are satisfied by desired electrolytic solutions comprised of two sets of solutes in which the most abundant solutes are in the major set and the lesser abundant salutes are in the minor set such that a quantity of a final solution is made by mixing weighed amounts of each set of salutes in a quantity of water, such as two pounds of the mixed solutes in two gallons of water to yield a solution with 35% solutes, 80% of which came from the major set of salutes comprising predominately potassium hydroxide and potassium carbonate and in which iron and calcium compounds are minimized and the second set comprises a bicarbonate and sodium chloride in comparatively small amounts.

Generally, the invention is an electrolytic solution comprising:

a major solute and a minor solute combined proportionately and dissolved in a predetermined quantity of water;

said major solute comprising dry pellets, flakes or combinations thereof comprising about 83% to 87% potassium hydroxide and about 0.4% to 0.7 of a carbonate, said major solute further comprising minimal amounts of iron compounds and minimal amounts of calcium; and

said minor solute comprising about 4.0% to 6.0% of a bicarbonate and up to 3.0% sodium chloride,

wherein said solutes are combined with said predetermined quantity of water to yield said electrolytic solution.

The dry pellets, flakes or combinations thereof comprise about 86 % potassium hydroxide and about 0.6 % of the carbonate. The carbonate of the major solute is preferably potassium carbonate. The minimal amounts of iron compounds in the major solute is preferably less than 0.005%.

The minor solute preferably comprises about 5.0% of the bicarbonate and up to 3.0% of the sodium chloride.

The electrolytic solution can be made with approximately two pounds of combined solutes being dissolved in approximately two gallons of water to yield an electrolytic solution comprising approximately 28% of the major solute and 7% of the minor solute totaling 35% total solutes.

The resultant solution is stable in reaction with an electrolysis system, has a freezing point of at least 54 °F below the freezing point of water, generates hydrogen gas output in an efficient manner with respect to energy input and with respect to hydrogen output, is readily modified in terms of the composition of its major solute to yield superior performance in response to changes in the composition and configuration of electrical conducting elements of the electrolysis system, and minimizes production of hydrogen sludge in the electrolysis system and scaling of conductive and other surfaces exposed to said electrolytic solution.

The major solute can be modified to best adapt the solution to an electrolytic system in which the content of nickel in conductor elements has been altered from 14.0%.

A chemical composition of the solution can be modified by changing the composition of the minor solute.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following examples, descriptions and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

All generators depending on the electrolysis of water to produce some form of hydrogen gas use some formulation of generic electrolytic solution. Commonly, the solute is potassium hydroxide, sodium hydroxide, or sodium bicarbonate. Little attention has been accorded the specific formulation of generic electrolytic solutions or to possible relationships between the formulation and unique characteristics of an electrolysis system, particularly to the nature of the electrical conductive elements of the system with respect to efficiency of the system as well as to maintenance issues.

Both the system efficiency and maintenance of the electrolysis system described in US Patent No. 6,689,259 issued February 10, 2004 to Klein and hereby incorporated in its entirety by reference are affected by the formulation of the desired electrolytic solution. In one example of formulations, a described electrolytic solution comprises two sets of solutes and a solvent. Although "tap water" can be used, in situations in which such water is high in dissolved salts, the use of distilled, deionized water may be appropriate.

The two sets of solutes comprise a first major set of solutes and a second minor set of solutes. The major set provides the majority of the reactive, dry, flaked or powdered (ionizing) materials. In the present example, the first set comprised

potassium hydroxide and a carbonate, preferably potassium carbonate. The dry material preferably comprises over 85 percent potassium hydroxide and less than 1 percent, preferably less than 0.66 percent potassium carbonate. The remaining approximately 14 percent is non-essential to the major solute and resulting solution, except iron compounds and calcium compounds are held to a minimum. Other materials include, but are not limited to nitrogen, phosphorous, sulfates, heavy metals, sodium, silicates, aluminum, arsenic, and mercury. The first set of solutes is commercially available as potassium hydroxide tablets.

The second set of solutes comprises a bicarbonate, preferably potassium bicarbonate and sodium chloride.

Example 1

An example of an electrolysis solution in which the analysis of the first set of solutes are as follows:

compound	percent by weight	
	limits	typical
potassium hydroxide	86.00	86.30
potassium carbonate	0.60	0.50
nitrogen	0.0005	0.0003
phosphorous	0.0002	0.0001
sulfates	0.0005	0.0005
heavy metals (as Ag.)	0.0005	0.0005
iron (Fe)	0.0005	0.0005
sodium (Na)	0.02	0.02
silicates	0.002	0.0001
aluminum	0.0001	0.0001
calcium	0.001	0.0004
arsenic	0.002	0.0001
mercury	0.1 ppm	0.1 ppm
identification	to pass (NF)	conforms
insoluble substances	to pass (NE)	passes
sodium	to pass (NW)	passes

and in which the second solute includes:

a bicarbonate	5.00
sodium chloride	2.0

Quantities of each of the solutes commonly in dry form are combined to yield the active ingredients that in the above example were 80 percent of the first solute and 20 percent of the second. Two pounds of the active ingredients are added to approximately two gallons of water to produce an electrolytic solution that is 28 percent of the major solute and 7 percent of the minor solute, and a total of 35 percent of the solutes, total. One skilled in the art recognizes that this final composition can be reached by mixing other combinations of basic ingredients.

The freezing point of the above-described electrolytic solution was approximately -22°F , substantially lower than the freezing point of water, that is, at least 54°F below the freezing point of water, and at least comparable to the freezing point of generic electrolytic solutions, such as a 20% percent solution of potassium hydroxide with a freezing point of $+25^{\circ}\text{F}$.

The described electrolytic solution was used in an electrolysis system referenced in United States Patent 6,689,259 that generates a combustible gas from water for a welder. In that specific electrolysis system, the electrolyzer produced an amperage draw of 20 amps compared with a draw of 18 amps using a generic electrolytic solution. Amperage draw (electrical power) production is highly, positively correlated with the level of gas (fuel) generation; thus the described electrolytic solution caused the generation of more gas (fuel) than the same electrolysis system produced with a generic electrolytic solution. In this system, the conductive elements (plates) of the electrolyzer were ferrous with 14% nickel.

Changing, increasing the percent nickel to about 20% and using the a generic electrolytic solution, resulted in a reduced gas yield; however when the generic electrolytic solution was modified to have 85% of the major solute, or a total of 35% solutes, resultant gas production equaled or exceeded that of the initial system using the initially described conductive elements (plates). The combustible gas is stable with respect to a given electrolysis system but the use of described electrolytic solutions increases electrical efficiencies, therefore increasing combustible gas production.

The system in which the described electrolytic solution was used also operated more efficiently with respect to maintenance wear, and general upkeep. Compared with generic electrolytic solutions, less calcium induced scaling was detected in the electrolyzer and the production of hydrogen sludge was substantially reduced.

The reduced scaling and substantial reduction of hydrogen sludge production is a direct reflection of the effective elimination of iron and calcium compounds in the described electrolytic solutions. The reduced freezing point is a desired function of the level and types of solutes in the described electrolytic solutions. The increased power output and resultant increase in combustible gas production resulted from the stability of the described electrolytic solutions in the systems, the dissociation of the salts in specific proportions and an interaction between the formulation of the described electrolytic solutions and the composition and configuration of electrical conductor elements (plates) in the electrolysis system, specifically reflected in the reaction to moderate changes in the proportion of nickel in the conductor elements (plates).

Example 2

The above-described electrolytic solution was modified by altering the relative proportion of potassium hydroxide and potassium carbonate in the major solute as shown in the table below. The table shows ranges of the resultant increase of amperage draw across 14% nickel (6" x 6") plates. Amperage draw increase ranged from 140 amps to 165amp. More amperage draw produces more gas volume. Voltage remained constant at 12 volts DC.

Amperage Draw	140 amps	152 amps	158 amps	165 amps
Electrolyte Solution:				
Potassium Hydroxide	28%	28%	28%	28%
Bicarb	0%	2%	3%	5%
Sodium Chloride	0%	1%	2%	3%

In addition, the proportion of nickel in the conductive elements (plates) in the electrolysis system ranges from 14% to 99.99% percent. General performance decreased for the generic electrolytic solutions, but still was effective. However the new electrolytic solutions produced superior results. Amperage draw increased with parallel increases in combustible gas output, increased efficiency of the inputted electrical energy, and reduced maintenance continued.

The preceding descriptions and examples are for illustrative purposes, not limitations on the scope or intent of the invention. It is anticipated that various elements of the several examples may be combined to yield still more valuable, alternative electrolytic solutions all of which are anticipated by the invention. Thus is any interpretation of the examples results, formulations, and compositions of

equipment are to be accorded their widest possible meaning and not be interpreted as limitations on the scope or intent of the invention.

What I claim is:

1. An electrolytic solution comprising:
a major solute and a minor solute combined proportionately and dissolved in a predetermined quantity of water;
said major solute comprising dry pellets, flakes or combinations thereof comprising about 83% to 87% potassium hydroxide and about 0.4% to 0.7 of a carbonate, said major solute further comprising minimal amounts of iron compounds and minimal amounts of calcium; and
said minor solute comprising about 4.0% to 6.0% of a bicarbonate and up to 3.0% sodium chloride,
wherein said solutes are combined with said predetermined quantity of water to yield said electrolytic solution.
2. The electrolytic solution according to claim 1, wherein the dry pellets, flakes or combinations thereof comprise about 86 % potassium hydroxide and about 0.6 % of the carbonate.
3. The electrolytic solution according to claim 1, wherein the carbonate of the major solute is potassium carbonate.
4. The electrolytic solution according to claim 1, wherein the minimal amounts of iron compounds in the major solute is less than 0.005%.
5. The electrolytic solution according to claim 1, wherein the minor solute comprises about 5.0% of the bicarbonate and up to 3.0% of the sodium chloride.
6. The electrolytic solution according to claim 1, wherein approximately two pounds of combined solutes are dissolved in approximately two gallons of water to yield an

electrolytic solution comprising approximately 28% of said major solute and 7% of said minor solute totaling 35% total solutes.

7. The electrolytic solution according to claim 1, wherein said electrolytic solution

is stable in reaction with an electrolysis system,

has a freezing point of at least 54 °F below the freezing point of water,

generates hydrogen gas output in an efficient manner with respect to energy input and with respect to hydrogen output, and

minimizes production of hydrogen sludge in the electrolysis system and scaling of conductive and other surfaces exposed to said electrolytic solution.